4.01 Membrane Distillation and Osmotic Distillation

E Curcio, University of Calabria, Arcavacata di Rende (CS), Italy

G Di Profio, Institute on Membrane Technology, ITM-CNR, at University of Calabria, Rende (CS), Italy

E Drioli, Institute on Membrane Technology, ITM-CNR, University of Calabria, Rende (CS), Italy

4.01.1 Definition and Basic Principles

Membrane distillation (MD) is an emerging nonisothermal separation technique that uses microporous hydrophobic membrane in contact with an aqueous heated solution on the one hand (feed or retentate) and a condensing phase (permeate or distillate) on the other [1]. This technique belongs to the class of membrane contactors in which a nonwetting membrane does not act as a conventional barrier or filter, but promotes mass and energy exchange between two opposite interfaces according to principles of phase equilibrium.

In MD, the hydrophobic nature of the membrane prevents the mass transfer in liquid phase and creates a vapor–liquid interface at the entrance of each pore. Here, volatile compounds (most commonly water) evaporate, diffuse and/or convect across the membrane, and are condensed and/or removed on the opposite side of the system.

The specific method used to activate the vapor pressure gradient across the membrane characterizes four main different MD configurations. In the most common arrangement – known as direct contact membrane distillation (DCMD) – the permeate side of the membrane consists of a condensing fluid (often pure water) that is directly in contact with the membrane. Alternatively, the vaporized solvent can be recovered on a condensing surface separated from the membrane by an air gap (AGMD), vacuum (VMD), or removed by a sweep gas (SGMD). All these variants are schematized in **Figure 1**.

The selection of a specific configuration depends upon feed and permeate compositions and characteristics, as well as upon requested productivity. In general, DCMD (cheaper and easier to operate) is the best choice for applications in aqueous

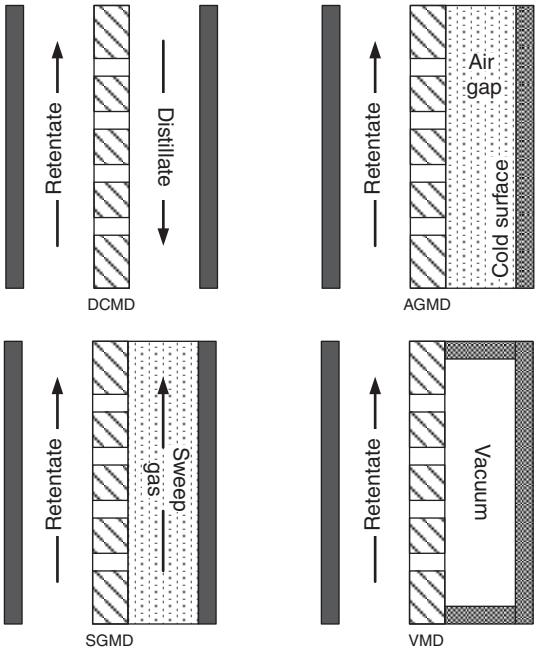


Figure 1 Scheme of the four most common membrane distillation (MD) configurations: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD), vacuum membrane distillation (VMD).

environments, SGMD and VMD are used to remove volatile organic components from aqueous solutions, and AGMD (the most versatile) can be employed to concentrate various nonvolatile solutes whenever high fluxes are not required. Compared to reverse osmosis (RO), MD does not suffer limitations of concentration polarization and can therefore be employed when high permeate recovery factors or high retentate concentrations are requested. Moreover, RO fluxes are drastically reduced at high concentration due to the increase in osmotic pressure, while MD fluxes slightly decrease as consequence of both reduction of the solution activity and increase of the solution viscosity.

With respect to traditional separation units and methods of the chemical industry, MD offers several important advantages. The nature of the driving force, coupled with the hydro-repellent character of the membrane, allow – at least theoretically – the complete rejection of nonvolatile solutes such as macromolecules, colloidal species, and ions. Lower temperature gradients (20–40 °C) with respect to those generally used in conventional distillation columns are generally sufficient to establish a transmembrane flux in the order of 1–20 kg m^{-2} h^{-1}, with consequent reduction of energy costs and mechanical requirements of the materials. Typical feed temperatures vary in the range of 40–60 °C and permit the efficient recycle of low-grade or waste heat streams, as well as the use of alternative energy sources (solar, wind, or geothermal) [2]. In addition, the possibility to use plastic equipments reduces or avoids erosion problems. On the other hand, MD suffers from some drawbacks. MD fluxes of permeate are usually lower than in RO, and a higher energy consumption is necessary to drive this thermal membrane operation. Moreover, only a restricted class of polymeric materials present a sufficient chemical resistance and operational stability and, despite the decreasing trend of membrane costs, commercial modules are still quite expensive.

4.01.2 Membrane Materials

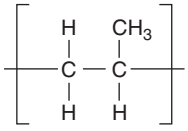
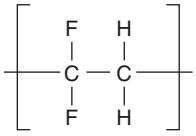
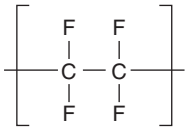
When producing microporous membranes for MD operations, the selection of the material is mainly driven by the necessity to achieve a high chemical and thermal stability, high hydrophobicity, and porosity. Typology and main characteristics of the polymers frequently used as starting material for microporous hydrophobic membranes are given in **Table 1**.

More recently, inorganic (stainless steel) membranes typically used in microfiltration, modified by depositing on their surface a very thin film of silicone compounds, have been tested for MD operations [3]. Microporous polymeric membranes are prepared by various techniques: sintering, stretching, and phase inversion.

Sintering is a simple technique: a powder of polymeric particles is pressed into a film or plate and sintered to just below the melting point [4]. The process yields a microporous structure having a porosity in the range of 10–40% and rather irregular pore sizes, ranging from 0.2 to 20 μm (**Figure 2(a)**).

Microporous membranes can also be prepared by stretching a homogeneous polymer film made from a partially crystalline material [5]. Films are obtained by extrusion of a polymeric powder at temperature close to the melting point, coupled with a rapid drawdown. Crystallites in the polymers are aligned in the direction of drawing. After annealing and cooling, mechanical stress is applied perpendicularly to the direction of drawing. This manufacturing process gives a relatively uniform porous structure with pore-size distribution in the range of 0.2–20 μm and porosity of about 90% (**Figure 2(b)**).

Table 1 Frequently used materials for MD membranes

Polymer	*Chemical Structure*	*Main Characteristics*
Polypropylene (PP)		Chemically resistant; hydrophobic
Polyvinylidenefluoride (PVDF)		High-temperature resistant; inherently hydrophobic
Polytetrafluoroethylene (PTFE)		High-temperature and chemical (acid) resistant; cannot be irradiated; inherently hydrophobic

MD membranes are often prepared by phase inversion technique from polymers that are soluble at a certain temperature in an appropriate solvent or solvent mixture, and that can be precipitated as a continuous phase by changing temperature and/or composition of the system [6]. These changes aim to create a miscibility gap in the system at a given temperature and composition; from a thermodynamic point of view, the free energy of mixing of the system becomes positive.

The formation of two different phases, that is, a solid phase forming the polymeric structure (symmetric, with porosity almost uniform across the membrane cross section, or asymmetric, with a selective thin skin on a sublayer) and a liquid phase generating the pores of the membrane, is determined by few and conceptually simple actions:

1. by changing the temperature of the system (cooling of a homogeneous polymer solution which separates in two phases) – temperature-induced phase separation technique (TIPS, see **Figure 2(c)**) and
2. by adding nonsolvent or nonsolvent mixture to a homogeneous solution – diffusion-induced phase separation (DIPS, see **Figure 2(d)**).

Although these procedures are practically dissimilar, the basics of the membrane formation mechanism is governed, in all cases, by similar thermodynamic and kinetic concepts: variations in the chemical potential of the system, diffusivities of components in the mixture, Gibbs free energy of mixing, and presence of miscibility gaps. **Table 2** reports the most frequently used commercial membranes in the MD lab activities.

4.01.3 Membrane Modification

A large part of commercial microporous hydrophobic polymeric membranes available in capillary and flat-sheet forms that are used for MD applications were originally manufactured and optimized for microfiltration purposes. The possibility to prepare new membranes specifically operated for MD is recently increasing in interest, and some significant results achieved in the preparation and modification of polymeric membranes have provided an increase of the reliability of MD.

4.01.3.1 Additives in the Casting Solution

The use of additives to the casting solution, for example, in the form of water-soluble polymers, such as polyvinyl pirrolidone (PVP), polyethylene glycol (PEG), or inorganic salts (LiCl), represents a practical way to modulate the structure of a membrane. This aspect has been investigated in the

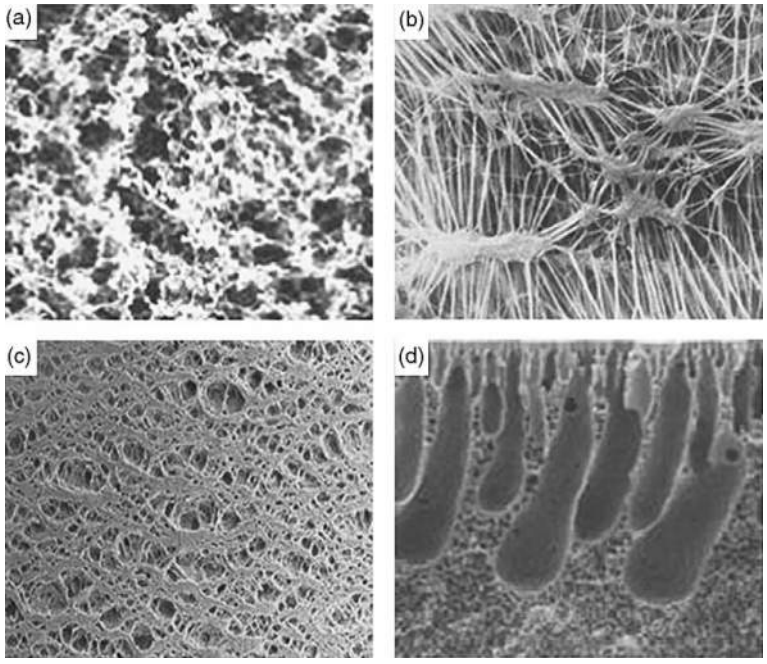


Figure 2 Cross-section micrographs of (a) sintered polytetrafluoroethylene (PTFE) membrane; (b) stretched polypropylene (PP) membrane; (c) PP membrane prepared by temperature-induced phase separation technique (TIPS); (d) polyvinylidenedifluoride (PVDF) membrane prepared by DIPS.

preparation of microporous polyvinylidenedifluoride (PVDF) membranes for MD applications, where high porosity is requested in order to obtain a significant flux [7–9]. In particular, it has been observed that the addition of significant amounts of LiCl increases the rate of PVDF precipitation during the immersion step that causes the formation of an open structure with large macrovoids and cavities. The accelerated precipitation is related to the high tendency of the additive to mix with water and to the interactions of the additive with polymer and solvent [10].

4.01.3.2 Copolymers

Copolymers of tetrafluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD), commercially known as HYFLON AD, have been used to obtain asymmetric and composite membranes showing

Table 2 Common commercial membranes for use in membrane distillation

Membrane type	*Trade name*	*Manufacturer*	*Material*	*Pore size (μm)*	*Porosity*
Flat sheet	TF200	Gelman	PTFE supported by PP	0.20	80
	TF450			0.45	80
	TF1000			1.0	80
	3MA	3M Corporation	PP	0.29	66
	3MB			0.40	76
	3MC			0.51	79
	3MD			0.58	80
	3ME			0.73	85
	FGLP	Millipore	PTFE supported by PE	0.20	70
	FHLP			0.50	80
	GVHP		PVDF	0.22	75
	HVHP			0.45	75
Capillary	Accurel S6/2	AkzoNobel Microdyn	PP	0.20	70
	Accurel BFMF	Enka AG		0.20	

a high hydrophobic character and contact angles to water greater than 120° [11]. Asymmetric hydrophobic microporous membranes from the copolymer of polytetrafluoroethylene (PTFE) and PVDF have been prepared by phase inversion process [12]. According to the experimental analysis, these membranes exhibit excellent mechanical properties (stretching strain and extension ratio at break approximately 6–8 times higher PVDF) and good hydrophobicity (contact angle to water of about 87°).

4.01.3.3 Surface Coating, Grafting, and Plasma Treatment

The work of Xu *et al.* [13] showed that hydrophobic PTFE membranes with a protective hydrophilic sodium alginate coating were resistant to wet out at least for 300 min during osmotic distillation tests using feeds containing 0.2, 0.4, and 0.8 wt.% orange oil. The reduction in the overall mass transfer coefficient due to the coating was less than 5%.

In order to prepare a hydrophilic/hydrophobic composite membrane, the surface of hydrophilic porous cellulose acetate was treated via radiation graft polymerization of styrene by Wu *et al.* [14].

Low-pressure plasma polymerization permits to apply a thin layer upon a porous sublayer: this generally results in a change of the chemical composition and properties of a material, such as wettability, refractive index, and hardness.

A very high hydrophobicity, somewhat higher than that of PTFE, was achieved by fluorinated coatings also named Teflon-like [15]. Kong *et al.* [16] have modified hydrophilic microporous cellulose nitrate membranes by plasma polymerization of octafluorocyclobutane. The performance of these membranes, tested in MD applications, was found comparable with that of usual hydrophobic polymers.

4.01.3.4 Surface Modifying Molecules

Khayet *et al.* [17] have modified the surface of hydrophilic membranes by adding oligomeric fluoropolymers synthesized by polyurethane chemistry and tailored with fluorinated end groups. During membrane formation, surface-modifying molecules (SMMs) migrate to the air-film surface according to the thermodynamic tendency to minimize the interfacial energy. These modified membranes exhibit low surface energies, good mechanical strength, and high chemical resistance [18].

4.01.4 Hydrophobicity and Nonwetting Properties

In MD, the penetration of liquid through the microporous structure of a polymeric membrane should be avoided. In general, a fluid does not pass through pores as long as the pressure is kept below a critical threshold known as breakthrough pressure (ΔP_{entry}). The Laplace equation offers a relationship between the largest pore size of the membrane $d_{\text{p,max}}$ and ΔP_{entry}:

$$\Delta P_{\text{entry}} = -\frac{4\Xi\gamma\cos\theta}{d_{\text{p,max}}} \tag{1}$$

where γ is the interfacial tension, Ξ is a geometric factor related to the pore structure (equal to 1 for cylindrical pores), and θ the liquid–solid contact angle.

For a typical water-hydrophobic membrane contact angle of 130°, the penetration pressure of a cylindrical pore of diameter 1 mm is only 185 kPa [19]. Breakthrough pressure data for several membranes type and fluids can be found in literature [20]; for MD applications, ΔP values range between 100 and 400 kPa (**Figure 3**).

Contact angle measurement is a traditional method to quantify the hydrophobic character of a material. In principle, it provides information about the wettability of an ideal (perfectly smooth) surface. In most cases, the intrinsic value of contact angle is perturbed by surface porosity and roughness, heterogeneity, etc. The value of the contact angle made by a liquid droplet deposited on a smooth surface (**Figure 4**) is greater than 90° if the affinity between liquid and solid is low; in the case of water, the material is considered hydrophobic. Wetting occurs at 0°, when the liquid spreads onto the surface.

At the triple point C where solid–liquid vapor interfaces are in contact, the thermodynamic equilibrium is expressed by the Young equation:

$$\gamma_{\text{LV}}\cos\theta = \gamma_{\text{SV}} - \gamma_{\text{SL}} \tag{2}$$

where γ_{LV}, γ_{SV}, and γ_{SL} are the surface tension for liquid–vapor, the surface energy of the polymer, and the solid–liquid surface tension, respectively. Surface tension values γ_{LV} for different test liquids are reported in **Table 3**.

Young's equation is rigorously applicable if the solid substrate is smooth, if the surface is homogeneous and rigid, chemically inert, and insoluble to contacting liquids. Courel *et al.* [22] demonstrated

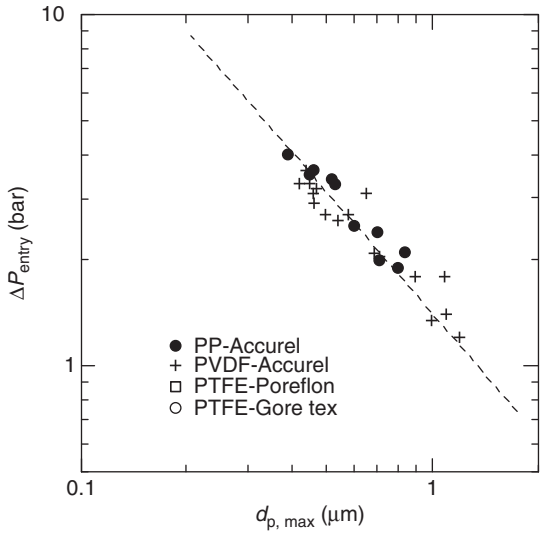


Figure 3 Water pressure entry for different membranes as a function of the maximum pore size. Modified from Schneider, K., Holz, W., Wollbeck, R. *J. Membr. Sci.* **1988**, *39*, 25–42.

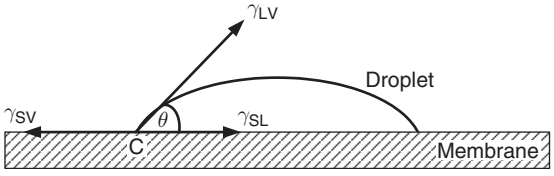


Figure 4 Contact angle (θ) of a liquid droplet deposited on the surface of a membrane. Thermodynamic equilibrium is established at the triple point C.

Table 3 Surface tension values γ_{LV} for different test liquids

Test liquid	γ_{LV} *(mJ^{-1}m)*
Water	72.8
Glycerol	64
Ethylene glycol	48
Formamide	58
Dimethylsulfoxide	44
Chloroform	27.2
Diiodomethane	50.8
A-bromonaphthalene	44.4

that the application of Young's equation to a porous surface leads to the following expression:

$$\cos\theta = y\cos\theta' - (1-y) \tag{3}$$

where y is the fraction of membrane surface made of solid material.

Under the assumption that the contact angles on the three-phase lines both on the outer drop border and over the pores are equal, Troger *et al.* [23] have obtained a general relation between the observed contact angle θ' and the ideal one θ (to be observed on ideally smooth surface):

$$\cos\theta = \cos\theta' - \frac{4\varepsilon}{1-\varepsilon}\frac{\cos\theta' + 1}{\cos\theta' - 1} \tag{4}$$

with ϵ being the porosity of the porous material; the validity of Equation (4) has been tested on porous PTFE membranes with appreciable results.

4.01.5 Mass Transfer

In a membrane operation, transport through membranes occurs if the system is not in thermodynamic equilibrium. In MD, coupled mass and heat transport is driven by a partial pressure difference between both sides of the membrane, established by temperature difference between the two contacting solution, or by vacuum, air gap, or sweep gas in the permeate side. According to the Raoult's law, the partial pressure of an ith component (p_i) is related to its vapor pressure as pure substance (p_i^0) through its molar fraction x_i and activity coefficient ξ_i:

$$p_i = p_i^0 \xi_i x_i \tag{5}$$

The accurate evaluation of activity coefficients is a critical issue in MD. The most flexible approach for determining the activity coefficients is probably given by UNIQUAC model [24]; it is based on a combinatorial term that contains pure-components parameters, and a residual contribute depending on adjustable parameters that are characteristic for each binary system.

NRTL model [25] is also used frequently in the description of vapor–liquid equilibrium of binary mixtures; for ethanol–water mixtures, Sarti *et al.* [26] reported the following expressions:

$$\ln\xi_i = x_k^2\left[\tau_{ki}\left(\frac{G_{ki}}{x_i + x_k G_{ki}}\right)^2 + \frac{\tau_{ik}G_{ik}}{(x_k + x_i G_{ik})^2}\right] \tag{6a}$$

$$\tau_{ik} = a_{ik} + b_{ik}/T;\ G_{ik} = \exp(-\alpha\tau_{ik}) \tag{6b}$$

where x_i and x_k are the mole fractions of ethanol and water, respectively; constant values are $a_{ik} = 0.49854$, $b_{ik} = -456.00$, and $\alpha = 0.24$.

Empirical correlations are very useful as well. For NaCl aqueous solutions, Schofield [27] proposed the

following correlation between the activity coefficient and molar fraction of solute:

$$\gamma_{\text{water}} = 1 - 0.5x_{\text{NaCl}} - 10x_{\text{NaCl}}^2 \quad (7)$$

For aqueous solution of $CaCl_2$, in the range of mass fraction (w) 32.2–46.2 %, Courel [28] found the following correlation:

$$a_{\text{w}} = 1.6941 - 0.0410w_{\text{CaCl}_2} + 2.4\cdot10^{-4}w_{\text{CaCl}_2}^2 \quad (8)$$

where a_w is the activity of the solution.

The vapor pressure of a pure substance varies with temperature according to the Clausius–Clapeyron equation:

$$\frac{\text{d}p^0}{\text{d}T} = \frac{p^0\lambda}{RT^2} \quad (9)$$

where λ is the latent heat of vaporization ($\lambda = 9.7$ cal mol^{-1} for water at 100 °C [29]), R the gas constant, and T the absolute temperature.

At the pore mouth, the curvature of the vapor–liquid interface is generally assumed to have a negligible effect on the vapor pressure; in any case, possible influences can be evaluated by the Kelvin equation:

$$p^0_{\text{convex surface}} = p^0\exp\left[\frac{2\gamma_{\text{L}}}{r\rho RT}\right] \quad (10)$$

where r is the curvature radius, γ_{L} the liquid surface tension, and ρ the liquid molar density.

The usual conceptual approach to the study of mass transfer in MD considers it in terms of serial resistances upon the transfer between the bulks of two phases contacting the membrane. The permeability K, defined as the inverse of the total resistance to the mass transport, is thus expressed as a combination of the mass transfer coefficients in the feed side (k_{f}), in the membrane (k_{M}), and in the distillate side (k_{d}):

$$K = \frac{1}{1/k_{\text{f}} + 1/k_{\text{M}} + 1/k_{\text{d}}} \quad (11)$$

Mass transfer boundary layers adjoining the membrane generally offer a negligible contribution to the overall mass transfer resistance, whereas diffusion across the polymeric membrane often represents the controlling step. The resistance to mass transfer on the distillate side can be omitted whenever MD operates with pure water as condensing fluid in direct contact with the membrane, or in VMD.

When solvent molecules are transferred through the membrane, the retained solute tends to accumulate at the membrane surface where its concentration gradually increases. Such a concentration gradient generates a diffusive counter-flow that, under steady-state conditions, balances the net convective solute flow into the system: this phenomenon is known as concentration polarization. In a thermally driven MD process, the concentration polarization has generally a limited effect on the process performance [30].

Concentration polarization is usually quantified by a CPC coefficient, defined as

$$\text{CPC} = \frac{C_{\text{m}}}{C_{\text{b}}} \quad (12)$$

where C_{m} and C_{b} are the solute concentrations at the membrane interface and in the bulk, respectively.

Referring to **Figure 5**, if the solute is completely retained by the membrane (an assumption theoretically valid in MD), the mass balance in the boundary layer with thickness δ gives

$$\frac{\mathcal{J}}{\rho} = k_x\ln\frac{C_{\text{m}}}{C_{\text{b}}} \quad (13)$$

where $\mathcal{J}$ is the transmembrane molar flux, k_x the mass transfer coefficient (given by D/δ, D being the diffusion coefficient), and ρ the solution density.

The literature provides several correlations [31] often derived by analogy with those evaluated for the heat transport, that are practical for determining the mass transfer coefficient. These empirical relationships are usually expressed in the form:

$$Sh = \alpha Re^{\beta}Sc^{\gamma} \quad (14)$$

where Sh is the Sherwood number, Re the Reynolds number, and Sc the Schmidt number (more details in Reference 32).

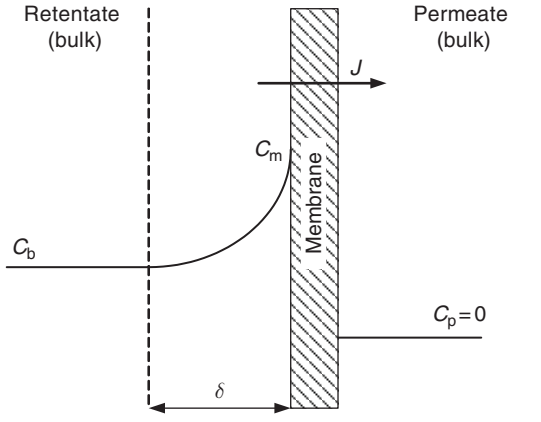


Figure 5 Development of a concentration profile into the boundary layer under steady-state conditions: concentration polarization.

Table 4 Predictive equations for mass transfer coefficients in MD

Correlation	α	β	γ	k_x (10^{-5} m^{-1} s)	*Comment*	*Reference*
$k_x = \beta Q^{\gamma}$	-	$4.02 \cdot 10^{-5}$	0.38	3.5–7.6	Q: volumetric feed flow rate (L min^{-1}); for VMD; Stirred cell; Feed side	[33]
$Sh = \alpha Re^{\beta} Sc^{\gamma}$	2.0	0.48	0.33	-	Stirred cell (200–800 rpm). Aqueous LiBr solution (0–55% w/w)	[34]
$Sh = \alpha Re^{\beta} Sc^{\gamma}$	1.86	0.38	0.38	-	Tangential flow	[35]
$Sh = \alpha Re^{\beta} Sc^{\gamma}$	0.96–0.45	0.55	0.33	17.5	Helicoidal hollow fibres φ: angle of inclination. $50<Re<400$ Feed side	[36]
$Sh = \alpha Re^{\beta} Sc^{\gamma}$	0.023	0.33	0.33	6.6–7.4	Tubular module. Water/NaCl (2–4% w/w) For VMD; feed side	[37]

Some specific correlations found in MD literature are reported in **Table 4**.

Mass transfer in a porous medium, assuming surface diffusion negligible, is affected by viscous resistance (resulting from the momentum transferred to the membrane), Knudsen diffusion resistance (due to collisions between molecules and membrane walls), and/or ordinary diffusion (due to collisions between diffusing molecules) [38]. The Knudsen number (Kn), defined as the ratio between the mean free path of diffusing molecules and the average pore size of the membrane, allows one to discriminate the eventual predominance of one peculiar mechanism.

If $Kn < 1$, the free mean path of the gas is small if compared with the average membrane pore diameter, and molecule–molecule collisions predominate over molecule–wall collisions. If $Kn > 1$, the situation is reversed: the mean free path of the gas is large with respect to the average membrane pore diameter, and molecule–wall collisions predominate over molecule–molecule collisions.

Dusty gas model (DGM) is probably the best mathematical tool for describing gaseous molar fluxes through porous media; in the most general form (again neglecting surface diffusion), DGM is expressed as [39]

$$\frac{\mathcal{J}_i^{\mathrm{D}}}{D_{i\mathrm{e}}^{k}} + \sum_{j=i\neq i}^{n} \frac{p_j \mathcal{J}_i^{D} - p_i \mathcal{J}_j^{\mathrm{D}}}{D_{ij\mathrm{e}}^{0}} = -\frac{1}{RT}\nabla p_i \tag{15a}$$

$$\mathcal{J}_i^{\mathrm{v}} = -\frac{\varepsilon r^2 p_i}{8RT\tau\mu}\nabla P \tag{15b}$$

$$D_{i\mathrm{e}}^{k} = \frac{2\varepsilon r}{3\tau}\sqrt{\frac{8RT}{\pi M_i}} \tag{15c}$$

$$D_{ij\mathrm{e}}^{0} = \frac{\varepsilon}{\tau} P D_{ij}^{0} \tag{15d}$$

where $\mathcal{J}^{\mathrm{D}}$ is the diffusive flux, $\mathcal{J}^{\mathrm{v}}$ the viscous flux, D^{k} the Knudsen diffusion coefficient, D^0 the ordinary diffusion coefficient, p the partial pressure, R the gas constant (8.314 J mol^{-1} K^{-1}), T the temperature, P the total pressure, μ the gas viscosity, r the membrane radius, ϵ the membrane porosity, and τ the membrane tortuosity. Underscript e indicates the effective diffusion coefficient, calculated by taking into account the structural parameters of the membrane as shown in Equations (15c) and (15d).

In most cases, simpler empirical correlations are preferred. The transmembrane flux is thus expressed as a linear function of the vapor pressure difference across the membrane [40]:

$$\mathcal{J} = \Theta \Delta p \tag{16}$$

where Θ is the MD coefficient, and Δp the vapor pressure gradient evaluated at the membrane surfaces. The coefficient Θ is a function of the membrane properties (pore size, thickness, porosity, and tortuosity), properties of the vapor transported across the membrane (molecular weight and diffusivity), and operative temperatures [41].

4.01.6 Heat Transfer

MD involves a simultaneous transport of heat and matter that is generally described in terms of serial and parallel resistances through the boundary layers of the membrane and through the membrane itself.

The total heat flux Q transferred across the membrane is expressed as

$$Q = \left[\frac{1}{h_f} + \frac{1}{h_m + \mathcal{J}\lambda/\Delta T_m} + \frac{1}{h_p}\right]^{-1} \Delta T \qquad (17)$$

where ΔT is the (bulk) temperature difference among feed and permeate sides, ΔT_m the transmembrane temperature, $\mathcal{J}$ the transmembrane molar flux, λ the molar heat of vaporization, and h_f, h_m, and h_p are the heat transfer coefficients on the feed side, membrane, and permeate side, respectively.

The most unfavorable effect due to boundary layer resistances is the creation of a temperature difference between the bulk and the membrane surface where vapor–liquid transition occurs; in particular, the evaporation reduces the temperature at the interface of the membrane and, therefore, decreases the driving force of the process. A temperature polarization coefficient (TPC) is commonly used to quantify the extent of the boundary layer resistances over the total heat transfer resistance. It is defined as

$$\mathrm{TPC} = \frac{T_f^m - T_p^m}{T_f - T_p} \qquad (18)$$

where superscript m indicates the temperature at the membrane surface.

TPC is also employed to evaluate the efficiency for MD process indirectly: it falls between 0.4 and 0.7 for well-designed systems, and approaches to unity for mass transfer limited operations [40].

Literature provides a large variety of empirical correlations that can be used to evaluate the heat transfer coefficients in the boundary layers. These correlations are usually expressed in the form:

$$Nu = \alpha Re^{\beta} Pr^{\gamma} \qquad (19)$$

where Nu is Nusselt number, Re the Reynolds number, and Pr the Prandtl number (more details are available in Reference 32). A brief summary of useful empirical relationships is proposed in **Table 5**.

The total heat flux Q is transferred across the membrane by two mechanisms: conduction across the membrane material,and as latent heat associated to the vaporized solvent. The energy balance gives

$$Q = \mathcal{J} H_v(T) - k_m \frac{dT}{dx} \qquad (20)$$

where H_v is the (vapor) enthalpy at temperature T, k_m is the thermal conductivity of the membrane, and x the coordinate. Assuming T_0 as a reference temperature, and considering that temperature inside membrane changes within few degrees (so that the specific heat can be supposed constant), the vapor enthalpy at a generic temperature T is given by

$$H_v(T) = \lambda(T_0) + c_{pv}(T - T_0) \qquad (21)$$

where c_{pv} is the specific heat of vapor (for water: c_{pv}=8.22 + 0.00015 T + 0.00000134 T^2 cal kmol^{-1}) [48] and λ the heat of vaporization.

Table 5 Predictive correlations for heat transfer coefficients in MD

Equation (tube side)	*Fluid dynamics*	*Reference*
$Nu = 0.13Re^{0.64}Pr^{0.38}$	Laminar flow	[42]
$Nu = 0.097Re^{0.73}Pr^{0.13}$	Laminar	[43]
$Nu = 1.62\left(RePr\left(\frac{d}{L}\right)\right)^{0.33}$	Laminar, tangential flow	[44]
$Nu = 0.023Re^{0.8}Pr^{0.33}\left(\frac{\mu}{\mu_w}\right)^{0.14}$	Turbulent	[45]
$Nu = 0.036Re^{0.8}Pr^{0.33}\left(\frac{d}{L}\right)^{0.055}$	Turbulent	[46]
$Nu = 0.027\left(1 + \frac{6d}{L}\right)Re^{0.8}Pr^{0.33}\left(\frac{\mu}{\mu_w}\right)^{0.14}$	Turbulent	[46]
$Nu = 0.116\left(Re^{0.66} - 125\right)Pr^{0.33}\left[1 + (d/L)^{0.66}\right]\left(\frac{\mu}{\mu_w}\right)^{0.14}$	Transition region	[47]
$Nu = 0.298Re^{0.646}Pr^{0.316}$	Tangential flow	[35]
$Nu = 0.023Re^{0.80}Pr^{0.33}$	VMD	[37]
$Nu = 2.0Re^{0.483}Pr^{0.33}$	Stirred cell	[34]

d: diameter of the tubular/capillary membrane; L: length of the tubular/capillary membrane; μ: viscosity

The enthalpy of saturated water vapor and liquid can be calculated by the following equation in the range of 273–373 K [49]:

$$\lambda(T) = 1.7535\,T + 2024.3 \tag{22}$$

where T is expressed in K and λ in kJ kg^{-1}.

Whereas the latent heat of vaporization is effectively used to promote the permeate flux, the conduction of heat across the membrane is an energetic loss that must be minimized. According to the investigation of Fane *et al.* [50], the heat loss by conduction represents the 20–50% of the overall heat transferred in MD. Experimental investigations prove that the amount of heat loss by conduction decreases when feed temperature and flow rates are increased, and when the permeate temperature is reduced [51, 52].

The conduction heat transfer coefficient k_m for a two-phase composite material is generally calculated by the Isostrain model [53]:

$$k_m = (1-\varepsilon)\,k_s + \varepsilon\,k_g \tag{23}$$

assuming that both polymer (k_s) and gas (k_g) contribute to k_m; ϵ is the membrane porosity.

For water vapor (k_{H_2O}), the gas of major interest in MD applications [19]:

$$k_{H_2O} = 2.72 \times 10^{-3} + 5.71 \times 10^{-5}\,T \tag{24}$$

The values of membrane thermal conductivity found by Equation (23) agree with measured ones within 10% [54].

The thermal conductivity of polymers strongly depends upon their degree of crystallinity. Data at 296 K for some common hydrophobic polymers span in a relatively narrow range: polypropylene (PP): 0.11–0.16 W m^{-1} K^{-1}; PVDF: 0.17–0.19 W m^{-1} K^{-1}; PTFE: 0.25–0.27 W m^{-1} K^{-1} [55]. Loss by conduction is reduced by increasing membrane porosity, since the water vapor thermal conductivity is one order of magnitude lower than that of polymeric materials in the range of typical MD working temperatures. Heat transferred by convection is generally considered negligible with exception of AGMD process.

4.01.7 Performance of Different MD Variants

4.01.7.1 Direct Contact Membrane Distillation

In DCMD, the warm feed solution is separated by the membrane from the colder permeate. Both feed and permeate solutions are circulated tangentially to the membrane surface (usually in counter-current flow, in order to maintain as much as possible constant the temperature gradient across the module) or stirred inside the membrane cell in small lab-scale MD devices. In this configuration, the transmembrane flux is driven by the temperature difference between the hot and cold sides of the membrane.

The possibility to carry out DCMD in any desired membrane configuration (flat sheets, spiral wound, tubular, capillaries, and hollow fibers) is a significant advantage of this configuration. A schematic representation of DCMD is shown in **Figure 6**.

In DCMD with air-filled micropores, the DGM reduces to the Knudsen molecular diffusion transition form under the assumptions that (1) the net flux of air across the membrane is very small with respect to the transmembrane flux of the volatile component and (2) the viscous flux is negligible. For aqueous solutions

$$\mathcal{J} = \frac{D^0_{\text{air-water,e}}}{\delta R \bar{T}} \ln\left[\frac{p^{\text{permeate}}_{\text{air}} D^{\text{k}}_{\text{water,e}} + D^0_{\text{air-water,e}}}{p^{\text{feed}}_{\text{air}} D^{\text{k}}_{\text{water,e}} - D^0_{\text{air-water,e}}}\right] \tag{25}$$

where $\mathcal{J}$ is the molar flux (of water), D^0 the molecular diffusion coefficient, D^{k} the Knudsen diffusion

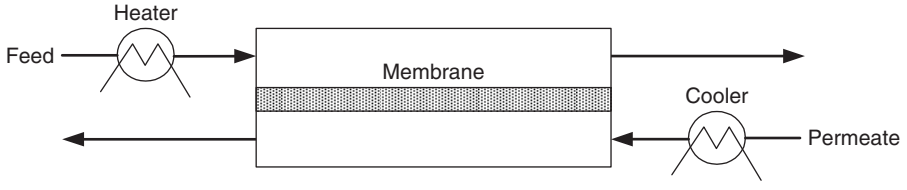


Figure 6 Scheme of direct contact membrane distillation (DCMD).

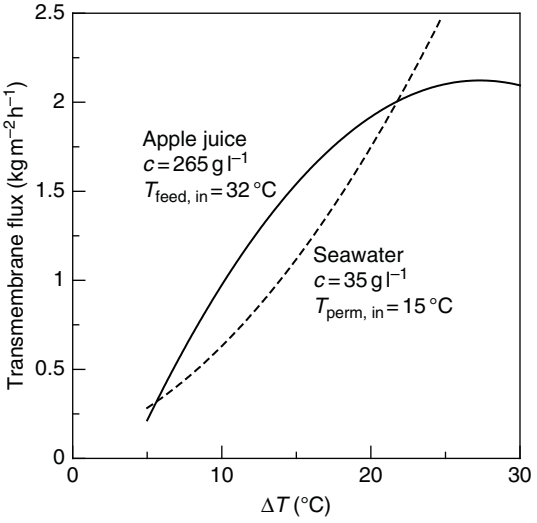


Figure 7 Effect of the temperature gradient ΔT on the transmembrane flux of water. Curves exhibit a different shape if feed (solid line) or permeate (dotted line) temperature is kept constant.

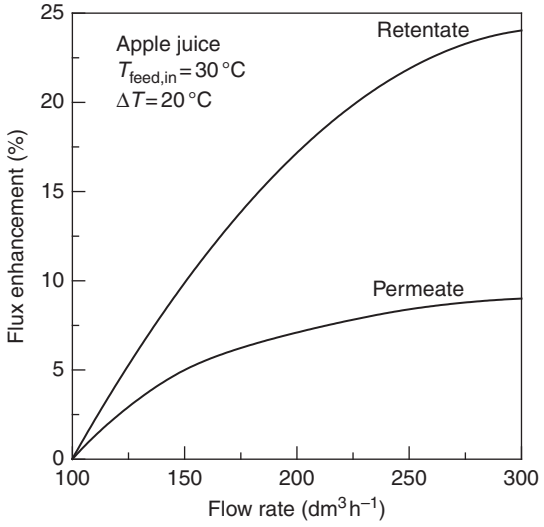


Figure 8 Variation of the transmembrane flux as a function of feed and distillate flow rate in DCMD.

coefficient, $\bar{T}$ the average temperature in the membrane, δ the membrane thickness, p the partial pressure.

TPC in DCMD assumes different values for different plant geometries and operative conditions: ~0.3 for well stirred cells, from 0.4 to 0.7 for flat membrane cross-flow systems, from 0.6 to 0.9 for tubular or hollow-fiber configurations [40].

According to the literature, the magnitude of water flux varies in the range from $\sim 1\,l\,m^{-2}\,h^{-1}$ [56] to $\sim 40\,l\,m^{-2}\,h^{-1}$ [57] for feed temperatures approaching the normal boiling point.

Feed and permeate temperatures and flow rates are the main operating parameters influencing the DCMD performance. **Figure 7** shows the effect of the bulk temperature difference between retentate and permeate ΔT on the transmembrane flux. The shape of the curves depends on the way to set ΔT. The net flux inverts its direction whenever ΔT is not sufficient to compensate the reduction of activity on the retentate side.

The transmembrane flux increases with increasing the axial flow rate both in the feed and distillate sides. **Figure 8** illustrates this behavior as result of the improvement of heat and mass transfer coefficients; consequently, both concentration and temperature polarization phenomena are reduced.

Mass flux is more sensitive to the flow-rate variation induced in the stream having the highest concentration and/or viscosity. The permeate flux moderately decreases with increasing feed concentration due to the concomitant reduction of the solution activity.

4.01.7.2 Sweep Gas Membrane Distillation

In this configuration, a cold inert gas sweeps the permeate side, carrying the vapor molecules outside the module. The sweeping gas increases its temperature along the module due to the heat transferred from the feed side across the membrane; in some cases, the sweep gas is thermostated by using a cold wall in the permeate side.

The configuration of SGMD (**Figure 9**) combines a relatively low conductive heat loss with a reduced mass transfer resistance. SGMD involves four serial stages: (1) evaporation of the volatile compound (usually water) at the hot feed side; (2) transport of vapor through the membrane pores; (3) collection of the permeate by an inert cold sweeping gas, generally humid air; and (4) condensation of the permeate out of the membrane module (in a external condenser).

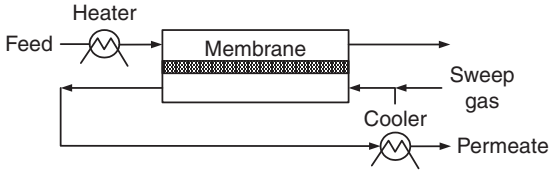


Figure 9 Scheme of sweep gas membrane distillation (SGMD).

The efficiency of this technical solution is generally low, since a little amount of permeate is condensed from a large volume of sweep gas.

On the sweep gas side, if the water vapor pressure $p_{water,air}$ is written as a function of the total pressure P and the humidity ratio w [58]:

$$p_{water,air}(T_{air}) = \frac{wP}{w + 0.622} \tag{26}$$

The humidity ratio along the membrane module length increases its inlet value w_{in} as a result of the transmembrane flux of vapor:

$$w_{in} = w + \frac{\mathcal{J}A}{\dot{m}_{air}} \tag{27}$$

where $\dot{m}_{air}$ is the massive flux of air and A the membrane area. Khayet combined equations (26) and (27) to derive the transmembrane mass flux $\mathcal{J}$:

$$\mathcal{J}^2 + \left[(w_{in} + 0.622)\frac{\dot{m}_{air}}{A} + \Theta\left(P - p_{water,feed}\right)\right]\mathcal{J} + \Theta\frac{\dot{m}_a}{A}\left[Pw_{in} - p_{water,air}(w_{in} + 0.622)\right] = 0 \tag{28}$$

where Θ is the MD coefficient (according to Equation (16)).

For the hot feed recirculating under laminar flow in the lumen side of a hollow-fiber module, correlations in **Table 5** can be used to calculate the heat transfer coefficient. For the cold air recirculating in the shell side of the membrane module, Khayet proposed the following equation [59]:

$$Sh = 0.206(Re\cos\alpha)^{0.63}Pr^{0.36} \tag{29}$$

where α is the yaw angle ($\alpha = 0°$: pure cross-flow; α=90°: pure parallel flow).

Experimental data and calculations demonstrate that temperature polarization in the feed side has a relatively small effect compared to the influence of the air flow rate. The increase of the SGMD flux as a function of the sweeping air velocity is illustrated in **Figure 10**.

In SGMD the main temperature polarization effect is generally located in the gas phase. The resistance exerted by the membranes becomes the controlling step for the mass transfer only at high gas flow rate.

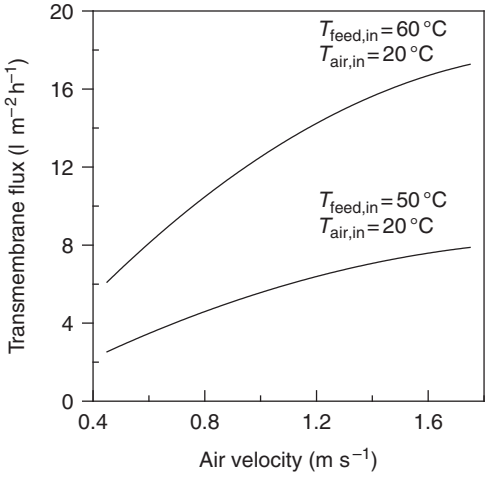


Figure 10 Transmembrane flux of water vs. sweeping air velocity (test on pure water) in SGMD.

4.01.7.3 Air Gap Membrane Distillation

In this configuration, a stagnant air gap is interposed between the membrane and a cooling (metallic) surface in the permeate side. Molecules evaporating from the feed side cross the membrane and the air layer, and finally condense on the metallic surface (**Figure 11**).

Among the four MD configurations described, AGMD exhibits the lowest driving force at constant feed temperature (and, consequently, the lowest transmembrane flux) due to the additional resistance to mass transport represented by the air gap. The rather complicated design and construction of the module (due to the presence of the cooling surface) is an additional drawback of AGMD, and applications are practically limited to the use of plate-and-frame or spiral-wound membrane modules.

For water diffusing through a stagnant air gap, the molar flux can be expressed by Equations (15a)–15(d) modified in order to take into account of some structural parameters such as porosity (ε), thickness (δ), tortuosity (τ), and air gap thickness (β):

$$\mathcal{J} = \frac{\varepsilon D_{water,air}}{RT|p|_{m,ln}}\left[\frac{1}{\delta\tau + \beta}\right]\Delta p \tag{30}$$

The effects of feed temperature and flow rate are similar to those described in Section 4.01.7.1 for DCMD. Theoretical and experimental studies

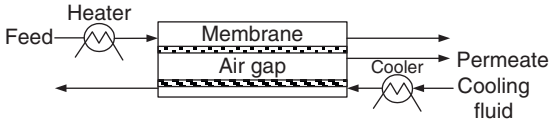


Figure 11 Scheme of air gap membrane distillation (AGMD).

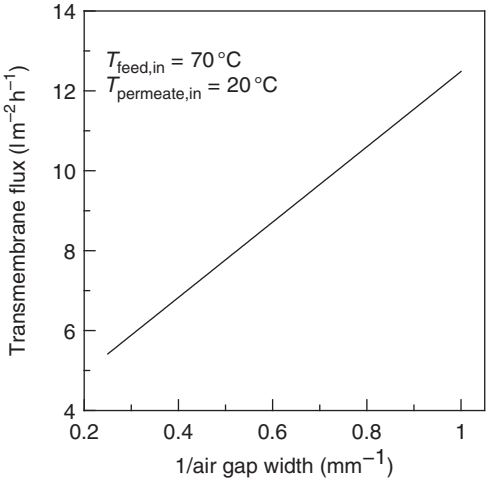


Figure 12 Effect of air gap width on the transmembrane flux (test on pure water) in AGMD.

specifically dedicated to SGMD [60, 61] demonstrate a linear correlation between the flux and the reciprocal of the air gap width (**Figure 12**).

4.01.7.4 Vacuum Membrane Distillation

In vacuum membrane distillation, vacuum is applied in the permeate side, and the condensation of molecules takes place outside the module (**Figure 13**). Among the four MD configurations described, VMD exhibits the highest driving force at constant feed temperature and, therefore, the highest transmembrane flux.

In VMD, assuming that the mass transfer through the membrane is dominated by Knudsen diffusion mechanism, the molar flux $\mathcal{J}_i$ of a permeating ith species is linearly related to the partial pressure gradient Δp across the membrane. The total molar flux $\mathcal{J}_t$, sum over all the components, can be expressed as

$$\mathcal{J}_t = \frac{K_m}{\sqrt{M}}\Delta p \qquad (31)$$

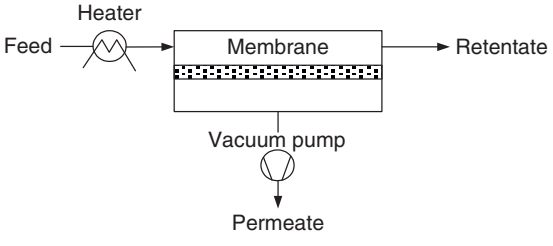


Figure 13 Scheme of vacuum membrane distillation (VMD).

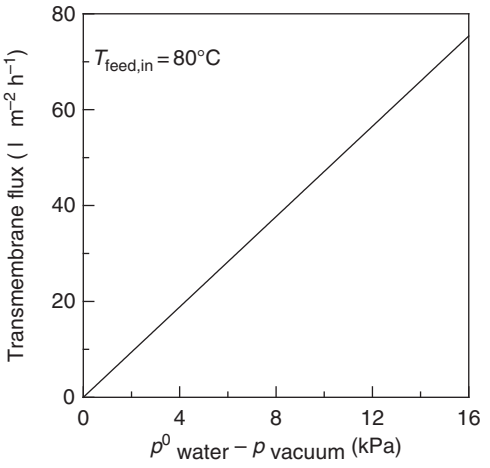


Figure 14 Effect of the VMD driving force (difference between the water vapor pressure and the pressure at vacuum side) on the transmembrane flux (test on pure water).

where K_m is a permeability coefficient that depends on the membrane properties and temperature, and M is an average molecular weight in the permeating stream, evaluated as [37]

$$\sqrt{M} = \sum_i \frac{\mathcal{J}_i}{\mathcal{J}_t}\sqrt{M_i} \qquad (32)$$

where $\mathcal{J}_t$ is the total flux across the membrane.

The transmembrane flux is enhanced when the pressure of the permeate side decreases; the linear trend of $\mathcal{J}$ versus the driving force is shown in **Figure 14**.

4.01.7.5 Osmotic Distillation

OD is a concentration technique for aqueous mixtures in which a volatile component (commonly water) is removed from the feed side by using a hypertonic solution flowing downstream a microporous hydrophobic membrane. Vapor diffuses through the membrane pores under a driving force given by the vapor pressure difference between both membrane sides generated by the different activities of feed and permeate streams (**Figure 15**).

OD is not an athermal mass transfer operation: transport involves an evaporation at the feed side and a condensation at the stripping side. A temperature difference at the membrane interfaces is thus created, even if the bulk temperatures of the two liquids are equal. In general, the temperature difference in aqueous systems is lower than 1 °C, leading to a negligible decrease of the vapor flux.

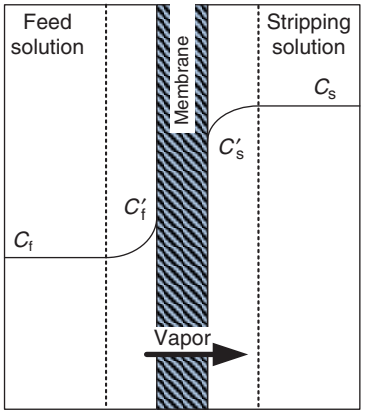


Figure 15 Concentration profile in osmotic distillation (OD) (C_f: solute concentration in the bulk of the feed side; C'_f: solute concentration at the membrane interface of the feed side; C_s: concentration of the stripping component in the bulk; C'_s: concentration of the stripping at the membrane interface).

Assuming a simplified approach, the transmembrane flux can be expressed in terms of membrane permeability K_m, partial pressures p'_{water} at feed (1) and stripping (2) fluid–membrane interfaces, and log mean pressure of air entrapped into pores $\bar{p}_{air}$:

$$\mathcal{J} = K_m \frac{p'_{water\ 1} - p'_{water\ 2}}{\bar{p}_{air}} \tag{33}$$

Referring to a series expansion cut at the first-order term, and assuming that the temperature difference through the membrane is small, the following relationship can be derived [62]:

$$\mathcal{J} = \frac{K_m}{\bar{p}_{air}} \left\{ p^0_w(\bar{T}) \cdot [a'_{water\ 1} - a'_{water\ 2}] - a_{water}(\bar{T}) \cdot \left[\frac{dp^0_{water}}{dT} \right]_{\bar{T}} \times (T_2' - T_1') \right\} \tag{34}$$

where p^0_{water} is the water vapor pressure, a'_{water} is the water activity at the membrane interface, and $\bar{T}$ is the average temperature through the membrane.

Film-theory model can be used to describe the mass transport through boundary layers:

$$\mathcal{J} = k_x \rho \frac{a_{water} - a'_{water}}{\xi_{water} \bar{x}} \tag{35}$$

assuming that water activity coefficients ξ_{water} are constant in the layers; $\bar{x}$ is the logarithmic mean value of solute molar fraction, k_x the mass transfer coefficient, and ρ the solution density. Apex refers to value at the membrane interface. Some useful empirical correlations for k_x are reported in **Table 6**.

Temperature and activity gradients can act in a synergistic way, or can operate in an antagonistic way to each other. Heat transfer phenomena are described as in MD operations. The salts chosen as osmotic pressure agents are in general NaCl, $MgCl_2$, $CaCl_2$, and $MgSO_4$, due to their relatively low cost [66]; in same cases, organic liquids (glycerol and polyglycols) are preferred [67]. In osmotic evaporation carried out at room temperature, transmembrane fluxes generally range between 0.2 and 1 l m^{-2} h^{-1} [68] and increase at higher stripping solution concentration (**Figure 16**).

4.01.8 Applications

4.01.8.1 Water Purification

The production of demineralized water for drinking purposes represents today an promising MD application. In 1982, Gore proposed the use of two different MD membrane modules for desalting NaCl aqueous solutions: a plate-and-frame module (production rate: 7 l m^{-2} h^{-1}, $T_{feed} = 30\,^{\circ}C$,

Table 6 Examples of empirical correlations for mass transfer coefficient in OD

Correlation	*α*	*β*	*γ*	k_x *(10^{-5} m s^{-1})*	*Comment*	*Reference*
$k_x = \omega^y$	-	-	1.09±0.17	54÷78.10^{-3}	ω = 0–350rpm aqueous NaCl solution 0.5–5M	[63]
$Sh = \alpha Re^{\beta} Sc^{\gamma}$	1.62(shell) 1.86(tube)	0.33	0.33	-	Shell: water–sucrose 0–70wt.% Tube: water–$CaCl_2$:26–40wt.%	[64]
$Sh = \alpha Re^{\beta} Sc^{\gamma}$	1.86	0.33	0.33	k_f = 0.17;0.9;0.37	For NH_3, SO_2, H_2S:1–20 10^{-3} M	[65]

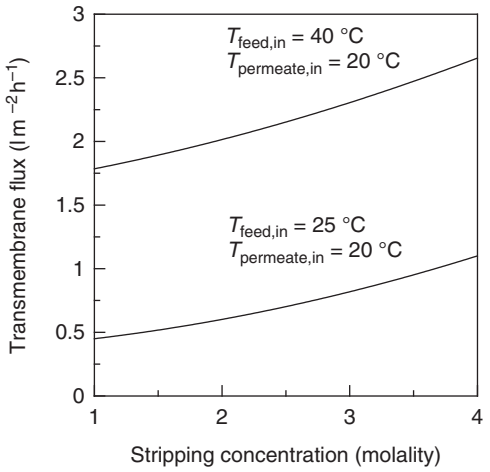


Figure 16 Transmembrane flux vs. stripping concentration (feed: 1 wt.% NaCl) in osmotic distillation (OD).

$T_{distillate}$= 20 °C) and a spiral-wound module (production rate: 3 l m^{-2} h^{-1}, T_{feed} = 30 °C, $T_{distillate}$= 20 °C) in AGMD configuration [69]. Few years later, papers related to the use of MD in desalination processes increased exponentially. More recently, DCMD using PTFE microporous membranes was considered by Godino *et al.* [70]: their work investigated the influence of temperature, fluid dynamics, and salt concentration of the system efficiency. According to the obtained results, transmembrane flux doubled when the retentate temperature was increased from 30 to 50 °C, while flux decreased of about 20% when feed concentration increased from 0.5 to 2.0 mol l^{-1}.

The experimental analysis of Lawson and Lloyd [56] indicated that DCMD is a viable process for seawater desalination, with fluxes reaching up to 2.0 mol m^{-2} s^{-1} (two times higher than in SWRO) working at feed temperature of 75 °C and distillate temperature of 20 °C. On the other hand, the work of Schneider *et al.* [71] stated that thermal MD for seawater desalination is not energetically competitive against large-scale multi-effect evaporators. Small and portable desalination units utilizing waste heat, which are simple in design and afford easy access, have been identified as market niches for MD.

Today, the interest of using MD process coupled with solar energy or utilizing low-grade heat source for desalination is increasing worldwide. Already in 1991, the combined use of DCMD and solar energy was theoretically investigated by Morrison *et al.* [72] by combining a mathematical model of MD with TRNSYS solar simulation system. More recently, the sensitivity of the permeate flux on the brine temperature, flow rate, salt concentration, and solar irradiation was evaluated by Banat *et al.* [73].

In 2004, researchers at the University of Texas at El Paso (UTEP) in collaboration with the Swedish firm SCARAB DEVELOPMENT AB [74] investigated methods for coupling solar pond technology with MD desalination to create a zero discharge. Coupling MD with solar energy is also the basic concept of FP6 MEDESOL (Seawater Desalination by Innovative Solar-Powered Membrane Distillation System) project; the goal is to develop an environmentally friendly desalination technology for fresh water supply in arid and semi-arid regions. The layout involves the concept of multi-step MD, to be implemented in the solar platform of Almeria (Spain), in order to minimize specific energy and membrane area required [75].

The MEDIRAS (MEmbrane DIstillation in Remote AreaS) project aims at optimizing a solar desalination system applicable for small distributed desalination systems in the capacity range between 0.1 and 20 m^3 d^{-1} (a scheme is illustrated in **Figure 17**). MD technology is claimed to be very robust against different raw water conditions and suitable for operation with solar energy [76].

The SMAll-scale, stand-alone DEsalination System (SMADES system) was designed to provide potable water in remote coastal areas with low infrastructure and without connection to a grid. The desalination units were based on MD modules with internal heat recovery function; the required energy was supplied by solar thermal collectors in the form of heat on a temperature level of 60–80 °C with 72 m^2 of collector area and a solar heat storage water tank of 3 m^3. The electrical auxiliary energy required to drive the pumps and valves was supplied by photovoltaic (PV) panels [77]. Memstill® is a recently developed membrane-based distillation concept, claimed to have the potential to improve the economy and ecology of existing desalination technologies for seawater and brackish water to a large extent (**Figure 18**). This technology combines MSF and MED modes into AGMD configuration. The process promised to decrease desalination costs to 0.26$ m^{-3}, using low-grade waste steam or heat as driving force [78].

The integration of DCMD and/or solar-powered VMD with conventional pressure-driven

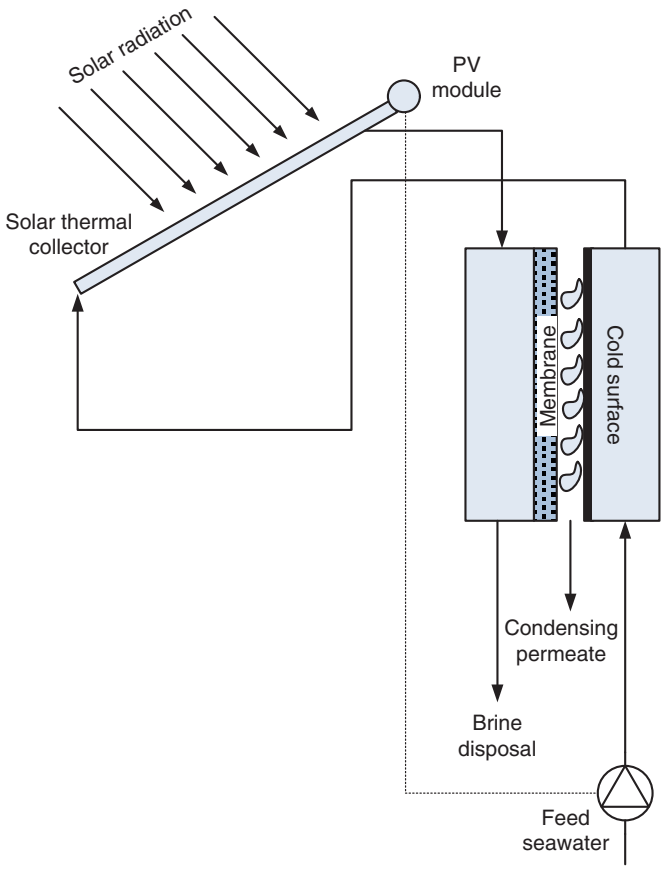


Figure 17 Conceptual scheme of the membrane distillation (MD) compact desalination system.

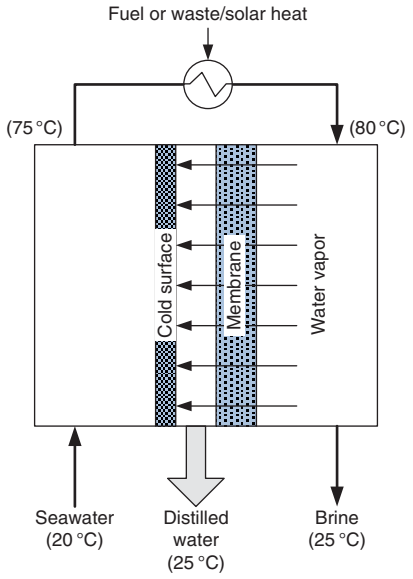


Figure 18 Conceptual scheme of Memstill desalination system.

membrane operations (such as MF, UF, NF, RO, and MBR) is one of the key issues of the MEDINA (MEmbrane Desalination Systems: an INtegrated Approach) project, implemented by a consortium of 14 partners, aimed to limit the brine disposal problem and to drastically enhance the water recovery factor [79].

4.01.8.2 Wastewater Treatment

MD has been tested for the recovery of HCl from acidic spent solutions generated by cleaning of electroplated surfaces. Concentration experiments, carried out at inlet feed and distillate temperatures of 70 and 20 °C, respectively, resulted in a solution with concentration of $\sim$100 g HCl dm^{-3}; the volumetric permeate flux progressively decreased from 80 to 40 $dm^3\,m^{-2}\,d^{-1}$ [80].

The possibility to remove heavy metals from wastewater has been investigated by Zolotarev

et al. [81]. In particular, a rejection coefficient close to unity was obtained by treating aqueous solutions of nickel sulfate in the range of 0.1–3.0 N.

MD process has been used to concentrate sulfuric acid obtained after apatite phosphogypsum extraction used to recover lanthane compounds. The concentration process was protracted up to 40% of H_2SO_4; lanthane compounds were then precipitated by cooling [82].

MD has also been investigated as treatment method for radioactive liquid wastes, generated from the nuclear industry, or by other end user of radioactive materials (hospitals, nuclear R&D centres, etc.).

MD was successfully applied also to textile wastewater contaminated with dyes [52]. The dependence of distillate fluxes, rejection, and polarization phenomena on the retentate concentration, operation temperatures, and axial flow rates suggested the opportunity of integrate MD operation in a production cycle with RO preconcentration stage. Gryta *et al.* [83] proposed a combination of ultrafiltration (UF) and MD to treat oily wastewater. Results showed that the permeate obtained from the UF process generally contains less than 5 ppm of oil. Further purification of the UF permeate by MD results in a complete removal of oil from wastewater and a very high reduction of the total organic carbon (99.5%) and total dissolved solids (99.9%).

MD operating under vacuum is an effective method for removing volatile organic components from dilute aqueous solutions such as acetone and isopropanol, ethanol, methylterbutylether, ethylacetate, methylacetate, and benzene traces from contaminated water.

The ability of microporous hydrophobic membranes to strip chloroform, tetrachloroethylene, carbon tetrachloride, 1,1,2-trichloroethane, and trichloroethylene from aqueous solutions has also been verified [84].

High volume reduction and decontamination factors (~4300 for ^{60}C, ~44 for ^{137}Cs, $\rightarrow \infty$ for other investigated compounds) have been reached by MD, as well as significant rejection values toward nuclides such as tritium or some forms of iodine and ruthenium [85].

Zakrzewska-Trznadel *et al.* [86] also observed the existence of a diffusion isotope effect in MD that enhances the separation factor for H_2O/DHO and $H_2^{16}O/H_2^{18}O$ enrichment.

4.01.8.3 Concentration of Agro-Food Solutions

Low-temperature MD operations (including OD) are of potential interest in the food industry, where the most part of substances are sensitive to thermal treatments. With respect to standard concentration methods, involving a significant energy consumption and often determining a partial degradation of the organoleptic properties, MD represents a competitive alternative, able to increase the quality of concentrates. DCMD was successfully tested in the concentration of many fruit juices: orange [87], apple [30], sugarcane [88], kiwifruit [89], etc.

The technical feasibility to concentrate the must by VMD was considered by Bandini and Sarti [90], with the objective of increasing the alcoholic potential, while preserving quality and quantity of the aromas. The concentration levels (50–60 °Brix) were significantly higher than those achieved by RO. On the other hand, MD fluxes were in the range of 1–3 l m^{-2} h^{-1} at low concentration and moderate temperatures, significantly lower than those experienced by using RO (10–15 l m^{-2} h^{-1}). A loss in taste and flavors of the concentrate juice was also observed, due to the evaporative nature of MD process.

The possibility to operate OD at room temperature makes this process more attractive than MD itself. For the preparation of the striping solution, a number of salts are suitable ($CaCl_2$, $MgCl_2$ etc.); recently, potassium salts of ortho- and pyrophosphoric acid have gained in interest due to their safe use in foods [91, 92]. Flavor and fragrance compounds can be conveniently preserved in OD concentration process, mainly because of the low temperature used; in addition, they have high molecular weights and, consequently, a low diffusive permeability through the membrane.

The integration of UF, RO, and OD units has been tested in fruit juice concentration in order to obtain high recovery factors. The investigations carried out in Melbourne (Australia) during the last few years have shown the potentiality of the membrane system for the production of grape juice concentrate and dealcoolized wine ferments; an optimized pilot plant has also been developed for the treatment of viscous concentrates [93]. The use of integrated membrane processes for the clarification and concentration of citrus (orange and lemon) and carrot juices has also been proposed [94]. A limpid phase obtained by ultrafiltration of

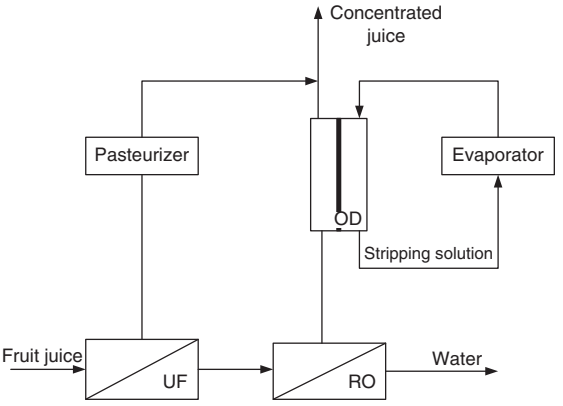


Figure 19 Integrated membrane system for fruit juice concentration.

the raw juice is concentrated up to 15–20 g TSS/100 g by RO. Finally, OD is operated on the RO retentate that increases its concentration up to 60–63 g TSS/100 g at an average transmembrane flux of $\sim 1\,kg\,m^{-2}\,h^{-1}$. A little decrease of the total antioxidant activity (TAA) has been observed during the RO treatment, probably due to the mechanical stress induced by the high operative pressure. Further analyses have shown that the subsequent treatment by OD did not induce any significant change to TAA independently of the final concentration achieved (**Figure 19**).

4.01.8.4 Concentration of Biological Solutions

MD has been applied in the concentration of biological solutions in order to selectively extract volatile solutes or solvents.

MD has been applied by Capuano *et al.* [95] to purify physiological solutions produced during treatments of patients affected by chronic renal failure. The aim of the work was to recover at the permeate side the patient's own water, purified from toxins, and to re-inject it to patient after addition of electrolytes, therefore avoiding the use of external water that could lead, with time, to inflammatory problems. During all experimental tests performed on microporous polypropylene membranes, water at the permeate side was toxins free.

Blood and plasma treatment by MD was considered in order to obtain a solute-free extraction of water from biomedical solutions without loss in quality[96].

References

[1] Curcio, E., Drioli, E. *Sep. Purif. Rev.* **2005**, *34*, 35–86.
[2] Gálvez, J. B., García-Rodríguez, L., Martín-Mateos, I. *Desalination* **2009**, *246*, 567–576.
[3] Hengl, N., Mourgues, A., Pomier, E. *et al. J. Membr. Sci.* **2007**, *289*, 169–177.
[4] Zubir, N. A., Ismail, A. F. *Songklanakarin J. Sci. Technol.* **2002**, *24*, 823–831.
[5] Gore R. W. Very Highly Stretched Polytetrafluoroethylene and Process Therefor. US Pat. 3,962,153, 8 June 1976.
[6] Ortiz de Zarate, J. M., Pena, L., Mengual, J. I. *Desalination* **1995**, *100*, 139–148.
[7] Tomaszewska, M. *Desalination* **1996**, *104*, 1–11.
[8] Feng, C., Shi, B., Li, G., Wu, Y. *J. Membr. Sci.* **2004**, *237*, 15–24.
[9] Fontananova, E., Jansen, J. C., Cristiano, A., Curcio, E., Drioli, E. *Desalination* **2006**, *192*, 190–197.
[10] Bottino, A., Capannelli, G., Munari, S., Turturro, A. *Desalination* **1988**, *68*, 167.
[11] Arcella, V., Colaianna, P., Maccone, P., *et al. J. Membr. Sci.* **1999**, *163*, 203–209.
[12] Feng, C., Shi, B., Li, G., Wu, Y. *Sep. Purif. Technol.* **2004**, *39*, 221–228.
[13] Xu, J. B., Lange, S., Bartley, J. P., Johnson, R. A. *J. Membr. Sci.* **2004**, *240*, 81–89.
[14] Wu, Y., Kong, Y., Lin, X., Liu, W., Xu, J. *J. Membr. Sci.* **1992**, *72*, 189–196.
[15] Favia, P., D'Agostino, R. *Surf. Coat. Technol.* **1998**, *98*, 1102–1106.
[16] Kong, Y., Lin, X., Wu, Y., Chen, J., Xu, J. *J. Appl. Polym. Sci.* **1992**, *46*, 191–199.
[17] Khayet, M., Mengual, J. I., Matsuura, T. *J. Membr. Sci.* **2005**, *252*, 101–113.
[18] Khayet, M., Suk, D. E., Narbaitz, R. M., Santerre, J. P., Matsuura, T. *J. Appl. Polym. Sci.* **2003**, *89*, 2902–2916.
[19] Lawson, K. W., Lloyd, D. R. *J. Membr. Sci.* **1997**, *124*, 1–25.
[20] Reed, B. W., Semmens, M. J., Cussler, E. L. Membrane Contactors. In: *Membrane Separation Technology. Principles and Applications*; Elsevier: Amsterdam, 1995; vol. 2, pp 467–498.
[21] Schneider, K., Holz, W., Wollbeck, R. *J. Membr. Sci.* **1988**, *39*, 25–42.
[22] Courel, M., Tronel-Peyroz, E., Rios, G. M., Dornier, M., Reynes, M. *Desalination* **2001**, *140*, 15–25.
[23] Troger, J., Lunkwitz, K., Burger, W. *J. Colloid Interface Sci.* **1997**, *194*, 281–286.
[24] Abrams, D. S., Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116–128.
[25] Prausnitz, J. M. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1969.
[26] Sarti, G. C., Gostoli, C., Bandini, S. *J. Membr. Sci.* **1993**, *80*, 21–33.
[27] Schofield, R. W. Membrane Distillation. PhD Thesis, The University of New South Wales, 1989.
[28] Courel, M. Etudes des transferts de matière en évaporation osmotique: Application a la concentration des jus de fruits. PhD Thesis, University of Mompelier, 1999.
[29] Reid, R. C., Prausnitz, J. M., Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd edn.; McGraw-Hill: New York, 1977.
[30] Laganà, F., Barbieri, G., Drioli, E. *J. Membr. Sci.* **2000**, *166*, 1–11.
[31] Gekas, V., Hallstrom, B. *J. Membr. Sci.* **1987**, *30*, 153–170.
[32] Bird, R. B., Stewart, W. E., Lightfoot, E. N. *Transport Phenomena*, 2nd edn.; Wiley: New York, 2007.

[33] Bandini, S., Gostoli, C., Sarti, G. C. *J. Membr. Sci.* **1992**, *73*, 217–229.
[34] Sudoh, M., Takuwa, K., Iizuka, H., Nagamatsuya, K. *J. Membr. Sci.* **1997**, *131*, 1–7.
[35] Tomaszewska, M., Gryta, M., Morawski, A. W. *J. Membr. Sci.* **1995**, *102*, 113–122.
[36] Costello, M. J., Hogan, P. A., Fane, A. G. *Proceedings of Euromembrane '97*, Twente, The Netherlands, 23–27 June 1997.
[37] Lawson, K. W., Lloyd, D. R. *J. Membr. Sci.* **1996**, *120*, 111–121.
[38] Kast, W., Hohenthanner, C. R. *Int. J. Heat Mass Transfer* **2000**, *43*, 807–823.
[39] Mason, E. A., Malinauskas, A. P. *Gas Transport in Porous Media: The Dusty-Gas Model*; Elsevier: New York, 1983.
[40] Schofield, R. W., Fane, A. G., Fell, C. J. D. *J. Membr. Sci.* **1987**, *33*, 299–313.
[41] Martinez, L., Vazquez-Gonzalez, M. I. *J. Membr. Sci.* **2000**, *173*, 225–235.
[42] Gryta, M., Tomaszewska, M., Morawski, A. W. *Sep. Purif. Technol.* **1997**, *11*, 93–101.
[43] Gryta, M., Tomaszewska, M. *J. Membr. Sci.* **1998**, *144*, 211–222.
[44] Rimura, S., Nakao, S. *J. Membr. Sci.* **1987**, *33*, 285–298.
[45] McCabe, W. L., Smith, J. C., Harriot, P. *Unit Operations of Chemical Engineering*, 4th edn.; McGraw-Hill: New York, 1985.
[46] Ozisik, M. N. *Heat Transfer*; McGraw-Hill: New York, 1985.
[47] Mengual, J. I., Khayet, M., Godino, M. P. *Int. J. Heat Mass Transfer* **2004**, *47*, 865–875.
[48] Perry, R. H. *Perry's Chemical Engineering Handbook*, 6th edn.; McGraw-Hill: Singapore, 1984.
[49] de Andrés, M. C., Dria, J., Khayet, M., Pena, L., Mengual, J. I. *Desalination* **I998**, *115*, 71–81.
[50] Fane, A. G., Schofield, R. W., Fell, C. J. D. *Desalination* **1987**, *64*, 231–243.
[51] Martinez-Diez, L., Florido-Diaz, F. J., Vasquez-Gonzalez, M. I. *Desalination* **1999**, *126*, 193–198.
[52] Calabrò, V., Drioli, E., Matera, F. *Desalination* **1991**, *83*, 209–224.
[53] Warner, S. B. *Fiber Science*; Prentice-Hall: Englewood Cliffs, NJ, 1995.
[54] Schofield, R. W., Fane, A. G., Fell, C. J. D. *J. Membr. Sci.* **1990**, *53*, 173–185.
[55] Brandrup, J., Immergut, E. H. *Polymer Handbook*, 3rd edn.; Wiley: New York, 1989.
[56] Lawson, K. W., Lloyd, D. R. *J. Membr. Sci.* **1996**, *120*, 123–133.
[57] Drioli, E., Wu, Y. *Desalination* **1984**, *53*, 339–346.
[58] Basini, I., D'Angelo, G., Gobbi, M., Sarti, G. C., Gostoli, C. *Desalination* **1987**, *64*, 245–257.
[59] Khayet, M., Godino, M. P., Mengual, J. I. *Desalination* **2003**, *157*, 297–305.
[60] Banat, F. A., Simandl, J. *Desalination* **1994**, *95*, 39–52.
[61] Bouguecha, S., Chouikh, R., Dhahbi, M. *Desalination* **2002**, *152*, 245–252.
[62] Celere, M., Gostoli, C. *Desalination* **2002**, *147*, 133–138.
[63] Mengual, J. I., Ortiz de Zarate, J., Pena L., Velazquez, A. *J. Membr. Sci.* **1993**, *82*, 129–140.
[64] Hogan, P. A. Thermal and Isothermal Membrane Distillation. PhD Thesis, University of New South Wales, 1996.
[65] Zhang, Q., Cussler, E. L. *AIChE J.* **1985**, *31/9*, 1548–1553.
[66] Sheng, J. *Aust. Chem. Eng. Conf.* **1993**, *3*, 429–432.
[67] Gryta, M. *J. Membr. Sci.* **2005**, *246*, 145–156.
[68] Kunz, W., Benhabiles, A., Ben-Aim, R. *J. Membr. Sci.* **1996**, *121*, 25–36.
[69] Gore, D. W. *Proceedings of the Tenth Annual Conference of the Water Supply Improvement Association*, Honolulu, HI, USA, 25–29 July 1982.
[70] Godino, M. P., Pena, L., Rincon, C., Mengual, J. I. *Desalination* **1996**, *108*, 91–97.
[71] Schneider, K., Holz, W., Wollbeck, R., Ripperger, S. *J. Membr. Sci.* **1988**, *39*, 25–42.
[72] Morrison, G. L., Fane, A. G., Hogan, P. *Proceedings of the Biennal Congress of ISES*, Denver, CO, USA, 19–23 August 1991.
[73] Banat, F., Jumah, R., Garaibeh, M. *Renew. Energy* **2002**, *25*, 293–305.
[74] Scarab Development AB, http://www.scarab.se (accessed February 2010).
[75] Plataforma Solar de Almeria, MEDESOL Project, http://www.psa.es/webeng/projects/medesol/index.html (accessed February 2010).
[76] Mediras, http://www.mediras.eu (accessed February 2010).
[77] Banat, F., Jwaied, N., Rommel, M., Koschikowski, J., Wieghaus, M. *Desalination* **2007**, *217*, 29–37.
[78] Hanemaaijer, J. H., van Medevoort, J., Jansen, A. E., Dotremont, C., van Sonsbeek, E. *Desalination* **2006**, *199*, 175–176.
[79] MEDINA (Membrane-Based Desalination an Integrated Approach), http://medina.unical.it (accessed February 2010).
[80] Tomaszewska, M., Gryta, M., Morawski, A. W. *Sep. Purif. Technol.* **2001**, *22/23*, 591–600.
[81] Zolotarev, P. P., Ugrozof, V. V., Yolkina, I. B., Nikulin, V. N. *J. Hazard. Mater.* **1994**, *37*, 7–82.
[82] Tomaszewska, M. *J. Membr. Sci.* **1993**, *78*, 277–282.
[83] Gryta, M., Karakulski, K., Morawski, A. W. *Water Res.* **2001**, *35*, 3665–3669.
[84] Semmens, M. J., Qin, R., Zander, A. *J. Am. Water Works Assn.* **1989**, *81*, 162–167.
[85] Zakrzewska-Trznadel, G., Harasimowicz, M., Chmielewski, A. G. *J. Membr. Sci.* **1999**, *163*, 257–264
[86] Zakrzewska-Trznadel, G., Chmielewski, A. G., Miljevic, N. R. *J. Membr. Sci.* **1996**, *113*, 337–342.
[87] Drioli, E., Jiao, B. L., Calabrò, V. *Proc. Int. Soc. Citriculture* **1992**, *3*, 1140–1144.
[88] Nene, S., Kaur, S., Sumod, K., Joshi, B., Raghavarao, K. S. M. S. *Desalination* **2002**, *147*, 157–160.
[89] Cassano, A., Figoli, A., Tagarelli, A., Sindona, G., Drioli, E. *Desalination* **2006**, *189*, 21–30.
[90] Bandini, S., Sarti, G. C. *Desalination* **2002**, *149*, 253–259.
[91] Hogan, P. A., Canning, R. P., Peterson, P. A., Johnson, R. A., Michaels, A. S. *Chem. Eng. Prog.* **1998**, *94*, 49–61.
[92] Sirkar, K. K. *Chem. Eng. Commun.* **1997**, *157*, 145–184.
[93] Bailey, A. F. G., Barbe, A. M., Hogan, P. A., Johnson, R. A., Sheng, J. *J. Membr. Sci.* **2000**, *164*, 195–204.
[94] Cassano, A., Drioli, E., Galaverna, G., Marchelli, R., Di Silvestro, G., Cagnasso, P. *J. Food Eng.* **2003**, *57*, 153–163.
[95] Capuano, A., Memoli, B., Andreucci, V. E., Criscuoli, A., Drioli, E. *Int. J. Artif. Org.* **2000**, *23*, 415–422.
[96] Sakai, K., Muroi, T., Ozawa, K., Takesawa, S., Tamura, M., Makane, T. *Trans. Am. Soc. Artif. Intern. Org.* **1986**, *32*, 397–400.

Biographical Sketches

Efrem Curcio – Born in Cosenza (Italy) in 1975.
Educational background – 1999 Masters Degree in Chemical Engineering. 2005 PhD in Chemical Engineering and Materials. 2005-present. Assistant Professor at the University of Calabria – Faculty of Engineering, and Research associate at the Institute on Membrane Technology ITM-CNR.
Research topics – Integrated membrane systems for desalination and water treatment.
– Membrane-crystallization devices: applications in structural proteomics, polymorphs and enantiomers selection.
– Design and modelling of membrane bioreactors for cells culture. Recipient of the EMS Award 2004 for the best published paper in Membrane Science and Engineering. A member of the European Membrane Society, the American Filtration Society, and Instituto Nazionale Scienza e Tecnologie dei Materiali (INSTM). A Referee of the Journal of Membrane Science, Desalination, the Journal of Biotechnology, Separation and Purification Technology (all Elsevier), and the Journal of Crystal Growth and Design (ACS). A member of the Editorial Board of The Open Proteomic Journal (Bentham Open).
Publications – Author of 53 papers published in international Journals, one book published by Elsevier, and around 80 contributions in congress proceedings, predominantly international.

Dr. Gianluca Di Profio is a researcher at the Institute on Membrane Technology (ITM) of the Italian National Research Council (CNR). Graduated in physical chemistry in 2001 from the University of Calabria, he obtained his PhD in 2007 at the Chemical and Materials Engineering Department, working on the crystallization of organic materials by using membrane technology.

A tutor in chemistry at the Engineering Faculty of the University of Calabria, from 2001 to 2009, he was also worked at Akzo Nobel Chemicals Research Arnhem, the Netherlands. He was awarded the 'European Membrane Society Award 2004' for the best published paper in membrane science and engineering.

His main research activities relate to: study of phase transitions occurring in membrane operations; membrane contactor technology; membrane crystallization processes; integrated membrane systems for water treatments; membrane bioreactors and submerged membrane operations for water purification.

He is the coauthor of more than 35 scientific papers on membrane science and technology published in international journals and of more than 70 contributions to scientific conferences.

4.02 Membrane Crystallization Technology

G Di Profio, Institute on Membrane Technology, ITM-CNR, at University of Calabria, Rende (CS), Italy

E Curcio, University of Calabria, Arcavacata di Rende (CS), Italy

E Drioli, Institute of Membrane Technology, ITM-CNR, University of Calabria, Rende (CS), Italy

Glossary

Activity A measure of the interaction between different molecules in a nonideal gas or solution.

Antisolvent One or a combination of more fluids, which differs in chemical composition from the solvent, which, when mixed with the crystallizing solution, lowers the solubility of the material of interest.

Brine Water solution with a high concentration (typically saturated) of salts.

Concentration polarization Accumulation of retained components in proximity of the membrane surface during a membrane separation process. It is a reversible process and influences the retention that can decrease (especially with low-molecular-weight solutes) or increase (this is particularly true for mixtures of macromolecular solutes); moreover, the flux is always reduced by concentration polarization phenomena.

Convective flow The movement of particles forced by the action of a fluid.

Crystallizing solution A solution comprising the substance of interest to be crystallized which is solubilized in the solvent to form a homogeneous solution.

Electrochemical potential The sum of the chemical and electrical potentials for a component which, in the presence of a gradient of the electrochemical potential, tend to move from areas with higher electrochemical potential to areas with lower electrochemical potential. It is expressed with units of energy (usually J mol^{-1}).

Entry pressure limit Value of pressure in correspondence of which a solution contacting a porous membrane will flood the pores of the membrane and pass into the other side, thereby permeating in liquid phase.

Feed Liquid or gaseous stream submitted to a membrane process.

Hydrophobic membrane A membrane which exerts a tendency to repeal water or aqueous solutions. When a droplet of water or a droplet of an aqueous solution is deposited on the surface of the membrane or in any site inside the pores of the membrane, the contact angle between the said droplet and the membrane according to the present invention forms an angle higher than 90°.

Integrated membrane system Integration of various membrane operations in the same process, with overall important benefits in product quality, plant compactness, environmental impact, and energetic aspects. This term is also used to

indicate the integration of a membrane operation with a traditional one in a process.

Knudsen flow Transport mechanism of gases through porous membranes occurring when the mean free path of the molecules is similar or larger than the pore size.

Laminar flow The streamlined flow of a viscous incompressible fluid in which all particles of the fluid travel along distinct and separate lines. This flow regime is characterized by high momentum diffusion, low momentum convection, and pressure and velocity independence from time.

Mean free path The average distance the particle travels between their collisions with other particles.

Membrane contactors Membrane process in which a membrane facilitates the diffusive mass transfer between two contacting phases (liquid–liquid, gas–liquid, gas–gas, etc.) without dispersion of one phase within another. The membrane function in a membrane contactor is to create and sustain the interfaces immobilized at the mouth of the pores.

Membrane crystallization Membrane process in which volatile solvents (usually water) evaporate through microporous hydrophobic membranes in order to concentrate feed solutions above their saturation limit, thus attaining a supersaturated environment where crystals may nucleate and grow. The driving force of the process is a vapor pressure gradient.

Membrane distillation Membrane process where a microporous hydrophobic membrane is in contact with an aqueous heated solution. The hydrophobic nature of the membrane prevents the transport in liquid phase and creates a vapor–liquid interface at the entrance of each pore. Here, volatile compounds (typically water) evaporate, diffuse, and/or convect across the membrane, and are condensed and/or removed on the permeate or distillate side. The process is activated by a vapor pressure gradient across the membrane.

Polymorphs Different crystalline or noncrystalline structures of a solid material. It includes the amorphous form and various solvate, hydrate forms commonly referred to as pseudo-polymorphs. Different polymorphs have different free energy associated with them.

Process intensification It is one of the most interesting strategies offered today for realizing a sustainable industrial growth compatible with a desirable high quality of our life. It consists of innovative equipment, design, and process development methods that are expected to bring substantial improvements in chemical and any other manufacturing and processing, such as decreasing production costs, equipment size, energy consumption, waste generation, and improving remote control, information fluxes, and process flexibility.

Retentate The part of the feed stream which does not pass through the membrane.

Scale-up Design process in which the data of an experimental-scale operation (model or pilot plant) are used for the design of a large (scaled-up) unit, usually of commercial size.

Solubility The amount of a solute that will dissolve in a specific solvent under given conditions.

Supersaturation The ratio between the effective concentration of a solute dissolvent in a solution and its solubility in those conditions.

Nomenclature

a	activity
A	pre-exponential kinetic parameter
A_{12}	nucleus/solution interface area
A_{23}	solution/substrate interface area
A_m	membrane area
B	growth rate
c	liquid molar density
C_a	concentration of heterogeneous particles
G	variation of the Gibbs free energy
D_i^k	Knudsen diffusion coefficient
F	Faraday's constant
I	ionic strength
J	transmembrane flux
k_B	Boltzmann's constant
MW	molecular weight
n	number of moles
n^*	critical nucleus size
n_P	number of pores in the membrane
N	stationary nucleation rate
p	partial pressure
P	hydrostatic pressure

P_{entry}	entry pressure limit	γ	interface energy
r	curvature radius	γ_L	liquid surface tension
r_P	pore radius	Δa	activity gradient
R	gas constant	Δp	vapor pressure gradient
S	supersaturation	ΔT	temperature gradient
t	time	Δz	thickness of the membrane
t_{ind}	induction times	ϵ	overall surface porosity
T	absolute temperature	λ	latent heat of vaporization
T_{cry}	crystallization temperature	μ	electrochemical potential
T_{feed}	feed temperature	ξ	activity coefficient
T_d	distillate temperature	τ	tortuosity factor
υ_0	molecular volume	ϕ	electrical potential
V	volume	φ	ratio between heterogeneous and homogeneous nucleation free energy
W^*	nucleation work		
x	liquid mole fraction	Ψ	constant depending on temperature and permittivity
y	vapor mole fraction		
z	ion valence	Ω	molar volume
α	contact angle		

4.02.1 Introduction

The necessity to produce substances in the solid-crystalline state is today in demand in various areas of industry, technology, and scientific research. Numerous products in daily use such as additives for hygiene and personal-care, pharmaceuticals, fine chemicals, pigments, and several other foodstuffs are formulated as crystalline powders. This is because the solid state makes these products more stable for storage and more functional to be managed by users. In some technological fields, as for example, in microelectronics, nonlinear optics and sensoring, the solid state is the base in the realization of semiconductor single-crystal devices; furthermore, crystalline materials experience a wide diffusion in heterogeneous catalysis, in the controlled release of active substances, and, more generally, in the nanotechnologies. As regards scientific research, single crystals or crystalline powders are required in structure-based investigations, with particular emphasis on medical advancement by rationale drug-design strategy and to structure-based materials development.

Generally, crystal properties have a remarkable impact with respect to their effective use. In the case of crystalline powders, crystal morphology is the dominant characteristic. During manufacturing, preferred crystal shapes are required, e.g., for more efficient particles recovery filtration from mother solutions by filtration for improved compressibility when producing tablets and for optical behavior in the case of pigments. In heterogeneous catalysis small, highly mono-dispersed in size, and uniformly shaped crystals are better suitable to achieve the highest surface-to-volume ratio and increased catalytic efficiency [1, 2]. In the pharmaceutical industry, the different polymorphic forms of the same substance are considered different materials, with their characteristic physical, chemical and biological properties, making each of them a diverse and patentable drug. In the case of proteins, large crystals ($\sim$100 μm at least in two dimensions) with elevated order in their crystalline lattice are needed for structure determination at the atomic level by X-ray diffraction analysis [3].

Despite the importance of crystallization operation in many fields, several problems remain still open, especially when taking into account the more recent developments in this area concerning the crystallization of bio(macro)molecules and other high-added-value products. If, on the one hand, continuous strengths are addressed to understand the basic mechanisms of crystallization to increase control over the final properties of the materials produced, the increased interest toward the 'bio' area stimulates more efforts to improve strategies and tools, because of the intrinsic difficulty to

crystallize structurally complex organic or biomacromolecules [4]. It appears thus obvious that the possibility to develop new equipments and strategies by which crystallization can be operated in a well-controlled way even for biomolecules would represent a fundamental contribution in many areas, with a particular impact in the overall field of the life sciences. On these bases, in the past few years, an innovative crystallization concept, based on the use of membranes and which might respond to the demand for a more efficient crystallization technology, has been proposed and developed [5]. In fact, membranes, with their intrinsic characteristics of efficiency and operational simplicity, high selectivity and permeability for the transport of specific components, compatibility between different membrane operations in integrated systems, low energetic requirement, good stability under operating conditions and environmental compatibility, easy control and scale-up, and large operational flexibility, represent a technology whose operation well satisfies the concept of the rationalization of chemical productions, leading to significant innovation in both processes and products. Accordingly, membrane technology has been chosen as a valid and innovative tool to introduce significant improvements in industrial crystallization.

4.02.2 Time-Line Development of the Membrane Crystallization Concept

The occurrence of crystallization during membrane operations has been observed since the beginning of their utilization. The interest in this phenomenon, however, was primarily addressed to adopt strategies useful to avoid it, because crystal formation above the membrane or inside the pores would induce severe degradation and dramatic flux decline with the consequent failure of the process [6, 7]. This was the case yet in the mid-1960s, with the observation of scaling deposition on the surface of polymeric reverse osmosis (RO) membranes facing high concentrated brines in seawater desalination. Scaling phenomena and high membrane cost prevented the full employment of RO in seawater desalination until the development of successful anti-scaling methodologies which, in combination with the commercialization of low-cost asymmetric cellulose acetate membranes, allowed RO to become competitive with (and actually overcome!) traditional thermal desalination methods. In addition, for membrane distillation (MD) a number of papers, appeared in the past few decades, described the crystallization phenomena as a hindering factor generating flux decline [8–13]. On the bases of these initial experiences, crystallization occurring in membrane operations was considered only as a side effect while no significant effort was devoted to use membranes to improve crystallization.

The first application of a membrane unit properly as a crystallizer dates back to 1986, when the precipitation of calcium oxalate in RO hollow-fiber modules was used to simulate the early stages of stone formation in the renal tubules [14–17]. In 1987, the possibility to crystallize a solute in a controlled manner by using membrane distillation at sufficiently high concentration was explicitly proposed [8, 18]. In 1991, this concept was put into practice by recovering Taurine crystals during pharmaceutical wastewater purification by MD after the flux had reduced to essentially zero [9]. In the same year, RO membranes were also tested to perform the controlled crystallization of bio-macromolecules in an osmotic dewatering process [19, 20]. Other than MD and RO membranes, no significant applications of other membrane operations had been explored for crystallization until the end of the 1990s. As a rare example, Sluys *et al.* [21] described the use of microfiltration (MF) for increasing the concentration of the solution up to the level required for seeded crystallization in the softening of drinking water.

After these initial studies, in 2001, the term membrane crystallizer was coined [5]. It refers to the innovative concept by which crystal nucleation and growth are carried out via a well-controlled pathway, starting from an under-saturated solution, by controlling supersaturation with a membrane. The working principle of what is defined today as a membrane crystallizer can be considered as an extension of the membrane distillation or the osmotic distillation concepts. According to this design, porous hydrophobic membranes are used to crystallize inorganic salts [5] as well as organic and bio(macro)-molecules [22, 23]. High-quality protein crystals suitable for X-ray diffraction analysis were also grown by using this approach [24]. In the early 2000s, several papers describing the use of membrane crystallization technology and its advantages over conventional evaporative techniques have come to light [25–37]. The possibility to promote the formation of specific crystal structure of proteins [38] and to control morphology and polymorphism of small organic molecules [39, 40] by acting on the main operating conditions has been well documented.

In more recent years, some other works reported about the use of membranes in designing crystallization operations. Solid (nonporous) hollow fibers, where the feed solution flows through the lumen side and a cooling solution flows through the shell side, thus inducing solute nucleation and growth at a temperature below the saturation temperature, have been used for crystallization [41, 42]. Membrane-assisted crystallization operations based on nanofiltration (NF) [43] and RO [44, 45] stages to concentrate a stream prior to batch cooling crystallization have recently been used for some organic species.

A special application of membranes for crystallization relies on antisolvent processes. A crystallization apparatus, in which a crystallizing solution is forced through a membrane in one or more antisolvents for the specie which is likely to be crystallized or that one or more antisolvents are forced in the solution comprising the specie to be crystallized to produce particles with narrow crystal size distribution (CSD), has been proposed in 2004 [46, 47]. The same concept was used for the crystallization of L-asparagine monohydrate [48]. In this system, solutions (whatever the crystallizing solution or the antisolvent) are pressed directly in the liquid phase through the porous membrane by overcoming its breakthrough pressure. Accordingly, the hydrophobic/hydrophilic nature of the membrane is not an issue, except that hydrophilic membranes would achieve higher fluxes, and hence higher productivities, for aqueous solutions.

The extension of the membrane crystallization concept to antisolvent processes, where a porous membrane is used to dose the amount of antisolvent in the crystallizing solution, has been proposed very recently [49]. In this system, two operative configurations have been developed: solvent/antisolvent demixing and antisolvent addition membrane crystallization. In both cases, solvent/antisolvent migration occurs in the vapor phase, according to the general concept of membrane crystallization and, unlike the above-mentioned configuration, not by forcing it in liquid phase through the membrane. The selective and precise dosing of the antisolvent, controlled by the porous membrane, allows a more fine control of the solution composition during the process and at the nucleation point, with consequent improvement of the final crystal characteristics.

The concept of the membrane crystallizer has been used to produce microfluidic system for protein crystallization [50, 51]. These devices consist in traditional vapor diffusion apparatus where a polymeric membrane, generally made by poly(dimethylsiloxane) (PDMS), is used to separate the crystallizing and the reservoir solutions. The control of solvent evaporation rate from the macromolecular solution toward the reservoir, depending on several operative parameters, led to the production of high-quality crystals and/or with particular morphologies, suitable for X-ray diffraction analysis.

According to the considerations above, crystallization by using membranes can be classified depending on the different working principles such as:

1. membrane distillation/osmotic distillation-based processes where diffusion of solvent molecules in vapor phase through a porous membrane, under the action of a gradient of chemical potential as driving force, generates supersaturation in the crystallizing solution;
2. membrane-assisted crystallization in which pressure-driven membrane operations (MF, NF, and RO) are used to concentrate a solution by solvent removal in liquid phase, while crystals are recovered in a separate tank, often operated at lower temperature and with seeding;
3. solid (nonporous) hollow fibers used as heat exchanger to generate supersaturation by cooling;
4. antisolvent (or crystallizing solution) forced directly in the liquid state into the crystallizing solution (or into the antisolvent) through the pores of a membrane under a pressure gradient; and
5. antisolvent membrane crystallization, where dosing of the antisolvent in the crystallizing solution is carried out by means of a membrane, according to the working principle of point 1, in the two solvent/antisolvent demixing and antisolvent addition configurations.

Although membranes are used in several crystallization equipments working on the bases of diverse principles, the term membrane crystallization is defined as the process described in the points 1 and 5 (**Table 1**). Accordingly, only these systems will be discussed in this chapter.

4.02.3 Description of Technology and General Working Principle

In its current general conception, what is defined as a membrane crystallizer is a system in which a solution containing a nonvolatile solute that is likely to be crystallized (defined as the crystallizing solution or feed or retentate), is in contact with, by means of a (macro)porous membrane, a solution on the distillate

Table 1 Time-line development of membrane-assisted crystallization processes

Year	*Mean achievement*	*Membrane process*	*References*
1986	Precipitation of calcium oxalate in hollow fiber modules	RO	[14–17]
1987	Introduction of the concept of MD properly for crystallization	MD	[8,18]
1991	Crystallization of Taurine	MD	[9]
1991	Development of an osmotic dewatering system	RO membranes	[19,20]
1996	MF–membrane-assisted crystallization	MF	[21]
2001	Definition of a membrane crystallizer	MCr (MD–OD)	[5]
2002	Crystallization of lysozyme	MCr	[22,23]
2004	Antisolvent membrance-assisted crystallization	MF	[46,47]
2005	NF–membrane-assisted crystallization	NF/cooler	[43]
2006	Solid hollow fiber cooling crystallization	Nonporous heat exchanger	[41,42]
2006	Promotion of the growth of unknown crystal forms of proteins	MCr	[38]
2007	Control of polymorphism of organic molecules	MCr	[39,40]
2009	RO–membrane-assisted crystallization	RO/cooler	[44]
2009	Antisolvent membrane crystallization	MCr	[49]

side. The membrane might be made by polymeric or inorganic materials or by a combination of both in a hybrid or composite configuration. Hollow fibers as well as flat-sheet membranes can be employed in a similar manner.

When the membrane is prevented from becoming wet due to the adjacent solutions, no mass transfer through its porous structure is observed directly in liquid phase, but the two subsystems, which are in contact, are subjected to mass inter-exchange in the vapor phase. Wetting of the membrane, with the consequent deleterious direct passage of liquids, can be avoided when the pressure of the solutions facing it is lower than the entry limit (P_{entry}), defined by Young–Laplace's equation [52]:

$$P_{entry} = -\frac{2\gamma_L}{r_p}\cos\alpha \qquad (1)$$

where γ_L is the liquid surface tension, r_p is the pore radius, and α is the contact angle between the membrane and the solution (see **Figure 1**).

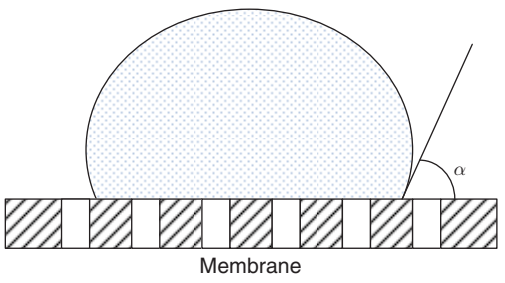


Figure 1 Definition of contact angle α between the liquid crystallizing solution and the surface of the membrane.

According to Equation (1), P_{entry} is positive for $\alpha = 90–180°$. This means that hydrophobic membranes can be used for hydrophilic (aqueous) crystallizing solutions and hydrophilic membrane materials are suitable for hydrophobic (or oleophilic) solutions.

For a pressure lower than P_{entry}, the two liquids are stopped at the entrance of each pore on both membrane sides, thus generating a curved profile as shown in **Figure 2**.

Generally, crystal nucleation and growth in the feed solution is induced by generating supersaturation. This can be done either by removing the solvent from the crystallizing solution, thus increasing solute concentration up to the overcoming of its solubility limit, or by adding an antisolvent to it, which reduces the solubility of the solute in the mixed solvent/antisolvent solution. Accordingly, the role of the membrane is not simply as a sieving barrier to select the transport of specific components, but as a physical support which, by the removal of the vaporized solvent or by the addition of the antisolvent, generates and sustains a controlled supersaturated environment in which crystals can nucleate and grow.

Detailed relations and models for heat and mass transport through the membrane in MCr can be described by using the same concepts developed for membrane distillation and osmotic distillation. Therefore, their thorough description is outside the scope of this chapter. Further details can be found by readers in cited literature [53–69] or in other specific chapters of this book (*see*, e.g., Membrane Distillation).

As a general description, heat and mass transport through membranes occurs only if the overall system

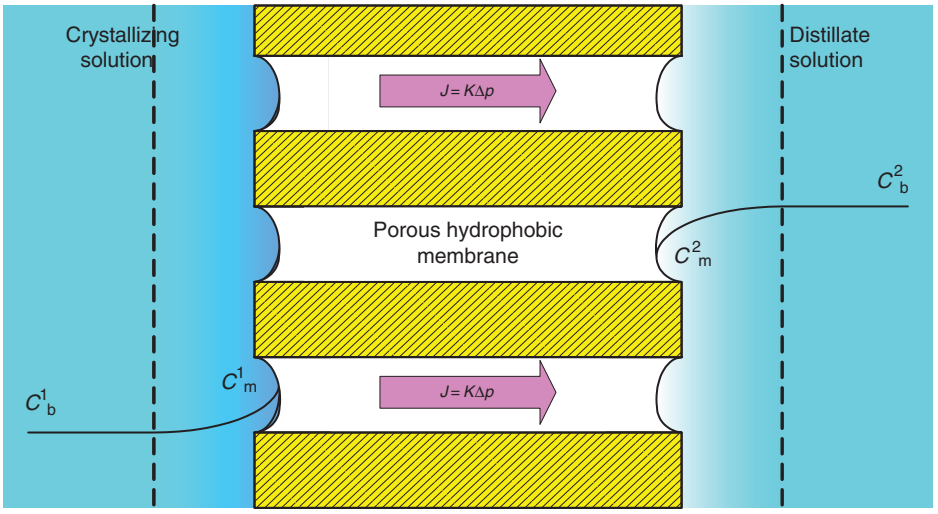


Figure 2 General principle of a membrane crystallizer: c_b, bulk concentration; c_m, concentration close to the membrane surface; J, transmembrane flux; K, phenomenological constant; Δp, gradient of partial pressure between the two sides of the membrane.

is not in thermodynamic equilibrium. In the two homogeneous subsystems separated by the membrane, indicated as the superscripts 1 and 2, the volatile species i has a defined value of electrochemical potential μ_i^1 and μ_i^2, defined as

$$\mu_i = \mu_i^0 + RT\ln a_i + PV + z_i F\phi_i \tag{2}$$

where a_i is the activity, P is the hydrostatic pressure, V is the volume, R is the gas constant, T is the absolute temperature, F is Faraday's constant, z_i is the ion valence, and ϕ_i is the electrical potential. For small changes of the number of moles in the two phases (caused by the mass transfer across the membrane), the variation of the Gibbs free energy (dG) is given by

$$dG = \sum_i (\mu_i^1 - \mu_i^2)\, dn_i^1 \tag{3}$$

where n_i^1 is the number of moles of the ith component transferred and it is related to transmembrane flux $\mathcal{J}_i$ by

$$\frac{dn_i^1}{dt} = A_m \mathcal{J}_i \tag{4}$$

where t is the time and A_m the membrane area. In the frequent case of nonideal mixtures, the vapor–liquid equilibrium is mathematically described in terms of partial pressure (p_i), vapor pressure of pure i (p_i^0), and activity coefficient ξ_i, according to the well-known thermodynamic relationship:

$$p_i = Py_i = p_i^0 a_i = p_i^0 \xi_i x_i \tag{5}$$

where x_i and y_i are the liquid and vapor mole fractions, respectively.

The vapor pressure p^0 of a pure substance varies with temperature according to the Clausius–Clapeyron equation

$$\frac{dp^0}{dT} = \frac{\lambda}{RT^2} \tag{6}$$

where λ is the latent heat of vaporization (9.7 cal mol^{-1} for water at 100 °C [70]). At the pore entrance, the pressure of the vaporized solvent in equilibrium with the liquid phase depends on the curvature of the vapor–liquid interface ($p^0_{\text{convexsurface}}$) as described by the Kelvin's equation [52]:

$$p^0_{\text{convexsurface}} = p^0 \exp\left(\frac{2\gamma_L}{rcRT}\right) \tag{7}$$

where r is the curvature radius, γ_L the liquid surface tension, and c the liquid molar density. Activity coefficients ξ_i can be deduced by a large variety of equations aiming to evaluate the excess Gibbs function of mixtures [71]. The expression for activity coefficient in diluted aqueous ionic solutions can be derived from the Debye–Hückel's theory:

$$\log\xi_\pm = -|z_+ z_-|\Psi\sqrt{I} \tag{8}$$

Here, $\xi_\pm$ is the activity coefficient of the electrolyte, Ψ is a constant, which depends on the temperature

and solution permittivity (in an aqueous solution at 25 °C, the constant Ψ is 0.509 $mol^{1/2}$ $kg^{-1/1}$) [52], z is the ion valence, and I the ionic strength of the solution, given by

$$I = \frac{1}{2}\sum_i z_i^2 c_i \tag{9}$$

According to Equations (2)–(6), the driving force for the mass transport of a component from one phase to the other is given by the difference in its electrochemical potential in the two phases and it is generated by changes in temperature, pressure, activity, or electrical potential. The hydrostatic pressure gradient across the membrane is negligible in MCr to avoid wetting while electrical gradients do not hold, so that the driving force of the process is the partial pressure difference across the membrane, established by a temperature or activity difference between the two contacted solutions. In the case of a driving force generated by a temperature gradient, the system is termed as thermal membrane crystallizer; when the driving force is obtained by an activity gradient, generated by a difference in ionic strength (as from Equations (8) and (9)), the system is named as osmotic (or isothermal) membrane crystallizer.

Under the action of the driving force, solvent or antisolvent molecules migrate, in vapor phase through the porous membrane structure, from the site where their chemical potential is higher toward the lower chemical potential subsystem, thus generating supersaturation and, hence, nucleation and crystal growth in the crystallizing solution. The specific mechanism for mass transport depends on the operational configuration of the membrane crystallizer. Two cases exist: (1) solvent evaporation membrane crystallizer (thermal or isothermal) in which solvent is removed in vapor phase from the crystallizing solution and (2) antisolvent membrane crystallizer where an antisolvent is dosed inside the crystallizing solution by means of the membrane. (Actually both solvent evaporation and antisolvent membrane crystallizer configurations are based on mass inter-exchange in the vapor phase, so that in the antisolvent configuration also the mass transfer process occurs by evaporation.) In the latter case, two more versions of the system exist: (a) solvent/antisolvent demixing configuration and (b) antisolvent addition configuration. For both solvent evaporation and antisolvent membrane crystallizers, static (quiescent) and dynamic process can be performed. In the first case, the feed and the distillate solutions are quiescent while, in the second case, those two solutions are circulated in forced solution flow environment, generally in a condition of laminar flow.

4.02.4 Operational Configurations

4.02.4.1 Solvent Evaporation Membrane Crystallizer

In this configuration, the substances to be crystallized are dissolved in an under-saturated solution located at the feed side of the membrane, as depicted in **Figure 2**. Generally, in order to avoid wetting, hydrophobic membrane materials are preferred for aqueous feed solutions while hydrophilic membranes can be used for oleophilic solutions. In the most common arrangement, the distillate side of the membrane consists of a condensing fluid, often the pure solvent at a lower temperature than the feed side, in the case of thermal activation of the driving force, or in a stripping solution consisting in a hypertonic solution of inert salts (NaCl, $MgCl_2$, $CaCl_2$, etc.) in the case of the isothermal configuration. The gradient of chemical potential between the two subsystems therefore induces a mechanism of evaporation of the solvent at the first interface on the feed side, the migration of the solvent in vapor phase through the porous membrane, and, finally, its recondensation at the second interface on the distillate. The continuous removal of solvent from the feed solutions increases solute concentration, thus generating, at a certain point, supersaturation. As solvent evaporates from the first subsystem and recondenses on the other side, the establishment of the concentration polarization layers adjacent to the two faces of the membrane occurs. Accordingly, the solute concentration in the polarization layer close to the membrane surface, c_m, is higher with respect to the bulk solute concentration, c_b, on the feed sides. As a change in the physical state of the molecules of the volatile component (solvent) occurs near the interface between the solutions and the membrane, heat is respectively absorbed by vaporized molecules on the feed side and released on the distillate side after condensation, so that a temperature polarization also exists across the membrane. Both concentration and temperature polarization might affect locally the degree of supersaturation, so that the mechanism of crystallization can develop in a different way with respect to the bulk of the solution. Accordingly, the

properties of the crystal nucleated and grown on/near the membrane might display characteristic features that can be controlled by modulating the heat and mass concentration profiles adjacent to the membrane.

For the crystallization of inorganic substances or low-molecular-weight organic compounds, the thermal system can be effectively used, while for the crystallization of heat-sensitive molecules, such as proteins, the osmotic configuration appears more appropriate thanks to its milder operating conditions [24–27].

4.02.4.2 Antisolvent Membrane Crystallizer

The system operates according to the two schemes depicted in **Figure 3**. In the solvent/antisolvent demixing configuration (**Figure 3(a)**), a certain solute is dissolved in an appropriate mix of a solvent and an antisolvent whose composition is chosen in such a way that the solute remains indefinitely in solution in the original conditions. When a gradient of chemical potential is generated between the two sides of the membranes, for example by a temperature difference, the solvent, which is supposed to have a higher vapor pressure than the antisolvent at the same temperature, evaporates at a higher flow rate, thus producing solvent/antisolvent demixing. As the amount of solvent in the mixture decreases, the lower solubility of the solute generates supersaturation and a phase separation occurs when the antisolvent exceeds a certain volume fraction. The requirements for this configuration are that: (1) the antisolvent and the solvent are miscible; (2) the initial solvent/antisolvent balance in the mixture guarantees that the solute is under its solubility limit; and (3) the solvent evaporates at velocity higher than the antisolvent. The crystallization of a solute from an aqueous/organic extraction mixture can be successfully carried out by this system.

In antisolvent addition configuration (**Figure 3(b)**), a solute is dissolved in a solvent and then an antisolvent is gradually evaporated from the other side of the membrane by applying a gradient of chemical potential. As the antisolvent mixes with the solvent, the

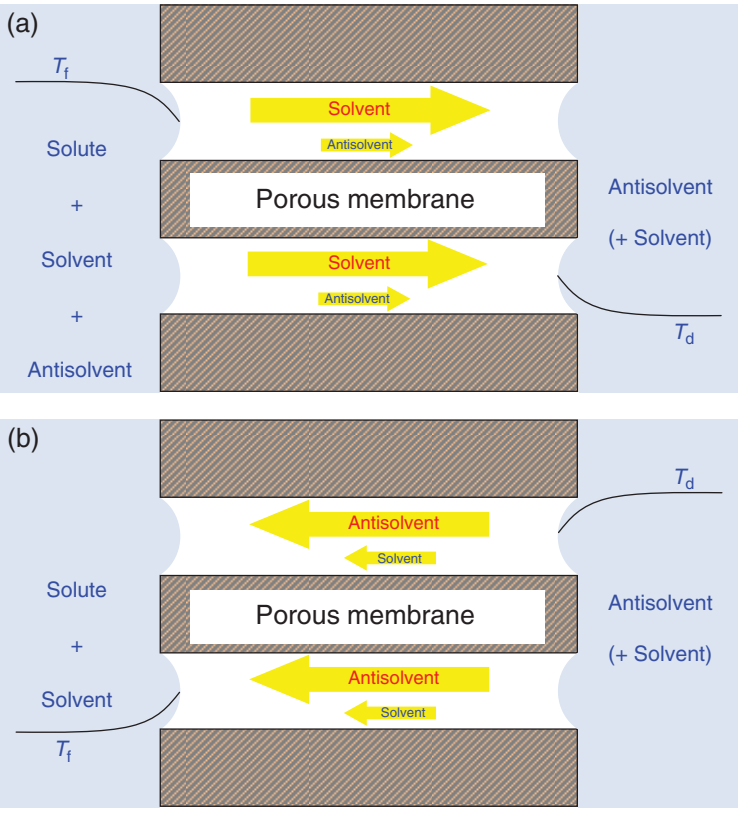


Figure 3 Principle of an antisolvent membrane crystallizer: (a) solvent/antisolvent demixing and (b) antisolvent addition configurations. T_f: feed temperature; T_d: distillate temperature. Reproduced with permission from Di Profio, G., Stabile, C., Caridi, A., Curcio, E., Drioli, E. *J. Pharm. Sci.* **2009,** *98*, 4902.

solute dilutes but, at the same time, the composition of the mixture changes. At a certain point, the excess of antisolvent creates supersaturation and solute crystallization. This configuration requires that the antisolvent and the solvent are miscible. In this case, the species to be crystallized can be soluble in aqueous solutions and poorly soluble in organic low-boiling liquids.

In the antisolvent addition configuration, a certain amount of solvent might be present initially on the distillate side for some reasons, for example, to modulate the rate of antisolvent dosage in the crystallizing solution, thus controlling the process kinetics; another reason might be to avoid wetting of the membrane when using the pure antisolvent. This is the case when the antisolvent is ethanol, which is known to wet the surface of a wide compilation of hydrophobic materials when used as pure liquid. A mixture of water/ethanol on the distillate side, in which ethanol has a volume fraction below 35% v/v, might be useful to avoid wetting of, for example, polypropylene membranes.

4.02.5 Control of Supersaturation

In membrane crystallization, the membrane does not behave as a selective separation medium, as in other conventional membrane operations, but it operates as a physical support which activates and sustains a mechanism of mass transfer in the vapor phase, thus generating supersaturation in the crystallizing solution. Vapor molecules sweep up from one side of the membrane to the other, passing through its porous structure under the action of a driving force whose extent is fixed by the combination of the operational parameters, and experiencing a resistance, which depends on the membrane properties.

Usually macroporous membranes, with average pore size around 0.1 μm, are used to provide consistent transmembrane flux. If considering that the diameter of the water molecule at room temperature and pressure is 2.75 Å, the approximate mean free path of water molecule passing through the membrane in vapor phase is in the same order of the pore size. Therefore, mass transport can be approximated by a Knudsen-like model [64]. According to this, the transmembrane flux $\mathcal{J}_i$ is directly proportional to the vapor-pressure gradient Δp across the membrane and to the physical membrane properties:

$$\mathcal{J}_i = \frac{\pi n_{\mathrm{P}} r_{\mathrm{P}}^2 D_i^{\mathrm{k}} \Delta p}{RT\tau\Delta z} \tag{10}$$

$$D_i^{\mathrm{k}} = 0.66 r_{\mathrm{P}} \sqrt{\frac{8RT}{\pi \mathrm{MW}}} \tag{11}$$

where n_{P} is the number of pores in the membrane, r_{P} the pore radius, Δz the thickness of the membrane, τ the tortuosity factor, MW the molecular weight, and D_i^{k} the Knudsen diffusion coefficient. While membrane characteristics such as thickness, pore size, overall porosity, and pore tortuosity are fixed once a specific membrane had been chosen, Δp is directly proportional to the activity gradient Δa of the volatile component(s) between the two solutions. Accordingly the different parameters, which might affect the activity gradient of the solvent and/or the antisolvent, would influence both the extent and the rate of evaporation. As a consequence, the effective excess of solute concentration with respect to its solubility in the crystallization solution (supersaturation, S) and the rate of its variation can be properly adjusted.

Supersaturation is the driving force for crystallization and both nucleation and crystal growth rates depend on it. The extent of the crystalline population, its morphological (size, habit, and shape) and structural (polymorphism) properties purity, all characteristics and which depend on the crystallization kinetics, can be properly controlled by choosing the opportune membrane and operating on the transmembrane flux. Parameters, such as solute concentration, concentration of the precipitating agent (if any), concentration of the stripping agent (for the osmotic membrane crystallizer), solution velocity (for the dynamic system), nature and concentration of the antisolvent (for the antisolvent membrane crystallizer), crystallization solution temperature (T_{cry}), distillate temperature (T_{d}) (for the thermal system), and the transmembrane temperature gradient (ΔT), contribute to establish the initial working point. As these parameters change with the time during the same crystallization run, the working point inside the system is dynamic, moving with different trajectories in the phase diagram of the species to be crystallized (**Figure 4**) depending on the specific followed evolution. Accordingly, the patch which leads, starting from the undersatured solution, to crystallization, depends on the evolution of the parameters above leading to different results for the diverse routes. The effect would be the variation of the rate and the extent of nucleation over the crystal growth with the possibility to generate a broad

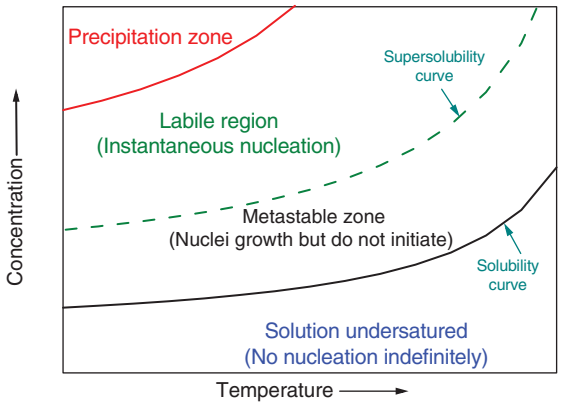


Figure 4 Generic concentration/temperature diagram of a substance to be crystallized. The metastable zone is the region where it is more convenient to perform crystallization.

set of trajectories for crystal nucleation and growth, that are not readily achievable in conventional crystallization formats and which would lead to the production of specific crystalline morphologies and structures.

4.02.5.1 Effect on Crystal Morphology and Purity

Figure 4 depicts the phase diagram for a generic substance to be crystallized. Under the solubility line, the solution is undersaturated and nucleation will not happen indefinitely. Between the solubility and the supersolubility curves is located the metastable zone, in which crystal growth occurs and nucleation might be observed after a certain time, defined as the induction time (t_{ind}). The induction time is defined as the elapsed time between the onset of supersaturation and the formation of the first crystalline nuclei and it is an important parameter affected by operating conditions. The metastable zone is the region in which it is more convenient to perform crystallization, as controlled nucleation and growth rate can be achieved. Above the supersolubility line is the labile region, where instantaneous nucleation (induction time is zero) is observed. Here, excess of nucleation with the formation of a large amount of tiny crystals is usually obtained and crystal morphology is out of the control of the operator. Above the labile zone is located the precipitation zone, in which the extremely high value of supersaturation generates the formation of amorphous precipitate instead of a solid-crystalline product. In the labile zone, the introduction of certain amounts of solution and/or impurities into the solid is more likely due to the rapid solidification process. Moreover, the excess of particles of reduced size may induce extensive aggregation phenomena, with the consequent production of particulates that are highly impure and have low uniformity. Accordingly, it is important, when designing a crystallization process, to exert a fine control over it and to operate in the more appropriate area of the phase diagram, in order to address some important properties of the final crystalline product.

Usually in membrane crystallization, all the variations which produce the decrease of the transmembrane flux, such as the increase of the initial solute and/or the precipitating agent (antisolvent) concentration in the crystallizing solution, the decrease of the stripping agent concentration on the distillate side, the decrease of the transmembrane temperature, and the decrease of the antisolvent volume fraction in the feed are associated with a reduced supersaturation generation rate and hence to a slower crystallization process. The deceleration of the crystallization kinetics translates in longer elapsed time for crystals' appearance and the encouragement of crystals' growth over nucleation with the production of fewer crystals of bigger size. However, some of these variations, such as the increase of the initial solute and/or antisolvent concentration and the decrease of the crystallization temperature, lead respectively to the increase of solute molecules in solutions and to the decrease of their solubility by salting out or temperature effect. The increased initial supersaturation will stimulate excessive nucleation at the expense of crystal growth with the appearance of very many small crystals. Therefore, changes which affect these two opposite aspects – the transmembrane flux (kinetic) and the solubility (thermodynamic) – have to be carefully balanced during the design of the crystallization process in such a way as to achieve the desired final crystals' size and number density population. On the other hand, however, variation of conditions exclusively related to the distillate side, such as changes of stripping agent concentration or distillate temperature, for the osmotic and the thermal systems respectively, would influence only transmembrane flux but not supersaturation in the feed. Accordingly, feed-related parameters can be referred to as "thermodynamic parameters" while distillate conditions can be considered "kinetic parameters". (This is not an absolute definition as the variation of the thermodynamic parameters also has a kinetic effect on the

transmembrane flux while changes of kinetic parameters also affect supersaturation, which is a purely thermodynamic property of the system.)

The effect of the transmembrane flux on the crystallization process in MCr has been studied in the case of hen-egg-white lysozyme (HEWL) [35, 36]. When increasing the initial protein concentration, while keeping other conditions constant, a reduced transmembrane flux, and its steeper decrease with the time, was observed. This would favor the production of a few big crystals. Although this reduction of flux, the increased solute concentration enhances supersaturation, leading to the undesirable excess of nucleation with the production of a huge amount of small crystals. A similar behavior was observed when increasing precipitant (NaCl) concentration or decreasing crystallization temperature, due to the reduced solubility of HEWL in these conditions. In this case, and generally in MCr, the variation of these thermodynamic parameters in the direction of decreasing flux produces at the same time a decrease of supersaturation generation rate by solvent removal, with the consequent tendency toward an extension of t_{ind}, but also a decrease of solubility, which leads to the increase of S. As t_{ind} is inversely proportional to supersaturation, crystals are stimulated to appear earlier. Accordingly, a parabolic behavior is usually observed in the curves displaying the relation between t_{ind} and one of the 'thermodynamic parameters,' due to the competition of the two opposite forces [28, 35]. This is shown in **Figure 5(a)** for the crystallization of HEWL [28]. When only 'kinetic parameters' are varied in the direction of increasing the transmembrane flux, supersaturation generation rate increases as well, and crystals are drawn to nucleate faster due to the rapid establishment of a high level of supersaturation. Accordingly, the dependencies of the transmembrane flux by these parameters show a monotonic trend (**Figure 5(b)**) [36]. In the latter case, as t_{ind} is proportional to $1/\mathcal{J}$, induction time maintains a monotonic variation with $\mathcal{J}$ as well.

Control of transmembrane flux in a MCr also has an influence on the purity of the crystals. Normally, crystal purity might be reduced by the high local level of supersaturation, which generates a growth velocity higher than the critical threshold value, which separates regions of impurity inclusion development and the growth of more pure crystals. For supersaturation above this critical value, inclusions will more probably occur, whereas at lower growth velocities, the tendency to grow purer crystals will rise and inclusions will be less effective. In MCr, the possibility to act on the transmembrane flux, by changing the driving force of the process, allows operating under proper growth conditions, thus achieving pure crystals. In the case of sodium chloride crystallization from NaCl/KCl solutions, low and gentle supersaturation generation rate in MCr leads to small and well-controlled growth rates and hence to the production of purer crystals in a onestep process [37]. In contrast, higher growth rates lead to rather impure crystals (see **Figure 6**).

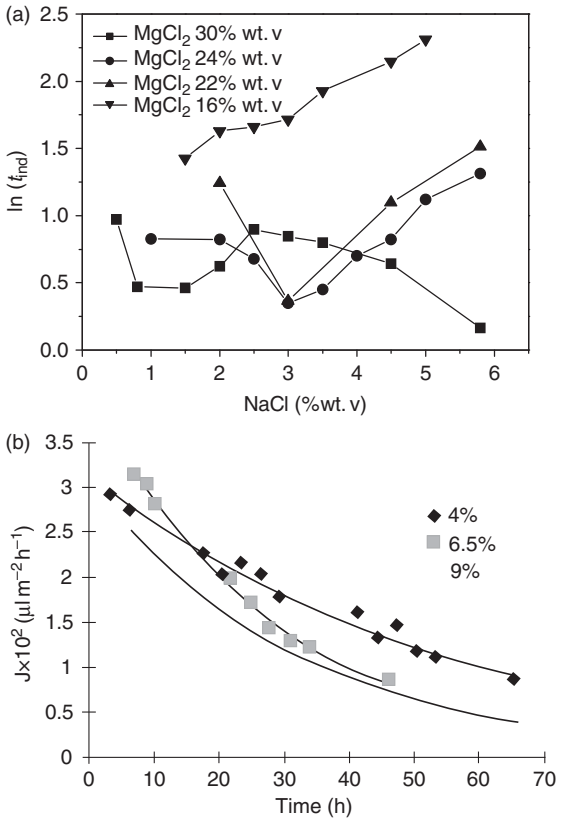


Figure 5 (a) Induction times t_{ind} vs. precipitant (NaCl) concentration for various stripping agent ($MgCl_2$) concentrations indicated in the legend. (b) Changes of transmembrane flux with time under various NaCl concentrations. (a) Reprinted from Di Profio, G., Curcio, E., Cassetta, A., Lamba, D., Drioli, E. *J. Cryst. Growth* **2003**, *257*(3–4), 362, Copyright (2003), with permission from Elsevier. (b) Reprinted from Zhang, X., Zhang, P., Wei, K., Wang, Y., Ma, R. *Desalination* **2008**, *219*(1–3), 105, Copyright (2008), with permission from Elsevier.

4.02.5.2 Influence on Polymorphism

Many substances can exist in solid crystalline state in several phases, a phenomenon named polymorphism.

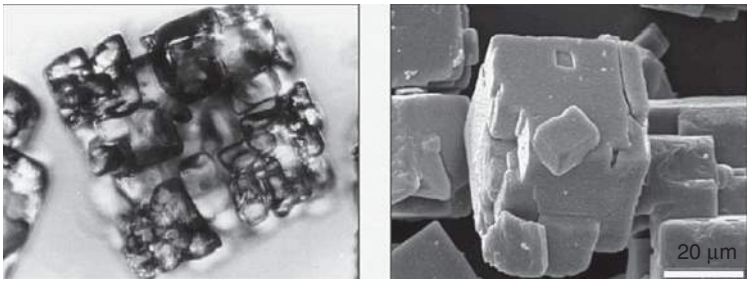


Figure 6 Sodium chloride crystals grown at high growth velocity with vacuum evaporation crystallization (left) compared to crystals grown by membrane-based evaporation crystallization (right). Reproduced with permission from Weckesser, D., König, A. *Chem. Eng. Technol.* **2008**, *31*, 157.

Each polymorph is characterized by its specific physical properties, such as solubility, dissolution rate, thermal and mechanical stability, and optical properties. Therefore, each form represents a specific material, different to some extent from the other phases of the same substance, with remarkable implications for its utilization in industrial, technological, and scientific applications. Among the different phases, the relative stability in a specific condition is ruled by thermodynamics, as described by the classical nucleation theory (CNT) [72]. However, the phase that will be effectively obtained depends on kinetics [73]. This is because of a competition between the thermodynamic and kinetic control of the nucleation phase which, in combination with the relative growth rates of the different polymorphs, will affect the final outcome of the crystallization process.

According to the CNT concept, the stationary rate of nucleation N can be described by

$$N = A\exp\left(\frac{-W^*}{k_B T}\right) \tag{12}$$

where k_B is Boltzmann's constant, A is a pre-exponential kinetic parameter, and W^* is the nucleation work. In the approximation of spherical particles, the nucleation work in the exponent is defined as

$$W^* = \frac{16\pi v_0^2 \gamma^3}{3(k_B T)^2 \ln^2 S} \tag{13}$$

where v_0 is the molecular volume and γ is the interfacial energy. This equation shows that the barrier height depends on the surface free energy γ and on supersaturation S. This means that the degree of supersaturation might govern the occurrence in the nucleation of the different forms of the same substance.

Let us consider, for the sake of simplicity, a dimorphic system, with the two polymorphs A and B having a different solubility with the stable polymorph A having the lowest. According to Equation (13), the height of the nucleation barrier that separates the stable and the metastable phases is increased by a large difference in solubility and interfacial energy between the two forms. This can be seen in a typical energy-reaction coordinate diagram as shown in **Figure 7**, where it is depicted the free energy variation ΔG of a solute in a supersaturated fluid which transforms, by crystallization, into one of two crystalline products, A or B.

Associated with each reaction pathway are a transition state and an activation free energy which is implicated in the relative rates of formation of the two structures. As A is the more stable (less soluble), its supersaturation is always higher than that of B: $S_A > S_B$. However, three situations might occur: (1) the interfacial energy of form A is lower than that of the metastable phase B, $\gamma_A < \gamma_B$, so that the activation energy for the stable polymorph is lower than that of the kinetic form $\Delta G_B^* < \Delta G_A^*$; (2) the interfacial energy of form B is much lower than that of the thermodynamic product A, $\gamma_B << \gamma_A$, so that the difference of interfacial energy in Equation (13) overcomes the difference in supersaturation with the final consequence that the activation energy for the stable polymorph is higher than that of the kinetic form $\Delta G_B^* > \Delta G_A^*$; and (3) the difference in solubility and interfacial energy for the two phases is very low ($S_A \sim S_B$ and $\gamma_A \sim \gamma_B$) so that the activation barriers for nucleation are very close each other: $\Delta G_B^* \approx \Delta G_A^*$.

In the first case, the formation of the stable form B is thermodynamically favored and it will be obtained at the end. In this situation, if the metastable phase is the desired product, a variation in solute solubility and/or in interfacial energy for example, by changing

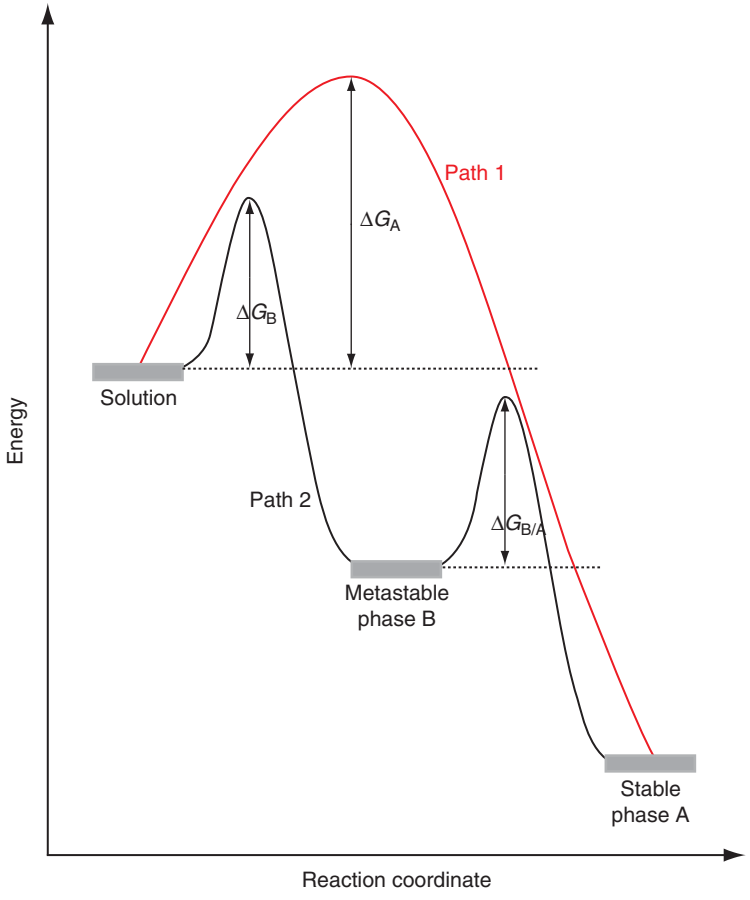


Figure 7 Different pathway in crystallization of stable and metastable phases in a dimorphic molecular system.

solution composition in antisolvent crystallization, can be appropriate to obtain it.

In the second case, the most stable form is not necessarily the first to appear and a scenario as that depicted in **Figure 7**, in which two different paths can be followed by the system, can occur. This arises since such systems are subject to the issue of the growth of one form over another, which is described by Ostwald's rule of stages, which states that "when leaving a metastable state, a given chemical system does not seek out the most stable state, rather the nearest metastable one that can be reached without loss of free energy" [73].

Although it is generally known that this rule is not a physical law and that more stable phases can form directly as stated above, it appears obvious that polymorphism adds a kinetic dimension to crystal growth. Unlike a chemical reaction, crystallization is complicated by the nature of the activated state since it relates to a collection of self-assembled molecules with not only a precise packing arrangement but which also exists as a new separate solid phase. It is the existence of the phase boundary that complicates matters since this is associated with an increase in free energy of the system, which must be offset by the overall loss of free energy. For this reason, the magnitudes of the activated barriers are dependent on the size (i.e., the surface-to-volume ratio of the new phase) of the supramolecular assembly (crystal nucleus). According to Volmer [74], the critical size n^*, which an assembly of molecules must have in order to be stabilized by further growth, is given by

$$n^* = \frac{32\pi v_0^2 \gamma^3}{3(k_B T)^2 \ln^3 S} \tag{14}$$

The higher the operating level of supersaturation, the smaller is the size (typically a few tens of molecules).

Although the supersaturation with respect to B is lower than that for A, if the critical size is lower for B than for A, for a particular solution composition, then the nucleation work is $W_A^* > W_B^*$ according to Equation (13) and $\Delta G_B^* < \Delta G_A^*$, so that kinetics will favor form B following Ostwald's behavior. The direct formation of the stable phase A will only occur if the system is able to overcome the activation barrier for the thermodynamic form.

The third situation is the case in which the activation-free energy for the two phases differs only slightly, so that the probability of the two forms to nucleate concomitantly is very high and the nucleation of both polymorphs occurs. In this last case, it is the relative growth rates of the diverse forms with respect to the rate of conversion of the kinetic product into the stable one that will influence the final outcome of the process. The conversion of form B into form A in solution, as derived by thermodynamics, is dependent on the dissolution of the metastable phase [75], (as stated in Equation (15)), driving the growth of the stable phase, as defined by Equation (16):

$$B_B = -k_d(S - S_{(B-A)}) \tag{15}$$

$$B_A = k_g S_{(B-A)} \tag{16}$$

where B is the growth rate and the subscripts g and d denote the growth and dissolution, respectively. The competitiveness of all these effects lead to the reduction of the nucleation process and the critical nucleus size, and the relative growth/dissolution velocities of the two phases will affect the polymorphic form that is effectively obtained. Therefore, while the degree of supersaturation states the thermodynamic tendency toward the formation of a specific polymorph, the phase that will actually be obtained depends on the rate at which the same level of supersaturation is generated with respect to the relative nucleation and growth/dissolution rates.

On these bases, it appears clear that the control of supersaturation and the rate of its variation in a crystallization process would represent a tool to impact on the thermodynamic/kinetic balance during the crystallization of a polymorphic system, with the consequent possibility to address the growth of a specific phase.

In a membrane crystallizer, this kind of control can be achieved by controlling the composition of the crystallizing solution through the management of the transmembrane flux. This provides an opportunity to systematically affect the rate of variation of the supersaturation which, in turn, affects the polymorphic composition of the precipitate. As this control can be produced very precisely, by fine-tuning the operating conditions and/or by choosing the opportune membrane properties, selective polymorph crystallization is an important possibility available with membrane crystallization technology. Namely, during a crystallization process, when the least stable structure (or a mixture of nuclei of the different polymorphs) forms following an Ostwald-like behavior, the relative growth rates of the different phases with respect to the supersaturation generation rate will decide which form will effectively be grown. When the rate of variation of supersaturation is low, due to the low evaporation rates, and nuclei of the more stable structure have time to grow at the expense of the less stable forms via solvent-mediated transfer of solute, a thermodynamic control, and the more stable polymorph will selectively (or prevalently) be obtained. However, for higher evaporation rates, the increase in the metastable zone width induces nucleation at higher values of supersaturation. In this situation, the conversion from the metastable to the stable phase could not be fast enough with respect to the growth of the former, so that the growth of the kinetically favored form (metastable), which might also be the first to appear according with the Ostwald rule of stages, is observed. In this case, the overall process is kinetically controlled. Accordingly, high control of the membrane-based process provides the possibility to induce polymorphic selection during crystallization by switching between a kinetic and a thermodynamic control of the nucleation stage, thus allowing the production of either a metastable or a stable structure.

Evidence of this possibility is reported in the selective crystallization, in a membrane crystallizer, of either the α or the γ polymorph of the amminoacid glycine (**Figure 8**) [39], the phases I and II of paracetamol [40], or the forms α and β of L-glutamic acid [76].

4.02.6 Heterogeneous Nucleation above the Membrane Surface

Two molecules that have to form a crystalline contact are brought together by translational diffusion inside the solution. In order to increase the chance for fine-tuning of the proper spatial positioning to establish the correct physical patches leading to aggregation, molecules need to be adjusted

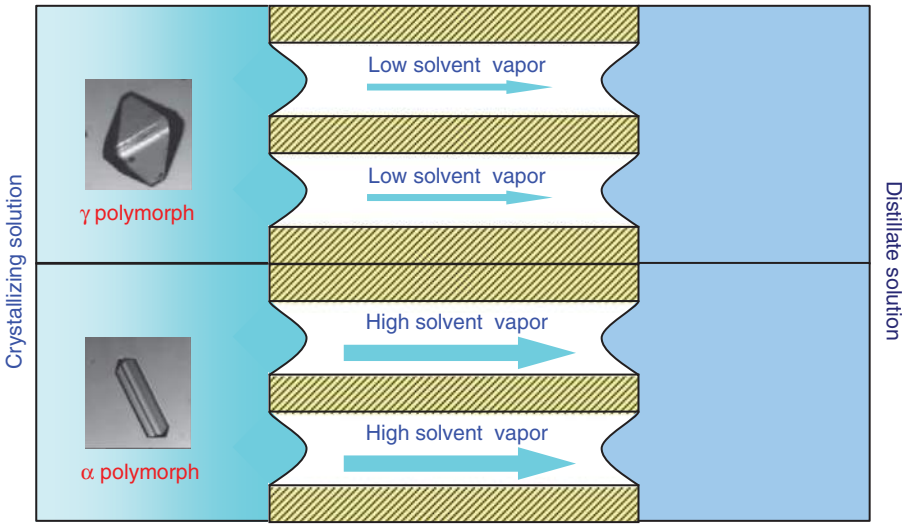


Figure 8 Effect of the solvent evaporation rate on the selective polymorphic crystallization of glycine: high solvent evaporation rate → kinetic product (α polymorph); low solvent evaporation rate → thermodynamic product (γ polymorph). Reprinted from Di Profio, G., Tucci, S., Curcio, E., and Drioli, E. *Cryst. Growth Des.* **2007**, *7*(3), 526–530, Copyright (2007), with permission from American Chemical Society.

spatially by a subsequent rotational diffusion. For this reason, a successful collision between the molecules, resulting in the formation of the crystalline bond, requires not only a sufficiently close approach of the two species but also a strict constraint on their spatial orientation. This is the ideal situation for what has been defined as homogeneous nucleation, which takes place fundamentally inside extremely pure solutions. A basic fact is straightforward that the random rotations of molecules, which also slow down very rapidly with larger complexes, lead to a reduced chance for proper and effective molecular interaction. This is a common case for proteins, even strengthened by the fact that the favorable aggregation of these complex bio-macromolecules is a process of highly precise self-assembly that requires highly selective and exact directional interactions. As a consequence, in many crystallization experiments, because the free-energy barrier to homogeneous nucleation is relatively large (of the order of $100k_BT$ or more), the required saturation levels are not reached, so that nucleation does not occur.

To create an environment that favors nucleation, the use of nucleation-inducing surfaces has become a common practice. Such nucleants could help to enhance the chances of any single trial producing crystalline material, thus reducing the amount of starting materials to be used for screening and/or to increase the nucleation rate, with consequent effect on crystal size and size distribution. In the nucleant-assisted interaction, the surface will support the proper molecular orientation, thus leading to the formation of crystalline clusters with a well-ordered organization of the building blocks. Furthermore, substrate–molecule interactions would reduce the surface tension of the growth units and hence will lower the activation energy for nucleation allowing the crystallization to occur under those conditions which would not be adequate for spontaneous nucleation [28]; this effect is termed heterogeneous nucleation, the process by which the surface of a foreign material lowers the nucleation barrier and facilitates aggregation under those conditions which would not be adequate for spontaneous (homogeneous) nucleation [77]. A primary reason for the attractiveness of heterogeneous nucleation for crystal growers is that nucleation induced at lower degree of supersaturation can occur inside the metastable zone. Because growth in the metastable zone affords kinetic advantages that often lead to the production of larger and better-ordered crystals than those grown at higher supersaturation, the aim of crystallizers is the possibility to induce heterogeneous nucleation in a controlled manner.

The mechanisms of heterogeneous nucleation might arise from both physical and chemical interaction between the solute molecules and the nucleant. Different surfaces may affect heterogeneous nucleation through different ways, for example: (1) introduction of spatial characteristics related to the

crystalline lattice [78]; (2) modification of the supersaturation profile near the surface due to the concentration polarization and/or adsorption of the solute onto the surface by specific interactions; and (3) the presence of a surface microstructure, for example, roughness or porosity, which facilitate nucleation. Control of heterogeneous nucleation has been attempted by using several substrates [78–84]; however, in spite of the preliminary positive results, which have been pursued for several years by employing a variety of substrates, none have proved to be generally applicable as an universal nucleant for controlled heterogeneous nucleation. This has induced difficulties and irreproducibility in the development of heterogeneous nucleation strategies, especially in protein crystallization.

In a membrane crystallizer, the crystallizing solution is in direct contact with the membrane surface; therefore, a solute–membrane interaction will occur in certain circumstances. The membrane provides, at the same time, the physical support for mass interexchange in vapor phase, thus generating supersaturation and the solid support to promote heterogeneous nucleation mechanism. This effect can be due to both the structural and the chemical properties of the membrane surface: (1) the porous nature might supply cavities where solute are physically entrapped leading, locally, to high supersaturation values suitable for nucleation and (2) the nonspecific and reversible chemical interaction between the membrane and the solute can allow to concentrate and orient molecules on the surface without loss of mobility [85], thus facilitating effective interaction appropriate for crystallization. In the case of complex molecular systems such as proteins, the different interaction mechanism is dependent on the patches, with different chemical properties, which are available on the molecular surface. Hydrophobic and hydrophilic spots, positively and negatively charged functional groups and hydrogen-bonding moieties, are known to provide affinity for almost any kind of nonbiological surface. Structural rearrangements of adsorbed molecules develop with solute–surface residence time and are considered as one of the driving forces of adsorption, which contributes significantly to nucleation free energy changes [86]. Furthermore, the solute–membrane interaction can provide specific solute–solute interaction pathways, which would lead to the formation of particular of crystal structures [38]. When inducing heterogeneous nucleation, generally both the induction time and solute concentration necessary for the nucleation decrease whereas the nucleation density increases on going from a predominantly homogeneous to a predominantly heterogeneous nucleation contribution.

From the classical nucleation approach, the energetic of nucleation concerns mainly the work to create a surface. If there is already a solid substrate in the system, this will decrease the work required to create critical nuclei and will increase locally the probability of nucleation with respect to other locations in the system. Quantitatively, the free energy required for the formation of two-dimensional nuclei, when lowered by the presence of an appropriate substrate, is described by [87]

$$\Delta G^{*}_{\text{het}} = \left(\frac{-\Delta\mu}{\Omega}\right) + \gamma_{12}A_{12} + (\gamma_{23}-\gamma_{13})A_{23} \qquad (17)$$

where Ω is the molar volume ($\Omega = 4\pi r^3/3\upsilon_0$), υ_0 is the molecular volume, $\Delta\mu$ is the driving force ($\Delta\mu = k_B T \ln S$), γ is the interaction energy per area, A_{12} and A_{23} are the surface areas of the interfaces, and the subscripts 1, 2, and 3 represent the solute, the solvent, and the substrate, respectively. The total change in surface free energy will be lowered by favorable interactions between the aggregate and the substrate and unfavorable interactions between the crystallization medium and the substrate, due to the negative value of the second term in the equation above. Consequently, nucleation will be enhanced by increasing the surface area of the substrate. According to Equation (17), the nucleation process depends on two main parameters: the externally controlled supersaturation ratio and the material surface/solution composition-dependent interfacial energy. According to Young's equation for an ideal smooth surface, interfacial energy γ_{12} can be estimated by

$$\frac{\gamma_{23}-\gamma_{13}}{\cos\alpha} = \gamma_{12} \qquad (18)$$

where γ_{12}, γ_{13}, and γ_{23} are the nucleus–liquid, nucleus–substrate, and liquid–substrate interfacial energies, and α is the angle the interface between the nucleus and the bulk phase makes with the surface (see **Figure 1**). The contact angle is determined by the interactions between the surface and the molecules in the nucleus. Attractions between the surface and the molecules that are stronger than those between the molecules in the nucleus will lead to a small angle α as the nucleus spreads into a thin droplet to maximize its contact area with the surface. However, if the surface tends to repel

the molecules, then the nucleus is pushed away from the surface, resulting in a contact angle $\alpha > 90°$. From Young's equations, the effective interfacial energy, γ_{eff}, for heterogeneous nucleation will be reduced by a factor $0 < \varphi < 1$ compared to the interfacial energy γ_{12} for a pure homogeneous process: $\gamma_{eff} = \varphi^{1/3}\gamma_{12}$. Because $\gamma_{eff} < \gamma_{12}$, the work of formation for heterogeneous nucleation is substantially reduced compared to that of a homogeneous process. Furthermore, the pre-exponential kinetic parameter, A_{het}, in Equation (12), is inversely proportional to the concentration of heterogeneous particles C_a, which is much smaller than the molecular volume v_0. Typically, $A_{het} \approx 10^{15}$–$10^{25} << A_{hom} \approx 10^{35}$. Therefore, heterogeneous nucleation on a substrate is generally energetically less demanding than homogeneous nucleation because of the lowering of the surface energy of the nucleus on the substrate upon interfacial contact [88]:

$$\Delta G^*_{het} = \varphi \Delta G^*_{hom} \tag{19}$$

$$N_{het} \propto \varphi N_{hom} \tag{20}$$

where φ is the ratio between the heterogeneous and the homogeneous nucleation mechanism contribution. Considering the interaction between solute and substrate in terms of the contact angle α that the nucleus forms with the ideally smooth and chemically homogeneous substrate, the reduction of the activation energy for nucleation by heterogeneous activation is given by

$$\Delta G^*_{het} = \Delta G^*_{hom}\left(\frac{1}{2} - \frac{3}{4}\cos\alpha + \frac{1}{4}\cos^3\alpha\right) \tag{21}$$

Figure 9 shows graphically the above expression for different polymeric materials used as heterogeneous nucleants. If the nucleus wets the substrate completely ($\alpha = 180°$), $\Delta G^*_{het} = \Delta G^*_{hom}$; when the contact angle is 90° (limit between hydrophobic and hydrophilic behavior), $\Delta G^*_{het} = 1/2\,\Delta G^*_{hom}$, and the smaller the contact angle α, the smaller the value of the activation energy for nucleation, which is zero for $\alpha = 0$.

When using membrane crystallization, Equation (21) is no longer applicable because nucleation takes place on a porous substrate. In this case, a modified version of the equation that takes into account the porous structure of the surfaces has to be considered [31]:

$$\frac{\Delta G^*_{het}}{\Delta G^*_{hom}} = \frac{1}{4}(2 + \cos\alpha)(1 - \cos\alpha)^2\left[1 - \epsilon\frac{(1 + \cos\alpha)^2}{(1 - \cos\alpha)^2}\right]^3 \tag{22}$$

where ϵ is the overall surface porosity, defined as the ratio of the total pore areas on the whole geometrical surface. If $\epsilon = 0$, Equation (22) reduces to the form

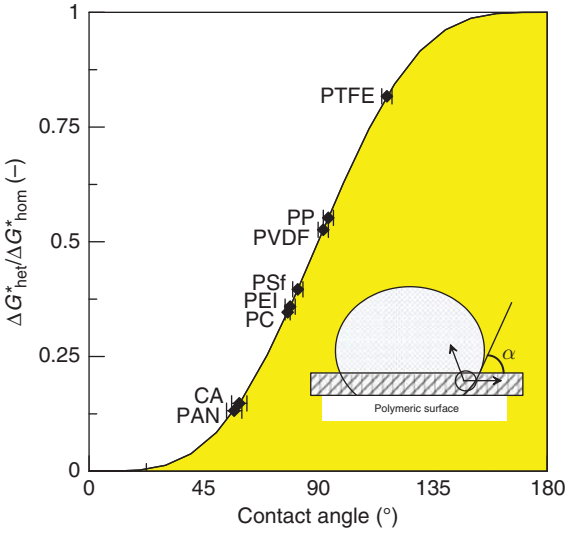


Figure 9 Reduction in the free energy of the nucleation barrier due to heterogeneous nucleation as a function of the water contact angle with the polymeric surface (CA, cellulose acetate; PAN, polyacrylonitrile; PC, polycarbonate; PET, polyetherimide; PES, polyethersulfone; PP, polypropylene; PSf, polysulfone; PTFE, polytetrafluoroethylene; PVDF, polyvinylidene fluoride).

reported in the literature (Equation (21)) for heterogeneous nucleation on nonporous surfaces.

Figure 10 shows the graphical representation of Equation (22) for various values of surface porosity. It can be seen from the figure that, if other solute/substrate interactions are not considered, the heterogeneous contribution to the free energy barrier for nucleation increases as surface porosity of the surface increases.

Figure 11 depicts a crystal of trypsin from porcine pancreas crystallized above the surface of a polypropylene membrane. From the figure, it is apparent the perfectly faceted morphology of the crystal embedded inside the porous irregularity of the surface where macromolecular aggregation started.

Figure 12 shows a possible nucleation mechanism generated by an irregular surface topography as that above a porous membrane. In this scheme, molecules dispersed in solution are first adsorbed on the surface by means of nonspecific attractive interactions. The irregular structure may physically block the lateral migration of the adsorbed protein molecules into the concaves, so that they are forced to be packed into compact aggregates. The trapping of molecules on

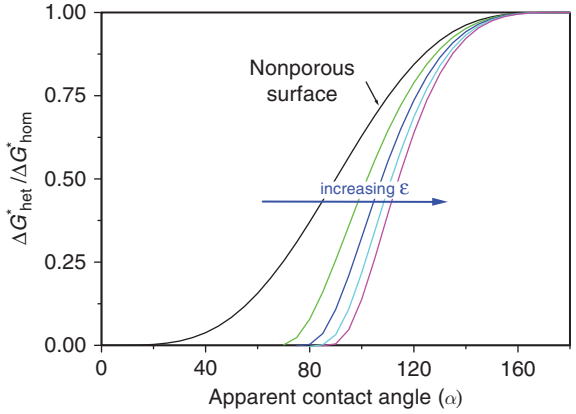


Figure 10 Effect of the surface porosity (ϵ) on the ratio $\Delta G^*_{het}/\Delta G^*_{hom}$ in the heterogeneous nucleation of protein on solid surfaces. The energetic barrier to nucleation decreases as porosity increases.

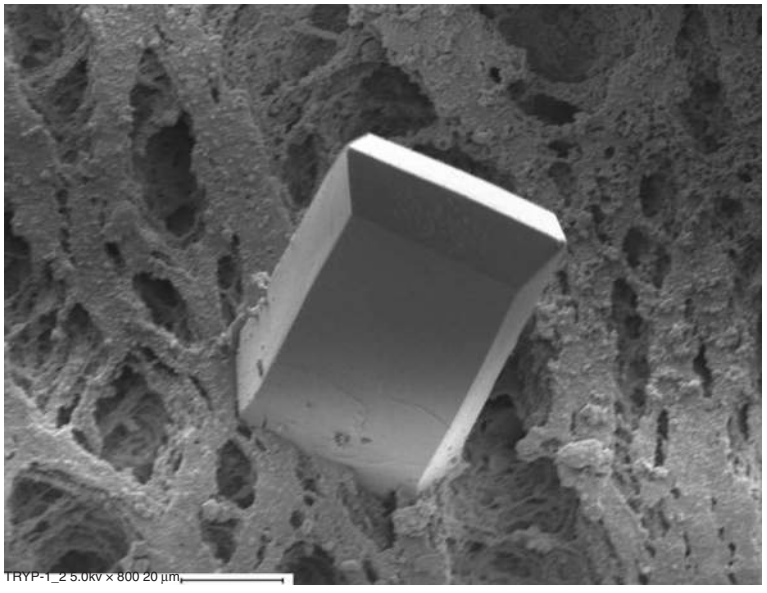


Figure 11 Porcine pancreas trypsin crystals grown on the surface of a macroporous hydrophobic polypropylene membrane.

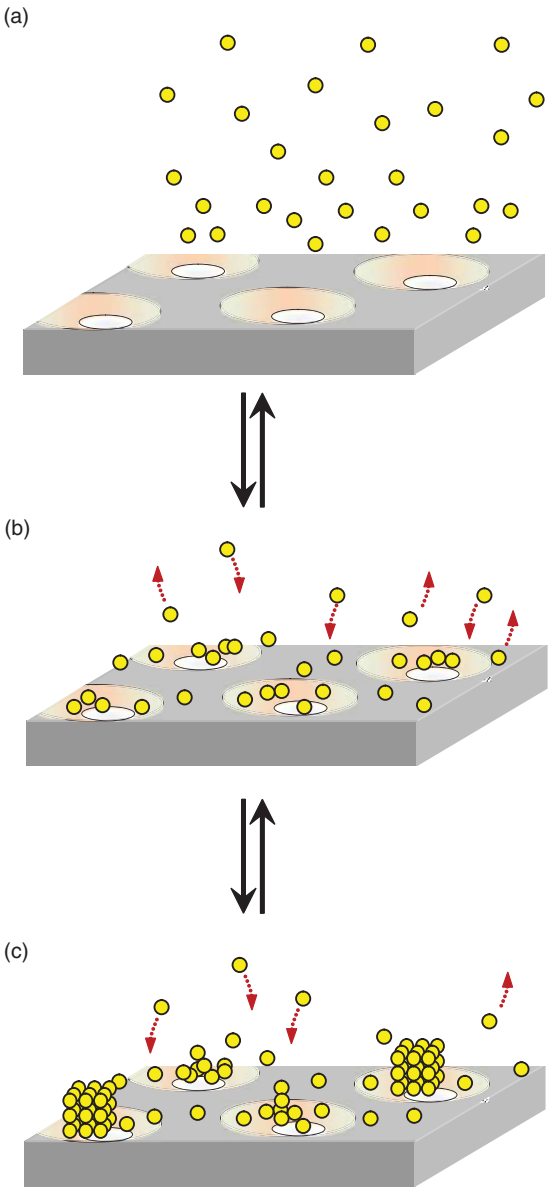


Figure 12 Schematic illustration of protein crystallization on irregular surfaces: (a) molecules dispersed in solution are first adsorbed on the surface; (b) the irregular structure may physically block the lateral migration of the adsorbed protein molecules into the concaves; (c) the trapping of molecules on the surface may result in a relatively higher local supersaturation, which would increase the possibility of aggregation.

the surface may result in a relatively higher local supersaturation, which would increase the possibility of nucleation compared with that on an ideally flat surface. Here, nucleation will follow with the formation of critical clusters comprising molecules forming suitable bond angles with their neighbors, while the molecules in a randomly packed compact structure may form a fractal cluster, which cannot work as a nucleus for crystal growth. Critical clusters then grow into crystals while the fractal clusters grow into larger clusters. This simple mechanism can be generalized to describe heterogeneous nucleation on irregular substrates such as porous membranes. From a technological point of view, the control of surface porosity in producing membranes can be easily achieved, so that specific nucleants, having the desired value of porosity which might be used to achieve the desired $\Delta G^*_{het}/\Delta G^*_{hom}$ ratio, can be produced.

4.02.7 Perspectives for Process Intensification

In the logic of the realization of improved productive cycles inspired to the process-intensification strategy, an important field where membrane crystallization could give a fundamental contribution is water treatment (both purification and desalination), which is becoming the most economically competitive way to resolve the potable water demand in regions which experience severe water scarcity. As environmental protection laws become more and more stringent, environmentally high-impacting wastes arising from industrial productions cannot be anymore discharged into the environment without preventive specific purification steps. This is the case of several industrial sectors where wastewaters containing high-polluting and/or high-value substances (fine chemicals, heavy metals, agro-food, tannery, desalination, petrochemicals, etc.) must be processed before being discharged into the environment. In this sense, membrane crystallization might be introduced in an integrated membrane system in which, after various separation steps, the selective crystallization and removal of some components might be achieved. The treated wastes can be purified by several pollutants, thus reaching the right characteristics for direct discharge and, on the other side, valuable materials with commercial implications can be recovered in crystalline state, and hence with high purity. Crystallization of marine salts from the brines of nanofiltration and/or RO steps used in seawater desalination is a typical example of such a strategy.

In seawater desalination, RO is the dominant technology to produce fresh water. However, some problems still exist related to this technique, such as the necessity to increase the recovery factors and to

resolve the problem of the disposal of the huge amount of the highly concentrated brine. Membrane contactor technology [89, 90], in the form of membrane crystallization, represents an additional option for realizing integrated membrane desalination systems, where a rational integration of different operations might determine substantial improvements in terms of water quality, product recovery factor, overall cost, brine disposal, and environmental impact. When a thermal membrane crystallizer follows an NF and/or a RO stage, the highly concentrate brine does not represent a waste to be disposed of, but rather the mother liquor in which crystals could nucleate and grow. With the integrated membrane system showed in **Figure 13**, the NF and/or the RO brine is further concentrated in a membrane crystallization unit, up to salt crystal formation in a controlled way. Sodium chloride, $CaCO_3$, and Epsom salts ($MgSO_4 \cdot 7H_2O$) are obtained as solid products from the NF retentate stream, while NaCl is the product from the RO brine [29]. If the presence of the NF as pretreatment for RO allows increasing the water recovery factor for the RO unit up to 50%, the introduction of a membrane crystallizer leads to a theoretical 100% recovery from the overall system, and therefore to the elimination of the problem of the brine disposal, as the pure crystals produced could represent a valuable product. Therefore, the adoption of membrane crystallization appears an interesting possibility for improving desalination operations and meeting the increasing demand for pure water at lower cost and with lower environmental impact [33] in the logic of the process-intensification strategy.

4.02.8 Other General Advantages of MCr Technology

Other general advantages of MCr technology over current state-of-the art crystallization processes, which are common for membrane operations and/or membrane contactor devices, are as follows:

Independence of operation. In MCr, although the membrane placed in contact the crystallizing solution with the distillate side, the two compartments are independent. This means that external manipulation on the crystallization kinetics, by tuning some of the operative parameters, can be carried out without disturbing the crystallizing solution, by acting for example, on the distillate side.

High and well-defined surface area. The high available specific area for mass transfer, and the possibility to control the evaporation rate during the operation, are additional advantages of this technology.

Forced solution flow environment. In the different cases, the crystallizing solution might be kept quiescent in a static configuration or it can be recirculated generating a condition of forced solution convection in a dynamic MCr. In this last case, the system is characterized by a laminar flow of the mother liquor through the membrane fibers; the low shear stress and an improved homogeneity are expected to promote a well-ordered organization of the molecules, resulting in the formation of a crystalline lattice exhibiting improved structural properties.

Low energy demand. Membrane crystallization technique requires low energy input for its operation. As an instance, in thermal membrane crystallizer, small temperature gradients between the feed and the distillate sides, in the order of 15 °C, are enough to produce transmembrane fluxes as high as several $l\,m^{-2}\,h^{-1}$. This means that a membrane crystallizer can be driven by using heat generated by other industrial processes (as, e.g., in cogeneration plants) and that would be, in normal cases, lost with high operating costs. On these bases, nonconventional alternative energy sources, such as wind, solar, geothermal, etc., might be potentially used to operate a membrane crystallization installation.

Mild operating conditions. In a thermal MCr, low feed temperature is sufficient to operate at high transmembrane fluxes. In an osmotic system, the supersaturation inside the crystallizing solution can be generated by using a stripping agent, which normally consists in a solution of an inert inorganic salt (NaCl, $MgCl_2$, $CaCl_2$, etc.). In both cases, the concentration of the feed is carried out in gentle conditions, without the solution experiencing thermal or mechanical stress. With the membrane-based system, labile or thermal-sensitive molecules, such as proteins, viruses, or other macromolecules, can be crystallized in large amounts, in very mild conditions, thus avoiding degradation and/or denaturation.

Possibility of scale-up and scale-down. As for every membrane operations, modularity might allow to scale-up or scale-down a process by simply adding or removing membrane modules. A similar case is for membrane crystallization techniques. In fact, this system would not suffer to any limitations for industrial-scale purposes by using well-designed multi-module system approach. On the other hand, the simple working principle of the system allows one

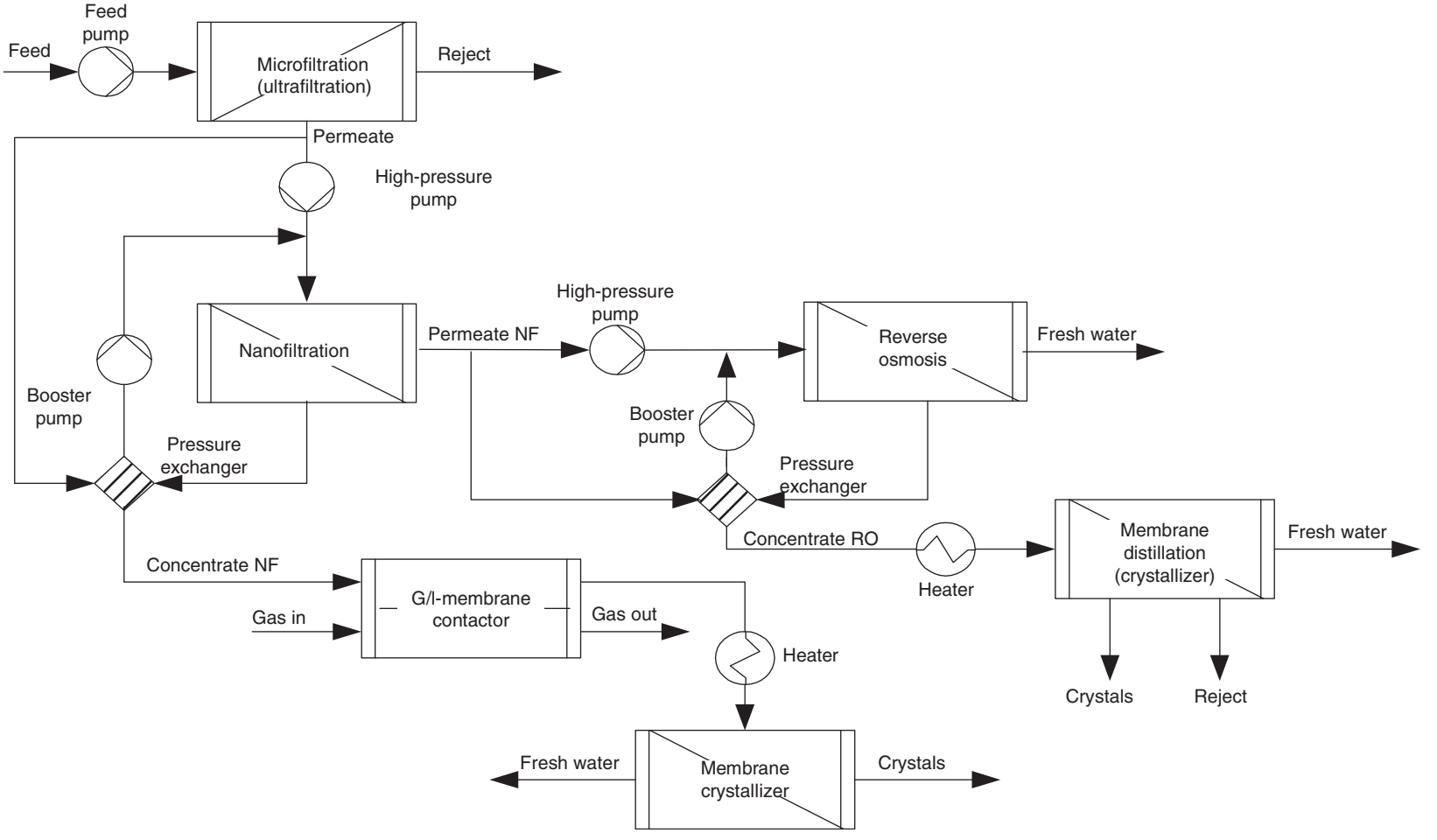


Figure 13 Integrated membrane system containing membrane crystallization units operating on the brine of the NF and/or of the RO stages.

to produce as small crystallization devices as microfluidic systems for the crystallization of little amounts of highly expensive materials, usually macromolecules, in high-throughput screening apparatuses.

4.02.9 Conclusions

Membrane crystallization is an effective method for performing well-behaved crystallization processes by a careful control of the operative parameters involved in the process, thus allowing the production of crystals with controlled shape, size, size distribution, and polymorphism. For example, the selective crystallization of one polymorph, for those molecular systems able to crystallize in several structures, can be achieved by controlling the rate of variation of the supersaturation. Crystals with different characteristics adapted to their specific uses can be selectively obtained even in the case of bio-macromolecules. Large crystals of high structural perfection for X-ray diffraction analysis or large amounts of biological material in the crystalline state and with controlled morphology can be grown. Further, the enhancement of the crystallization kinetics and/or the production of specific crystal forms by heterogeneous nucleation is another opportunity offered by this innovative technology. Membrane crystallizers also represent an interesting fundamental unit process to be introduced in integrated membrane systems operating in the logic of the process-intensification strategy such as, for instance, the recovery of fresh water from the sea by desalination.

References

[1] Margolin, A. L., Navia, M. A. *Angew. Chem. Int. Ed.* **2001**, *20*, 2204–2222.
[2] Falkner, J. C., Al-Somali, A. M., Jamison, J. A., *et al. Chem. Mater.* **2005**, *17*, 2679–2686.
[3] McPherson, A. *Crystallization of Biological Macromolecules*; Cold Spring Harbor Laboratory Press: Cold Spring Harbor, NY, 1999.
[4] Doye, J. P. K., Louis, A. A., Vendruscolo, M. *Phys. Biol.* **2004**, *1*, P9–P13.
[5] Curcio, E., Criscuoli, A., Drioli, E. *Ind. Eng. Chem. Res.* **2001**, *40*, 2679–2684.
[6] Boerlage, S. F. E., Kennedy, M. D., Bremere, I., Witkamp, G. J., Van der Hoek, J. P., Schippers, J. C. *J. Membr. Sci.* **2000**, *179*, 53–68.
[7] Boerlage, S. F. E., Kennedy, M. D., Bremere, I., Witkamp, G. J., Van der Hoek, J. P., Schippers, J. C. *J. Membr. Sci.* **2002**, *197*, 251–268.
[8] Wu, Y., Drioli, E. *Water Treat.* **1989**, *4*, 399–415.
[9] Wu, Y., Kong, Y., Liu, J., Zhang, J., Xu, J. *Desalination* **1991**, *80*, 235–242.
[10] Wu, Y., Kong, Y., Liu, J., Xu, J. *Water Treat.* **1991**, *6*, 253.
[11] Tomaszewska, M. *J. Membr. Sci.* **1993**, *78*, 277–282.
[12] Gryta, M. *Desalination* **2000**, *129*, 35–44.
[13] Gryta, M., Tomaszewska, M., Grzechulska, J., Morawski, A. W. *J. Membr. Sci.* **2001**, *181*, 279–287.
[14] Azoury, R., Garside, J., Robertson, W. G. *J. Cryst. Growth* **1986**, *79*, 654–657.
[15] Azoury, R., Garside, J., Robertson, W. G. *J. Cryst. Growth* **1986**, *76*, 259–262.
[16] Azoury, R., Garside, J., Robertson, W. G. *J. Urol.* **1986**, *136*, 150.
[17] Azoury, R., Robertson, W. G., Garside, J. *Chem. Eng. Res. Des.* **1987**, *65*, 342–344.
[18] Drioli, E., Wu, Y., Calabrò, V. *J. Membr. Sci.* **1987**, *33*, 277–284.
[19] Todd, P., Sikdar, S. K., Walker, C., Korzun, Z. R. *J. Cryst. Growth* **1991**, *110*, 283–292.
[20] Lee, C. Y., Sportiello, M. G., Cape, S. P., Ferree, S., Todd, P. *Biotechnol. Prog.* **1997**, *13*, 77–81.
[21] Sluys, J. T. M., Verdoes, D., Hanemaaijer, J. H. *Desalination* **1996**, *104*, 135–139.
[22] Curcio, E., Criscuoli, A., Drioli, E. *Proceedings of Euromembrane*, Hills of Jerusalem, Israel, 24–27 September 2000.
[23] Curcio, E., Criscuoli, A., Drioli, E. *Proceedings of 3rd Italy–Korea Workshop on Membrane Processes for Clean Energy and Clean Environment*, Cetraro, Italy, 23–27 September 2001.
[24] Curcio, E., Di Profio, G., Drioli, E. *Desalination* **2002**, *145*, 173–176.
[25] Gryta, M. *Sep. Sci. Technol.* **2002**, *37*, 3535–3558.
[26] Curcio, E., Di Profio, G., Drioli, E. *Sep. Purif. Technol.* **2003**, *33*, 63–73.
[27] Curcio, E., Di Profio, G., Drioli, E. *J. Cryst. Growth* **2003**, *247*, 166–176.
[28] Di Profio, G., Curcio, E., Cassetta, A., Lamba, D., Drioli, E. *J. Cryst. Growth* **2003**, *257*, 359–369.
[29] Drioli, E., Curcio, E., Criscuoli, A., Di Profio, G. *J. Membr. Sci.* **2004**, *239*, 27–38.
[30] Tuna, C. M., Fane, A. G., Matheickal, J. T., Sheikholeslami, R. *J. Membr. Sci.* **2005**, *257*, 144–155.
[31] Curcio, E., Fontananova, E., Di Profio, G., Drioli, E. *J. Phys. Chem. B* **2006**, *110*, 12438–12445.
[33] Drioli, E., Curcio, E., Di Profio, G., Macedonio, F., Criscuoli, A. *Chem. Eng. Res. Des.* **2006**, *84*, 209–220.
[34] Mariah, L., Buckley, C. A., Brouckaert, C. J., *et al. J. Membr. Sci.* **2006**, *280*, 937–947.
[35] Zhang, X., El-Bourawi, M. S., Wei, K., Tao, F., Ma, R. *Biotechnol. J.* **2006**, *1*, 1302–1311.
[36] Zhang, X., Zhang, P., Wei, K., Wang, Y., Ma, R. *Desalination* **2008**, *219*, 101–117.
[37] Weckesser, D., König, A. *Chem. Eng. Technol.* **2008**, *31*, 157–162.
[38] Simone, S., Curcio, E., Di Profio, G., Ferraroni, M., Drioli, E. *J. Membr. Sci.* **2006**, *283*, 123–132.
[39] Di Profio, G., Tucci, S., Curcio, E., Drioli, E. *Cryst. Growth Des.* **2007**, *7*, 526–530.
[40] Di Profio, G., Tucci, S., Curcio, E., Drioli, E. *Chem. Mater.* **2007**, *19*, 2386–2388.
[41] Zarkadas, D. M., Sirkar, K. K. *Ind. Eng. Chem. Res.* **2004**, *43*, 7163–7180.
[42] Sirkar, K. K., Zarkadas, D. M. Solid Hollow Fiber Cooling Crystallization System and Methods. US Pat. Appl. US20060096525A1.

[43] van der Gun, M. A., Bruinsma, O. S. L. Crystallization and Nanofiltration, Partners in Minerals Processing. In *Proceedings of 16th International Symposium on Industrial Crystallization*, Dresden, Germany, 11–14 September 2005.
[44] Cuellar, M. C., Herreilers, S. N., Straathof, A. J. J., Heijnen, J. J., van der Wielen, L. A. M. *Ind. Eng. Chem. Res.* **2009**, *48*, 1566–1573.
[45] Kuhn, J., Lakerveld, R., Kramer, H. J. M., Grievink, J., Jansens, P. J. *Ind. Eng. Chem. Res.* **2009**, *48*, 5360–5369.
[46] Bakker, W. J. W., Geertman, R. M., Reedijk, M. F., Baltussen, J. J. M., Batgeman, G., van Lare, C. E. J. Antisolvent Solidification Process. World Pat. Appl. WO2004096405A1.
[47] Mayer, M. J. J., Demmer, R. L. M., van Strien, C. J. G., Kuzmanovic, B. Process Involving the Use of Antisolvent Crystallisation. World Pat. Appl. WO2004096404A1.
[48] Zarkadas, D. M., Sirkar, K. K. *Chem. Eng. Sci.* **2006**, *61*, 5030–5048.
[49] Di Profio, G., Stabile, C., Caridi, A., Curcio, E., Drioli, E. *J. Pharm. Sci.* **2009**, *98*, 4902–4913.
[50] Hansen, C. L., Sommer, M., Quake, S. R., Berger, J. M. Microfluidic Protein Crystallography Techniques. World Pat. Appl. WO2005056813A3.
[51] Hansen, C. L., Classen, S., Berger, J. M., Quake, S. R. *J. Am. Chem. Soc.* **2006**, *128*, 3142–3143.
[52] Atkins, P. W. *Physical Chemistry*, 6th edn.; Oxford University Press: Oxford, 1998.
[53] Pena, L., Godino, M. P., Mengual, J. I. *J. Membr. Sci.* **1998**, *143*, 219–233.
[54] Martinez, L., Vazquez-Gonzalez, M. I. *J. Membr. Sci.* **2000**, *173*, 225–234.
[55] Ugrozov, V. V., Elkina, I. B. *Desalination* **2002**, *147*, 167–171.
[56] Schofield, R. W., Fane, A. G., Fell, C. J. D. *J. Membr. Sci.* **1987**, *33*, 299–313.
[57] Laganà, F., Barbieri, G., Drioli, E. *J. Membr. Sci.* **2000**, *166*, 1–11.
[58] Mulder, M. *Basic Principles of Membrane Process*; Kluwer: Dordrecht, 1996.
[59] Gekas, V., Hallstrom, B. *J. Membr. Sci.* **1987**, *30*, 153–170.
[60] Fujii, Y., Kigoshi, S., Iwatani, H., Aoyama, M. *J. Membr. Sci.* **1992**, *72*, 53–72.
[61] Kast, W., Hohenthanner, C.-R. *Int. J. Heat Mass Trans.* **2000**, *43*, 807–823.
[62] Kuhn, H., Fostering, H.-D. *Principles of Physical Chemistry*; Wiley: New York, 2000.
[63] Phattaranawik, J., Jiraratananon, R., Fane, A. G. *J. Membr. Sci.* **2003**, *215*, 75–85.
[64] Mason, E. A., Malinauskas, A. P. *Gas Transport in Porous Media: The Dusty-Gas Model*; Elsevier: New York, 1983.
[65] Fane, A. G., Schofield, R. W., Fell, C. J. D. *Desalination* **1987**, *64*, 231–243.
[66] Schofield, R. W., Fane, A. G., Fell, C. J. D. *J. Membr. Sci.* **1990**, *53*, 173–185.
[67] Warner, S. B. *Fiber Science*; Prentice-Hall: Englewood Cliffs, NJ, 1995.
[68] Jonsson, A. S., Wimmerstedt, R., Harrysson, A. C. *Desalination* **1985**, *56*, 237–249.
[69] Lawson, K. W., Lloyd, D. R. *J. Membr. Sci.* **1997**, *124*, 1–25.
[70] Reid, R. C., Prausnitz, J. M., Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd edn.; McGraw-Hill: New York, 1977.
[71] Perry, R. H. *Perry's Chemical Engineering Handbook*, 6th edn.; McGraw-Hill: Singapore, 1984.
[72] Kashchiev, D. *Nucleation, Basic Theory with Applications*; Butterworth: Oxford, 2001.
[73] Ostwald, W. Z. *Phys. Chem.* **1987**, *22*, 289–330.
[74] Volmer, M. *Kinetik der Phasenbildung*; Steinkopf: Leipzig, 1939.
[75] Cardew, P. T., Davey, R. J. *Proc. R. Soc.* **1985**, *398*, 415–428.
[76] Di Profio, G., Curcio, E., Ferraro, S., Stabile, C., Drioli, E. *Cryst. Growth Des.* **2009**, *9*, 2179–2186.
[77] Mullin, J. W. *Crystallization*, 4th edn.; Butterworth-Heinemann: Oxford, 2001.
[78] Kimble, W. L., Paxton, T. E., Rousseau, R. W., Sambanis, A. *J. Cryst. Growth* **1998**, *187*, 268–276.
[79] McPherson, A., Shlichta, P. *Science* **1988**, *239*, 385–387.
[80] Edwards, A. M., Darst, S. A., Hemming, S. A., Li, Y., Dkornberg, R. *Nat. Struct. Biol.* **1994**, *1*, 195–197.
[81] Chayen, N. E., Saridakis, E., El-Bahar, R., Nemirovsky, Y. *J. Mol. Biol.* **2001**, *312*, 591–595.
[82] Rong, L., Komatsu, H., Yoshizaki, I., Kadowaki, A., Yoda, S. *J. Synchrotron Radiat.* **2004**, *11*, 27.
[83] Vidal, O., Robert, M. C., Boùe, F. *J. Cryst. Growth* **1998**, *192*, 257–270.
[84] Sanjoh, A., Tsukihara, T., Gorti, S. *J. Cryst. Growth* **2001**, *232*, 618–628.
[85] Kornberg, R. D., Darst, S. A. *Curr. Opin. Struct. Biol.* **1991**, *1*, 642–646.
[86] Horbett, T. A. Adsorption of Proteins and Peptides at Interfaces. In *Stability of Protein Pharmaceuticals, Part 1: Chemical and Physical Pathways of Protein Degradation* Ahern, T. J., Manning, M. C., Eds.; Plenum: New York, 1992 Vol. 2, pp 195–214.
[87] Fletcher, N. H. *J. Chem. Phys.* **1963**, *38*, 237–240.
[88] Bonafede, S. J., Ward, M. D. *J. Am. Chem. Soc.* **1995**, *117*, 7853–7861.
[89] Drioli, E., Curcio, E., Di Profio, G. *Chem. Eng. Res. Des.* **2005**, *83*, 223–233.
[90] Drioli, E., Criscuoli, A., Curcio, E. *Membrane Contactors: Fundamentals, Applications and Potentialities*; Elsevier: Amsterdam, 2006.

Biographical Sketches

Dr. Gianluca Di Profio is a researcher at the Institute on Membrane Technology (ITM) of the Italian National Research Council (CNR). Graduated in physical chemistry in 2001 from the University of Calabria, he obtained his PhD in 2007 at the Chemical and Materials Engineering Department, working on the crystallization of organic materials by using membrane technology.

A tutor in chemistry at the Engineering Faculty of the University of Calabria, from 2001 to 2009, he was also worked at Akzo Nobel Chemicals Research Arnhem, the Netherlands. He was awarded the 'European Membrane Society Award 2004' for the best published paper in membrane science and engineering.

His main research activities relate to: study of phase transitions occurring in membrane operations; membrane contactor technology; membrane crystallization processes; integrated membrane systems for water treatments; membrane bioreactors and submerged membrane operations for water purification.

He is the coauthor of more than 35 scientific papers on membrane science and technology published in international journals and of more than 70 contributions to scientific conferences.

Efrem Curcio
Born in Cosenza (Italy) in 1975.

Educational background
1999 Masters Degree in Chemical Engineering.
2005 PhD in Chemical Engineering and Materials.
2005-present. Assistant Professor at the University of Calabria – Faculty of Engineering, and Research associate at the Institute on Membrane Technology ITM-CNR.

Research topics
– Integrated membrane systems for desalination and water treatment.
– Membrane-crystallization devices: applications in structural proteomics, polymorphs and enantiomers selection.
– Design and modelling of membrane bioreactors for cells culture.

Recipient of the EMS Award 2004 for the best published paper in Membrane Science and Engineering. A member of the European Membrane Society, the American Filtration Society, and Instituto Nazionale Scienza e Tecnologie dei Materiali (INSTM). A Referee of the Journal of Membrane Science, Desalination, the Journal of Biotechnology, Separation and Purification Technology (all Elsevier), and the Journal of Crystal Growth and Design (ACS). A member of the Editorial Board of The Open Proteomic Journal (Bentham Open).

Publications

Author of 53 papers published in international Journals, one book published by Elsevier, and around 80 contributions in congress proceedings, predominantly international.

Enrico Drioli is full professor at the School of Engineering of the University of Calabria. He has been professor of chemistry and electrochemistry at the School of Engineering of the University of Naples, dean of the School of Engineering of the University of Calabria, director of the Institute on Membranes and Chemical Reactors of the National Research Council, and director of the Institute on Membrane Technology of Consiglio Nazionale delle Ricerche (CNR).

His main research activities focus on membrane science and engineering; membranes in artificial organs; integrated membrane processes; membrane preparation and transport phenomena in membranes; membrane distillation and membrane contactors; and catalytic membrane and catalytic membrane reactors.

He received the following awards and honors: Doctorate Honoris Causa from the University of Paul Sabatier of Toulouse; International Cooperation Honor Award given by the Membrane Industry Association of China for his special dedication to the International Cooperation between China and Europe in the field of membrane and science technology; guest professor in the Environment and Safety Engineering Department at the Jiangsu Polytechnic University, China; honorary member of the A. V. Topchiev Institute of Petrochemical Synthesis at the Russian Academy of Sciences, Moscow; Doctorate Honoris Causa in Chemistry and Chemical Technology from the Russian Academy of Science; and honorary professor at the China Northwest University in Xi'an, Shaanxi, People's Republic of China.

He is involved in many international societies and scientific committees. Currently, he is member of various editorial boards and international advisory boards as well as chairman of the Working Party on Membranes of the European Federation of Chemical Engineering.

He is author of more than 530 scientific papers and 18 patents in the field of membrane science and technology.

4.03 Membrane Emulsification

E Piacentini and A Figoli, Institute on Membrane Technology, ITM-CNR, at the Universtity of Calabria, Rende (CS), Italy

L Giorno and E Drioli, Institute of Membrane Technology, ITM-CNR, University of Calabria, Rende (CS), Italy

Glossary

Capillary pressure The minimum pressure required to obtain dispersed phase permeation through the membrane.

Crossflow membrane emulsification Method in which the shear stress is generated by the recirculation of the continuous tangentially to the membrane surface, while a dispersed phase passes through the membrane.

Direct membrane emulsification Method to produce droplet emulsions by extruding the dispersed phase through the membrane pores into the continuous phase.

Emulsion An emulsion is a mixture of two or more immiscible phases (hydrophilic and hydrophobic) in which one liquid (the dispersed phase) is dispersed in the other (the continuous phase).

Membrane emulsification (ME) Method to produce emulsions by drop-by-drop mechanism, that is, the dispersed phase is added drop by drop through porous membranes in the continuous phase.

Multiple emulsion It is a mixture in which a simple emulsion (O/W or W/O) is dispersed as droplets in the continuous phase (W or O). These emulsions can be W/O/W and O/W/O emulsions. For example, a W/O/W emulsion consists of water droplets dispersed within larger oil droplets, which are themselves dispersed in a water continuous phase.

Premix membrane emulsification Method to produce fine droplet emulsion by extruding the course emulsion through the membrane pores into the continuous phase.

Simple emulsion It is a mixture in which oil droplets are dispersed in the water continuous phase (O/W emulsion) or water droplets are dispersed in the oil continuous phase (W/o emulsion).

Stirred membrane emulsification Method in which the shear stress at the membrane surface is generated using a paddle stirrer, while a dispersed phase passes through the membrane.

4.03.1 Definitions

An emulsion is a mixture of two or more immiscible phases (hydrophilic and hydrophobic) in which one liquid (the dispersed phase) is dispersed in the other (the continuous phase). Emulsions can be conveniently classified according to the relative spatial distribution of the hydrophobic (oil) and hydrophilic (water) phases: a system that consists of oil droplets dispersed in the water continuous phase is an oil-in-water (O/W) emulsion and a system that consists of water droplets dispersed in the oil continuous phase is a water-in-oil (W/O) emulsion. More complex systems are the multiple emulsions in which a simple emulsion (O/W or W/O) is used as the dispersed phase. These emulsions can be water-in-oil-in-water W/O/W and oil-in-water-in-oil O/W/O emulsions. For example, a W/O/W emulsion consists of water droplets dispersed within larger oil droplets, which are themselves dispersed in a water continuous phase. Some examples of emulsion types are shown in **Figures 1(a)** and **(b)**.

Furthermore, emulsions in which a solid phase is dispersed into a liquid phase can also be obtained (**Figure 1(c)**). The final product is composed of solid particles which can be classified (as shown in **Figure 2**) into: (1) capsules, for example, small, coated particles loaded with a solid, a liquid, a solid–liquid dispersion, or a solid–gas dispersion; and (2) microspheres or microbeads, for example, spherical particles composed of various natural and synthetic materials with diameters in the micrometer range: solid lipid microspheres, albumin microspheres, and polymer microspheres.

Some specific definitions can be considered in membrane emulsification (ME) process. Direct ME refers to the formation of droplets by extruding the dispersed phase through the membrane pores into the continuous phase (**Table 1**). Premix ME refers to the formation of fine droplet emulsion by extruding the course emulsion through the membrane pores into the continuous phase (**Table 1**). ME can be carried out in

1. A dynamic mode operation (**Figure 3(a)**) in which
   (a) static and fixed membranes are used and the continuous phase is moved (cross flow or stirred ME) and
   (b) moving membranes are used to generate relative motion between the membranes and the continuous phase.
2. A static mode operation (**Figure 3(b)**) in which droplets are detached from the membrane pore when they reach a certain size in the absence of additional moving force.

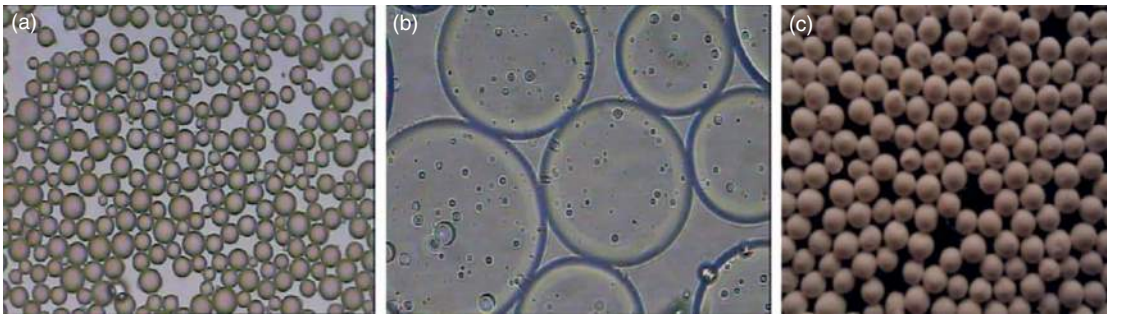


Figure 1 (a) Simple and (b) multiple emulsions; (c) microspheres picture.

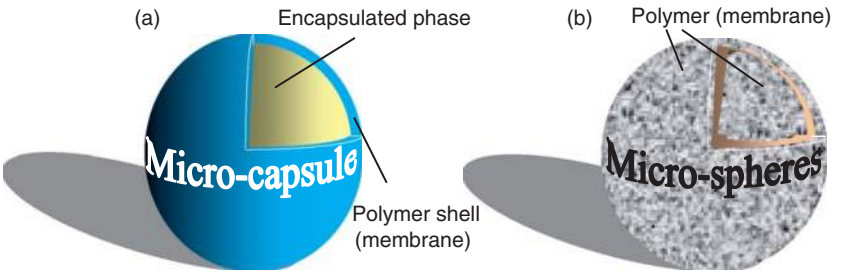
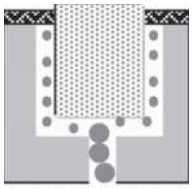
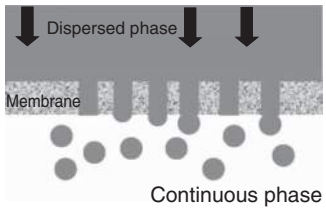
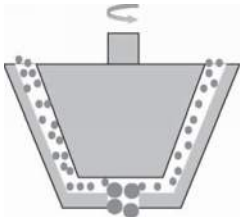
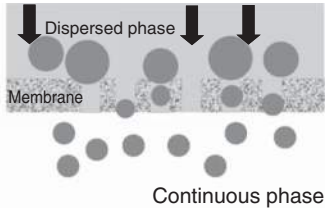
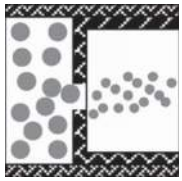


Figure 2 Schematic representation of the (a) microcapsule and (b) microspheres/beads.

Table 1 Schematic drawing of mechanical processes used to production emulsions

Emulsion production by mechanical process	
Droplet disruption	***Droplets formation at microporous***
Ultrasound	Direct membrane emulsification
	
High-pressure systems	Premix membrane emulsification
	
Rotor–stator systems	Microchannel
	

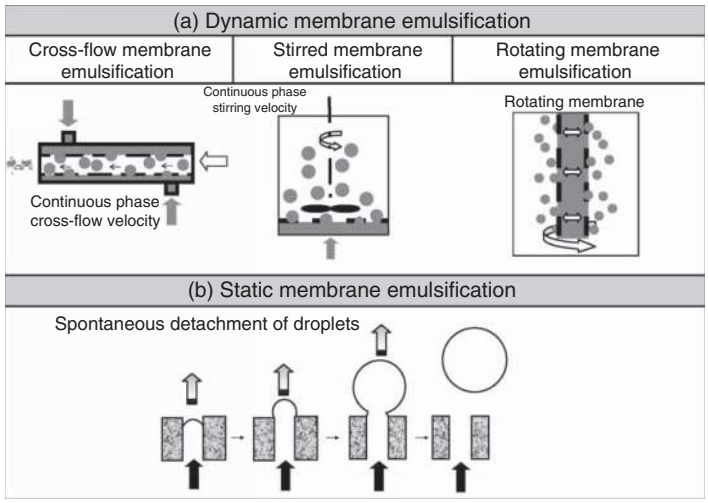


Figure 3 Membrane emulsification mode operation and mechanisms.

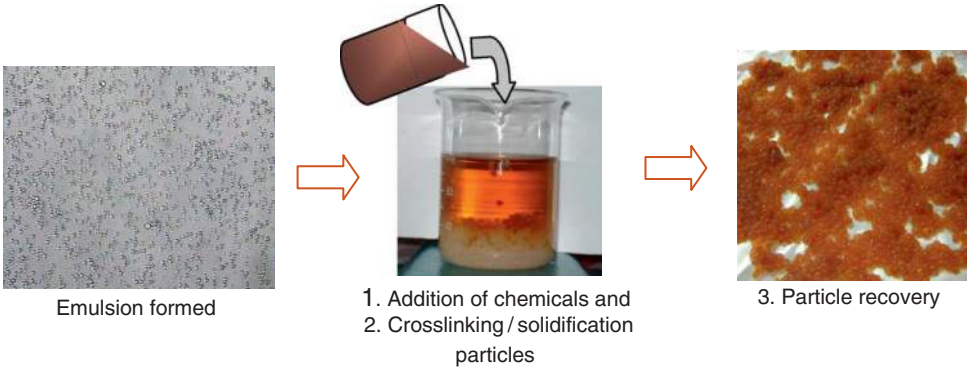


Figure 4 Flowsheet of microparticles formation.

Once the emulsion is formed, several methods are employed for preparing particles based exclusively on physical phenomena, polymerization reaction, or combining physical and chemical phenomena. However, they all have three main steps in common as schematically shown in **Figure 4**.

After the emulsion formation, specific chemicals and materials need to be added to the dispersion to form either the capsule wall or the microsphere (first step), then, the solidification or crosslinking of the droplets takes place (second step). The particles formed are, subsequently, separated and collected (third step).

4.03.2 Emulsions Production

Many different methods can be used to produce an emulsion (**Table 1**). There are several nonmechanical processes such as dispersed phase precipitation or phase inversion. Changes in the phase behavior of the substances to be emulsified, promoted by variation of temperature or composition or by mechanical stress, are used to achieve the desirable state of the system. It is possible to form an emulsion by homogenizing the dispersed phase and the continuous phase together in a premix emulsions and by disrupting big droplets in a fine emulsion. Rotor–stator systems, high-pressure system, and ultrasound are used as conventional mechanical devices to produce emulsions [1]. In rotor–stator systems, emulsions can be produced both continuously and discontinuously by applying a mechanical energy that is the driving force for droplet disruption. In high-pressure systems, the driving force is a high-pressure gradient. They can be subdivided into radial diffusers, counterjet dispergators, and axial nozzle aggregates, depending on the flow guidance. High-pressure systems are always continuously operated. In ultrasonic systems, the energy input takes place with the so-called ultrasonic sonotrodes. They are discontinuously operated.

Emulsions may also be produced drop by drop at membranes and microstructured systems. In this case, the dispersed phase is forced through the membrane pores and collected as droplets in the continuous phase (direct ME). ME process can be used also to produce fine droplets from a premix emulsion forcing a coarse emulsion through the membrane (premix ME). ME technology was introduced in the early 1990s by Nakashima and Shimizu [2] at the Autumn Conference of The Society of Chemical Engineering in Japan. In the late 1990s, Suzuki *et al.* [3] used the premix ME to obtain higher production rate than the other emulsification method. The fast progress in microengineering and semiconductor technology led to the development of microchannels, which Nakashima and co-workers [4] applied in emulsification technology. A comparison of the conventional mechanical method and membrane processes is presented in **Table 2**.

Here, a distinction between continuous and discontinuous processes is discussed. In the case of continuous emulsification, the ingredients are usually dosed separately or premixed in a stirrer (to obtain a coarse-disperse raw emulsion). Further distinctive features include the possible product throughput and the product stress during the emulsification process, which predestines the different processes again for the industrial production or the application in laboratories and/or product-form development. Rotor–stator systems and high-pressure systems are frequently used in industrial production. Due to the small product throughput, ultrasonic systems, ME, and microchannel are mainly applied in batch scale for

Table 2 Main properties of mechanical emulsification process

Process	*Membrane emulsification*	*Microchannel*	*Rotor–stator systems*	*High-pressure systems*	*Ultrasound*
Droplets formation mechanism	Droplet detachment by wall shear stress	Droplet detachment by instability phenomenon	Droplets break-up by shear-/inertia-stress in turbulent flow or shear stress in laminar flow	Droplets break-up by shear-/inertia-stress in turbulent flow; cavitation; laminar extension flow	Droplets break-up by cavitation; microturbulences
Modus operation	Continuous	Continuous	Discontinuous or continuous	Continuous	Discontinuous
Productivity	Laboratories/ product from development	Laboratories/ product from development	Industrial production	Industrial production	Laboratories/product from development
Droplets size	0.1–10 μm	>3 μm	>2 μm	<0.2 μm	≈0.4 μm
Energy density	10^3–10^6 Jm^{-3}	–	10^5–10^8 Jm^{-3}	10^6–10^8 Jm^{-3}	10^7–10^8 Jm^{-3}
Droplets size distribution	Narrow	Monodisperse	Polydisperse	Polydisperse	Polydisperse

niche productions. Most of the properties of emulsions depend on the droplet size and droplet-size distribution. They are of essential importance because of their great influence on physical stability, rheological and optical characteristics, bioavailability or dose–response, taste, texture, and other properties. In high-pressure homogenizers, the diameter of droplets is a direct function of energy density that equals the effective pressure difference at the homogenizing valve. With this system, mean droplet size <0.2 μm can be obtained with high product throughputs. However, the stress on the product is very high due to the high-pressure gradients and flow rate. In rotor–stator systems and ultrasound homogenizers, droplet size and energy density are only linked by approximations on the basis of experimental data [5]. With rotor–stator systems, mean droplet size below 2 μm cannot be obtained. The product throughput lies in the middle of the available range, whereas the product stress can be classified as medium. With ultrasound homogenizers, droplet size of approximately 0.4 μm can be obtained. Thereby the product stress is very high.

In ME process, droplet size is strictly controlled by the membrane pore size. Here, the diameter of droplets down to 0.2 μm with very narrow droplet-size distributions can be obtained. The possible product throughput, however, can be classified as small. The great advantage of emulsification process is the small shear stress applied, which corresponds to the lowest energy input. Microchannel emulsification distinguishes itself from ME only by a deliberate choice for a specific geometry of the channel that ends in a strongly noncylindrical geometry. The energy density of the emulsification process using microchannels is not reported in literature but it is expected that it could be in the range of ME. However, the microchannel process is very expensive compared to the common emulsification methods. Thus, the energy input is not important. The main advantage of the microchannel process is the possibility to produce nearly monodispersed emulsions.

4.03.3 Emulsion Manufacturing by ME Process

The main distinguishing factor in ME is that emulsion droplets are generated by forcing a dispersed phase through membrane pores into a continuous phase [6]. Many different parameters influence droplet size, droplet-size distribution, and emulsification productivity in ME processes (**Figure 5**). During droplet formation, the droplets grown at the pore opening become detached once they reach a certain size. Depending on whether a shear force is responsible for the droplet detachment from the pore opening or the droplets are spontaneously detached in the absence of shear flow at the membrane surface, it is possible to distinguish the dynamic or static ME, respectively.

4.03.3.1 Dynamic ME

Generally, in order to ensure a regular droplet detachment from the pore openings, cross flow is

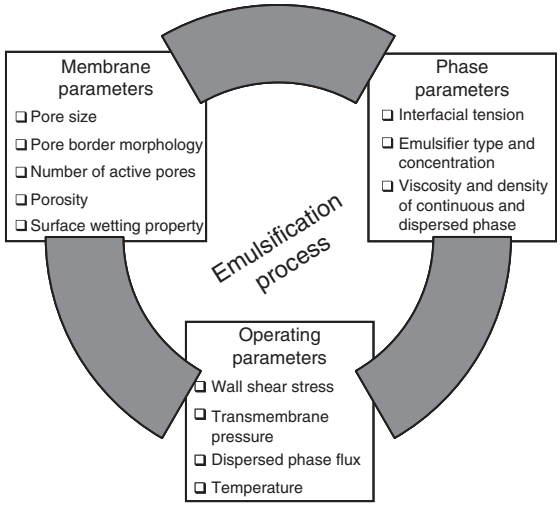


Figure 5 Main parameters influencing membrane emulsification process.

applied in the continuous phase along the membrane surface, where shear stress is generated by the recirculation of the continuous phase using a low shear pump. This technique is called cross-flow membrane emulsification. Alternatively, the shear stress at the membrane surface can be generated using a paddle-blade stirrer. This technique is called stirred membrane emulsification. A schematic representation of dynamic ME is shown in **Figure 3(a)**.

The main parameters involved in ME are presented in **Figure 5**.

A transmembrane pressure (ΔP_{tm}) is the force required to press the dispersed phase through the membrane pore into the continuous phase. It is defined as the difference between the pressure of the dispersed phase, P_d, and the mean pressure of the continuous phase ($P_{c,in}$ and $P_{c,out}$ are the pressure of the flowing continuous phase at the inlet and the outlet of the membrane, respectively):

$$\Delta P_{tm} = P_d - \frac{\left(P_{c,in} + P_{c,out}\right)}{2} \tag{1}$$

The minimum pressure required to obtain dispersed-phase permeation is the capillary pressure, P_c, that depends on O/W interfacial tension (γ_{ow}), contact angle (θ) of the dispersed phase against the membrane surface well wetted with the continuous phase, and average membrane pore diameter (d_p):

$$P_c = \frac{4\gamma\cos\theta}{d_p} \tag{2}$$

An important parameter related to the transmembrane pressure is the dispersed phase flux ($\mathcal{J}_d$). According to Darcy's law, the dispersed-phase flux depends also on membrane permeability (L_p), membrane thickness (L), and dispersed phase viscosity (μ):

$$\mathcal{J}_d = \frac{L_p \Delta P_{tm}}{\mu L} \tag{3}$$

When the pressure of the disperse phase is high enough, it sets in the droplet formation at the membrane surface. In dynamic ME, after the droplet has grown up to a critical diameter, it is detached by the wall shear stress (τ_w) of the continuous phase at the membrane surface.

The wall shear stress is calculated considering the friction factor correlation (λ), the density of emulsion (ρ), and the axial velocity (V_{ax}):

$$\tau_w = \frac{\lambda \rho V_{ax}}{2} \tag{4}$$

The friction factor correlation depends on Reynolds number (Re):

$$Re < 2000 \qquad \tau_w = \frac{\lambda \rho V_{ax}}{2} \tag{5}$$

and

$$Re < 2000 \qquad \lambda = 0.0792 Re^{-0.25} \tag{6}$$

The Reynolds number is a nondimensional parameter defined by the ratio of dynamic pressure ($\rho\ V_{ax}^2$) and shearing stress ($\eta\ V_{ax}/D_h$) and can be expressed as

$$Re = \frac{\rho V_{ax}^2}{\frac{\eta V_{ax}}{D_h}} = \frac{\rho V_{ax} D_h}{\eta} \tag{7}$$

where D_h is the hydraulic diameter and η the viscosity.

Among different forces holding the droplet at the membrane surface, the force caused by the interfacial tension ($F\gamma$) is the most dominant. It is caused by the time-dependent interfacial tension $\gamma(t)$:

$$F\gamma = \pi\, d\, \gamma(t) \tag{8}$$

Due to the influence of surfactants on the interfacial tension, surfactant dynamics strongly influence the droplet formation.

Emulsion droplet diameter (d_d) is a function of membrane pore diameter (d_p) according to a linear relationship in which the linear coefficient (c) is constant and depends on the membrane used:

$$d_d = c\, d_p \tag{9}$$

In dynamic ME, it is shown that the droplet size becomes smaller as the wall shear stress increases and that the influence is greater for low wall shear stresses [7, 8]. The effect of shear stress on reducing droplet size is dependent on the membrane pore size, being more effective for smaller membrane pore size [9].

A new dynamic emulsification method has been developed using rotating membrane [10–12]. Compared with cross-flow ME methods, the rotating ME can be particularly advantageous for the production of coarse emulsions and fragile structured products in which the droplets and/or particles are subject to breakage during the pump recirculation. The dispersed phase permeates the porous membrane wall radially and forms droplets moving into the continuous phase. Another novel approach is the application of transversal excitation to the membrane surface. When amplitude and frequency of the excitation are sufficiently large, the additional forces may

significantly reduce the average droplet size. Zhu and Barrow [13] reported the first investigation on the efficacy of transversal excitation in ME. They performed ME of hexadecane in water using Tween 20 as the surfactant, and micro-machined silicon nitride membranes excited by a piezoactuator system.

4.03.3.2 Static ME

In the absence of shear flow at the membrane surface, the important relationship referred to transmembrane pressure, dispersed phase flux, interfacial tension force, and membrane pore describes the main factor to consider in static ME (**Figure 3(b)**). This type of spontaneous droplet detachment has also been observed in droplet formation using grooved and oblong straight-through microchannel [14–15]. In this case, the interfacial tension is a driving force for droplet detachment. In particular, the flow of dispersed phase in membrane pores has a great influence on the spontaneous droplet formation behavior and depends on the viscosities of dispersed and continuous phases and flow velocity of the dispersed phase through the membrane pore [16]. In addition, with ME in the absence of continuous phase flow, the adsorption kinetics of surfactant, which is added in the continuous phase, has a more profound effect on the size and size distribution of the droplets generated. During the droplet formation process, the surfactant molecules adsorb to the newly formed oil–water interface to reduce the interfacial tension and consequently to facilitate droplet formation. The transfer rate of the surfactant molecules from bulk solution to the newly formed oil–water interface is mainly determined by their diffusional transfer because of the absence of continuous-phase flow. The surfactant type and concentration greatly influence the adsorption kinetics of the surfactant and thus the dynamic interfacial tension [17].

Sugiura *et al.* [16] presented a detachment mechanism for interfacial-tension-driven droplet formation, where the spontaneous droplet detachment from the pore openings is strongly dependent on the shape of the pore openings: noncircular pore openings cause the spontaneous detachment of droplets. This mechanism, termed as spontaneous-transformation-based droplet formation, is described by considering the free energy of the system: during droplet formation from tortuous pores with a noncircular cross section, the distorted dispersed phase is spontaneously transformed into spherical droplets by interfacial tension because of minimization of the interfacial free energy of the system. Spontaneous droplet formation from Shirasu porous glass (SPG) membranes was first observed by Christov *et al.* [18] using an optical microscopy. Yasuno *et al.* [19] visualized spontaneous droplet formation from SPG membrane at a low dispersed phase flux and proposed a mechanism for spontaneous-transformation-based droplet formation. Kukizaki and co-workers [20, 21] studied the influence of surfactant type and concentration, viscosity of dispersed and continuous phases, and transmembrane pressure on the droplet size, droplet-size distribution, and dispersed flux. Kosvintsev *et al.* [22] carried out experimental and theoretical studies using metallic membrane with a highly uniform pore spacing and uniform pore size under conditions of zero surface shear showing that an additional force to the buoyancy and capillary forces exists in ME. A push-off force, derived by consideration of the geometry of the drops as they deform at the surface of the pores, is the dominant detachment force in the force balance.

The emulsification method in static condition shows several advantages over cross-flow ME because no moving parts, such as cross-flow pump, are needed: (1) the experimental setup is generally simpler than in cross-flow ME; (2) the energy input needed would be lower; and (3) ME in the absence of shear flow at the membrane surface is potentially suitable for the production of less viscous and/or larger droplets with uniform size. This is because, during droplet formation in cross-flow ME, less viscous and/or larger droplets are liable to further break up due to the shear force caused by the cross-flow pump [23].

4.03.4 Advances Needed in ME Process

The main disadvantage of the ME process is a low dispersed phase flux through the membrane. **Table 3** shows typical values of dispersed phase flux during ME process. SPG membranes are the mostly common used membrane in emulsion preparation even if low flux of the dispersed phase is usually obtained in the preparation of O/W and W/O emulsion. Higher fluxes are obtained with ceramic membranes.

The flux through the membrane is determined by the applied transmembrane pressure, the permeability of the membrane, and the number of active pores (Darcy's law). The SPG membranes have a low permeability, because they are quite thick

Table 3 Typical dispersed phase flux membrane obtained during membrane emulsification method

Membrane	*Membrane pore*	*Emulsion type*	*Disperse phase flux* ($lm^{-2}h^{-1}$)	*Ref*
Hydrophilic SPG	0.2 μm	O/W	5–15	24
Hydrophilic SPG	0.5 μm	O/W	10–45	24
Hydrophilic ceramic Al_2O_3 membrane	0.2 μm	O/W	50–250	25
Hydrophilic SPG pretreated	0.5 μm	W/O	200	25
Hydrophilic SPG pretreated	1 μm	W/O	2300	25
Polypropylen	0.4 μm	W/O	0.05–0.2	26
Hydrophilic polyamide pretreated	10 kDa (NMWCO)[a]	O/W	2	27

[a] Nominal molecular weight cutoff.

(0.45–0.75 mm) and are homogeneous in structure. In addition, the number of active pores is reported to be very low, that is, 0.3–0.5% [28] and 2% [29]. For ceramic membranes, the permeability is expected to be higher, because the top layer with the smallest pores is very thin; this layer being mechanically supported by layers with larger pore diameters [30].

To overcome the limitation of low dispersed flux, various operating methods were introduced such as rotating or vibrating membranes and repeated premix ME.

The productivity (expressed as dispersed phase flux) is an important issue in commercial production. ME productivity can be enhanced by appropriate membrane design of pore size and pore shape [31]. In particular, noncircular pores can offer significant process benefits for the production of uniform droplets.

Fouling phenomena on the membrane surface and/or in the pores also represent an important issue in ME application. Membrane fouling can be caused by proteins used as emulsifier [32] or by interactions of the dispersed phases [33] with the membrane materials. The fouling phenomenon determines a decrease of dispersed phase flow rate. This problem is most evident for membranes with smaller pore size. In addition, fouling of the membrane must be avoided during emulsification in order to maintain a reasonably narrow size distribution of the droplets.

A small number of membranes are specifically developed for application in ME, including SPG membrane (SPG technology) and metallic membrane (micropore technology). In most cases, the membranes used are borrowed from other processes and adapted to this specific use. Advances needed in ME process include membranes, modules, and plants specifically designed and developed to fulfill properties required for emulsification applications: high fluxes, fouling resistance, appropriate membrane pore size, and pore shape design.

4.03.5 O/W Emulsion

O/W emulsions are the most versatile emulsions and exist in many formulations:

- mayonnaises, cream liqueurs, creamers, whippable toppings, and ice-cream mixes for application in the food industry;
- skin care emulsions for cosmetic application;
- pharmaceutical suspension for drug delivery; and
- multiphase system as chemical or biochemical reaction medium.

Most studies in ME report the preparation of O/W emulsion. Some of these studies are important because they help in understanding the theoretical bases of ME process [24, 25, 34–38]. Some examples of O/W emulsion preparation using ME are given in **Table 4**.

The studies show that increasing transmembrane pressure causes a faster droplet growth and larger droplets are obtained. However, this is observed only as long as the droplet formation is fast compared to the adsorption of emulsifiers. The longer the droplet formation time for the same emulsifier, the lower the influence of the transmembrane pressure on the droplet size [35]. When shear stress effect is investigated, experimental studies reveal that the droplet size becomes smaller as the wall shear stress increases and that the influence is much greater for wall shear stresses <30 Pa [35, 37]. However, this effect is dependent on the membrane pore size, being more effective for smaller membrane pore sizes [35, 39]. When faster emulsifiers are used, smaller droplet size is obtained. The faster the adsorption of the emulsifier molecules, the lower the probability

Table 4 Literature data of previous investigations dealing with the preparation of O/W emulsion by membrane emulsification

Parameter studied	*Method*	*Operation procedures*	*Membrane*	D_p (μm)	*Dispersed phase*	*Continuous phase*	*Emulsifier*	*Flux (l $h^{-1}m^{-2}$) or P_{tm} (kPa) of dispersed phase*	*Shear stress (Pa) of continuous phase*	*Dd (μm)*	*Ref*
ΔP_{TM}	Direct	Cross flow	Hydrophilic SPG membrane	4.8	Rapeseed oil	Demineralized water	Tween 80 2% wt	13.3–9.9 kPa	30	2.9–3.5	34
ΔP_{TM}	Direct	Cross flow	Hydrophilic Ceramic Al_2O_3 membrane	0.8	Vegetable oil	Demineralized water	SDS 2% wt	50–325 kPa	33	2.5–3.45	35
ΔP_{TM}	Direct	Cross flow	Hydrophilic Ceramic Al_2O_3 membrane	0.2	Vegetable oil	Demineralized water	Tween 20 0.1% wt	70–150 kPa		6.2–10.6	35
ΔP_{TM}	Direct	Cross flow	Hydrophilic Ceramic Al_2O_3 membrane	0.2	Vegetable oil	Demineralized water	SDS 2%wt	100–300 kPa	30	0.6	36
τ_w	Direct	Cross flow	Hydrophilic SPG membrane	4.8	Rapeseed oil	Demineralized water	Tween 80 2% wt	13.3 kPa	1.3–30	18–14	34
τ_w	Direct	Cross flow	Hydrophilic Ceramic Al_2O_3 membrane	0.5	Semper 131 Vegetable oil	Skin milk	Dimodan PVP 2%wt	20 kPa	6.1–102.4	40–4.6	37
τ_w	Direct	Cross flow	Hydrophilic Ceramic Al_2O_3 membrane	0.8	Vegetable oil	Demineralized water	LEO-10 0.7%wt	70 kPa	5–20	1.28–0.84	35
τ_w	Direct	Cross flow	Hydrophilic Ceramic Al_2O_3 membrane	0.1	Vegetable oil	Demineralized water	LEO-10 0.7%wt	33 kPa	5–20	0.36	35

τ_w	Direct	Cross flow	Hydrophilic MPG membrane	0.2	Sunflower oil	-	Milk protein 3%wt	450 kPa	2.7–13.5	8.1–3	24
							SDS 2% wt			1.25	
							LEO-10 0.7%wt			2.5	
γ	Direct	Cross flow	Hydrophilic Ceramic Al_2O_3 membrane	0.2	Vegetable oil	Demineralized water	Tween 20 0.1% wt	300 kPa	33	3.5	36
							Tween 20 2% wt			2.5	
							Lacprodan 60 0.1% wt			10	
							SDS 1% wt			2.26	
γ	Direct	Cross flow	alumina-based membrane	0.5	Sunflower oil	Aqueous solution	11 s globulin 0.02% wt	22.1 (l $h^{-1}m^{-2}$)	93.3	6.10	39
							Casein 0.02%wt			6.50	
				0.36						1.7	
				0.73						3.77	
dp	Direct	Cross flow	Hydrophilic SPG membrane	1.25	Corn oil;	Deionized water	SE at 0.3%wt	-	-	6	25
				1.9						9	
				2.34						11.62	
				0.36						1.1	
dp	Direct	Cross flow	Hydrophilic MPG membrane	0.73	Soybean oil	Deionized water	Phospholipid (PLs) 0.5% wt	-	-	2.2	38
				1.46						4.34	

of coalescence, especially during droplet formation [36]. Kato *et al.* showed the droplet diameter distribution in representative O/W emulsions, composed of deionized water/sucrose esters (SEs) or sodium dodecyl sulfate (SDS) or polyglycerol esters (PGEs)/corn oil, prepared by the SPG ME method using membranes of various pore diameters. The results demonstrated that the dispersion droplet diameter basically depends upon the membrane pore diameter. The same relationship between particle size distribution of the emulsion and pore-size distribution of the membrane used is found for the egg phospholipid (PL) emulsions when microporous glass membranes are used [38].

In addition, various formulations of food emulsions by ME are reported [18, 24, 25, 37, 40]. A limited number of studies are reported in the emulsion preparation specifically designed to other applications. O/W emulsions containing astaxanthin were prepared by repeated premix ME [41]. Astaxanthin is a natural carotenoid product with exceptional antioxidant properties. In the emulsification process, a pre-emulsion is repeatedly pushed through a hydrophilic or hydrophobic membrane. Pre-emulsions were produced by dispersing palm oil containing dissolved astaxanthin in water [41].

The technology also represents a suitable strategy for the preparation of microstructured multiphase reaction systems. Giorno *et al.* [42] reported on the use of ME to distribute a phase-transfer biocatalyst (lipase from *Candida rugosa*) at the O/W stable emulsion interface. The enzyme itself was used as a surfactant. The methodology allowed preservation of the catalytic performance of the biocatalyst as well as optimal enzyme distribution at the interface of stable, uniform, and small oil droplets to be achieved.

4.03.6 W/O Emulsion

W/O emulsification is an important process in food, cosmetic, pharmaceutical, and other chemical industries [43–45]. Moreover, W/O emulsions were applied to produce multiple emulsions [46], microcapsules for capsulizing medicines, microspheres for packing gel permeation chromatograph (GPC) and high-performance liquid chromatography (HPLC) columns [47, 48], immobilizing enzymes [49], and loading protein drugs [50]. The mean size and size distribution of emulsions are of special significance for fabrications of all these high-tech products. In addition, the characteristics and stability of emulsions are greatly affected by their size and size distribution [51].

Only a very small number of papers dealing with the preparation of W/O emulsions by an ME method are available. It can be explained by the fact that the preparation of W/O emulsions is difficult in comparison to O/W emulsions. It is because the water droplets are difficult to stabilize by an electrical double-layer repulsion force in an oil phase with low dielectric constant. In addition, diffusion of surfactant molecules through the continuous oil phase is slower because of the higher viscosity of oil compared to water. Thus, stabilization of the newly formed water droplets is a slower process and coalescence cannot be avoided sufficiently during droplet formation. On the other hand, droplet coalescence in the prepared emulsion is slower in the case of higher continuous-phase viscosity. Some of the data of previous investigations dealing with the preparation of W/O emulsions by an ME method are summarized in **Table 5**. Most studies mainly concern with the production of W/O emulsions by direct ME in static [52–55] or cross flow [56–61] operation procedures. In some cases, when cross flow was used, droplet size was below the mean pore size and this was attributed to the fact that (1) water which penetrates through the membrane cannot completely displace the oil phase from the interior of the pores due to the high oil viscosity compared with water [56] or (2) spontaneous emulsification occurred when the interfacial tension between the water and oil phases is less than $2\,\mathrm{mN\,m^{-1}}$ [53]. In addition, most results were referred to the use of hydrocarbons.

4.03.7 Multiple Emulsions

Multiple emulsions (or double emulsions) are very complex dispersion systems known as liquid membrane systems. Double emulsions have promising applications in the food industry (low-calorie products, improved sensoric characteristics, and taste masking), cosmetic industry (easily spreadable creams with encapsulated ingredients in both water and oil phases), pharmaceutical industry (drug delivery systems), and other fields such as agriculture and the production of multi-compartment microspheres. If a single emulsion (e.g., W/O) is used as the to-be dispersed phase, also double emulsions (e.g., W/O/W) can be produced by the ME method. The primary emulsion may be produced either by means of a conventional method or by ME. The mild conditions of

Table 5 Literature data of previous investigations dealing with the preparation of W/O emulsion by membrane emulsification

Method	*Operation procedures*	*Membrane*	*D_P (μm)*	*Dispersed phase*	*Continuous phase*	*Emulsifier*	*Flux ($l\,h^{-1}\,m^{-2}$) or P_{TM} (kPa) of dispersed phase*	*Flow rate ($l\,h^{-1}$) or shear stress (dines cm^{-2}) of continuous phase*	*Dd (μm)*	*Ref*
Pre-mix	Static	Hidrophobic PTFE	1	Water	Corn oil	Hexaglycerol polricinoleate (2 wt%)	1 10^{-7}–1.5 10^{-6} kPa		3	52
Direct	Stirred batch	Hydrophilic SPG	0.99	Water	Toluene	PE-64 (2–10 wt%)	-	-	0.66–0.70	53
Direct	Stirred batch	Hydrophilic SPG	2.70	Water	Toluene	PE-64 (2–10 wt%)	-	-	1.38–1.96	53
Direct	Stirred batch	Hydrophilic SPG	4.70	Water	Toluene	PE-64 (2–10 wt%)	-	-	1.59–1.87	53
Direct	Stirred batch	Hydrophobic SPG	4.8	Water + NaCl (0.017–0.855 M)	Kerosene	PGPR (5 wt%)	3 kPa	-	13.5–15.5	54
Direct	Stirred batch	Hydrophobic SPG	2	Water + NaCl (0 855 M)	Kerosene	PGPR (5 wt%)	7–10 kPa	-	6.5–7.5	54
Direct	Stirred batch	Hydrophobic SPG	4.8	Water NaCl (3% w)	Kerosene	PGPR (5 wt%)	3 kPa	-	15	55
Direct	Cross flow	Hydrophobic Polypropylene	0.4	Water	Mineral oil	PGPR (10 wt%)	0.5 $l\,h^{-1}\,m^{-2}$	130 $l\,h^{-1}$	0.42	56
Direct	Cross flow	Hydrophobic Polypropylene	0.4	Water	Mineral oil	PGPR (10 wt%)	0.12 $l\,h^{-1}\,m^{-2}$	130 $l\,h^{-1}$	0.31	56
Direct	Cross flow	Hydrophobic Polypropylene	0.4	Water	Mineral oil	PGPR (10 wt%)	0.2 $l\,h^{-1}\,m^{-2}$	130 $l\,h^{-1}$	0.26	56
Direct	Cross flow	Hydrophobic arrays of micro-orifices	2.5	Water	n-hexadeane	BolevMT (1wt%)	25 kPa	-	125	57
Direct	Cross flow	Hydrophobic arrays of micro-orifices	3.5	Water	n-hexadeane	Span 85 (1 wt%)	15 kPa	-	150	57
Direct	Cross flow	Hydrophobic MPG	1	Water + glucose (5%)	Soybean oil	PC + PGCR (5 wt%)	80 kPa	-	3.08	58
Direct	Cross flow	Hydrophilic SPG	0.99	Water	Toluene	PE-64 (2–10 wt%)	-	1.38 $l\,h^{-1}$	0.66–0.70	59

(*Continued*)

Table 5 (Continued)

Method	*Operation procedures*	*Membrane*	*D_P (μm)*	*Dispersed phase*	*Continuous phase*	*Emulsifier*	*Flux ($l\,h^{-1}\,m^{-2}$) or P_{TM} (kPa) of dispersed phase*	*Flow rate ($l\,h^{-1}$) or shear stress (dines cm^{-2}) of continuous phase*	*Dd (μm)*	*Ref*
Direct	Stirred cell	Hidrophobic metallic	30	Water + PVA (15%)	Kerosene	Hypermer B261 (0.3 wt%) Span 80 (2 wt%)	70 $l\,h^{-1}\,m^{-2}$	70 dynes cm^{-2}	77	60
Direct	Stirred cell	Hidrophobic metallic	30	Water + PVA (15%)	Kerosene/ soyabean oil (40%)	Hypermer B261 (0.3 wt%) Span 80 (2 wt%)	70 $l\,h^{-1}\,m^{-2}$	126 dynes cm^{-2}	71	60
Direct	Stirred cell	Hidrophobic metallic	30	Water + PVA (15%)	Kerosene/ soyabean oil (60%)	Hypermer B261 (0.3 wt%) Span 80 (2 wt%)	70 $l\,h^{-1}\,m^{-2}$	127 dynes cm^{-2}	65	60
Direct	Stirred cell	Hidrophobic metallic	30	Water + PVA (15%)	Kerosene/ soyabean oil (80%)	Hypermer B261 (0.3 wt%) Span 80 (2 wt%)	70 $l\,h^{-1}\,m^{-2}$	120 dynes cm^{-2}	5	60
Direct	Rotating	Nickel	5	Water	Sunflower oil	PGPR (1wt%)	–	–	–	61

ME are especially useful for the second emulsification step in order to prevent rupture of the double-emulsion droplets, which might even lead to inversion into a single O/W emulsion. Contrary to conventional emulsification methods, it becomes possible to produce small and monodisperse droplets without using high-shear stresses that cause escape of the internal droplets. ME may be a method of choice for the preparation of multiple emulsions, because of the low shear rates involved in ME.

Mine *et al.* [46] were the first to report that it is possible to produce double emulsions (W/O/W) by ME. They used a conventional mechanical emulsification method for the first W/O emulsion preparation and SPG membranes for the second emulsification step. They showed that the membrane has to be hydrophilic and needs to have an average pore size of at least twice the diameter of the primary water droplets of the W/O emulsion, otherwise these droplets will be rejected by the membrane. Okochi and Nakano [62] compared two W/O/W emulsions containing water-soluble drugs, which were prepared by either ME (for the second emulsification step) or a (traditional) two-stage stirring emulsification method. Double emulsions prepared by ME showed a smaller standard deviation of the mean particle size and a slightly lower viscosity. In addition, the entrapment efficiency for ME was somewhat higher. This makes the method of ME especially useful for low-molecular-weight drugs, which normally give a relatively low entrapment efficiency. Drug release from the emulsion prepared by ME was slower, which may be due to the more homogeneous particles and the sharper size distribution that make the emulsions more stable. Higashi and co-workers [63–65] published the first, very promising results for clinical studies of this new drug delivery system based on ME. Only one peer-reviewed paper is known to us, in which double emulsions were successfully prepared by ME for both emulsification steps. Nakashima *et al.* [66] reported the application of double-membrane emulsification, which means the preparation of a W/O emulsion using a hydrophobic membrane and completion of the W/O/W emulsion using a hydrophilic membrane. Shima *et al.* [67] investigated W/O/W emulsions to protect fragile bioactive compounds from stomach acid and intestinal digestive fluids. If the compound is isolated into the inner-water phase of the W/O/W emulsion, it is expected that the loss of its function during the delivery from oral uptake to the intestine can be suppressed or prevented. Thus, a W/O/W emulsion may be a promising carrier for a hardly adsorbed hydrophilic bioactive compound that was deactivated or digested during the digestive process. These authors prepared W/O/W emulsion as a carrier system for the daily uptake of a hydrophilic model compound of a bioactive substance (1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt). Membrane filtration of a coarse W/O/W emulsion prepared with a rotor/stator homogenizer produced a fine emulsion with a mean oil droplet diameter $<1\,\mu m$ and an encapsulation efficiency >90%. However, the authors observed that the included water phase disappeared during the membrane filtration of the coarse emulsion when preparing the fine emulsion. Vladisavljevic *et al.* [68] produced W/O/W emulsions using multistage premix ME with SPG membranes. Better results with regard to particle size distribution were obtained using several (two to four) passes at moderate pressures instead of a single pass at high pressures.

4.03.8 Particles Production

The microparticles are produced after the emulsion production. The micro-encapsulation technique can be applied in different industrial sectors, such as photocopy toners, optical recording, herbicides, animal repellents, pesticides, oral and injectable pharmaceuticals, cosmetics, food ingredients, adhesives, curing agents, and live cell encapsulation [69].

The size of the produced particles may range from 100 nm to about 1 mm and, depending on their size, can be classified as nano-, micro-, and macroparticles.

The micro-encapsulation process, depending on the way the particles are produced, can be divided in two main categories [69]:

1. *Chemical process.* This refers to using different approaches such as the complex conservation, polymer/polymer incompatibility, interfacial polymerization in liquid media, *in situ* polymerization, in liquid drying, and desolvation in liquid media. The particles produced by chemical process are formed entirely in a liquid-filled stirred tank or tubular reactor.
2. *Mechanical process.* This involves employing different systems such as spray drying, spray chilling, fluidized bed, electrostatic deposition, centrifugal extrusion, pressure extrusion, or spraying into

solvent extraction bath. Mechanical process uses a gas phase at some stage of the encapsulation process.

One of the major problems related to the particle formation is their agglomeration. It involves the irreversible or largely irreversible adhesion of the microparticles that can occur during the crosslinking/solidification step and/or during the recovery/drying step.

In this work, the particles (microspheres or microcapsules) produced by ME have been classified on the basis of polymer material biodegradability, as given in **Tables 6** and **7**.

Several works deal with the preparation of biodegradable polymer microcapsules or microspheres mainly for drug delivery system or chromatography applications. The dispersed phase is usually made of water polymer and additives, while the continuous phase is made of solvents and emulsifiers. The membranes used are usually hydrophobic type (**Table 6**).

The biopolymers employed are poly(lactide) (PLA) [71, 75, 94], poly(lactic-co-glycolic acid) (PLGA) [80, 85, 92, 96, 101], chitosan [72, 81], and agarose [88–90]. These polymers have been applied mainly for encapsulating proteins and peptides used as prophylactic and therapeutic agents in biomedical fields. So far, the delivery route is the injection, which not only causes distress and inconveniency to patients, but also induces unstable curative effective and side effects [72]. The use of microspheres as a controlled release system can be one of the prospect methods. In fact, it may prevent encapsulated drug from degradation by proteolytic enzymes, prolong its lifetime, and improve its bio-availability *in vivo* by controlling release rate of drug from the micro-spheres. Recently, Doan and Olivier [92] produced narrowly size-distributed PLGA, for rifampicin lung delivery, by combining the W/O solvent evaporation method with premix membrane homogenization microspheres. Using ethyl acetate as organic solvent, a coarse O/W emulsion (or premix) was prepared under magnetic stirring and homogenized by extrusion through an SPG membrane with a pore size of 5.9 μm. Microspheres were obtained after dilution and solvent evaporation. The emulsion was gradually reduced in size and homogenized with the membrane resulting in narrowly size-distributed microspheres. Six homogenization cycles and 10-ml emulsion (containing 3–5 ml dispersed phase) could be prepared within 1 h and the resulting microspheres were about 1–2 μm diameter. Once the optimal conditions were found, PLGA microspheres with rifampicin (up to a concentration of 20 wt.%) were also successfully produced and tested for lung delivery by intratracheal insufflation in rats.

Recently, Zhou and co-workers [88–90] reported the preparation of uniform-sized agarose beads (>14%) with small diameters (<10 μm) by premix ME. These types of particles have great significance in chromatography. The use of the high-flux premix method overcomes the production of beads by means of the conventional methods, including cross-flow ME. In their work, the importance of the transmembrane pressure, ingredient proportions between the dispersed and continuous phases to obtain uniform-sized agarose microbeads were exploited. The results showed, also in this case, that the membrane pore size directly affected the mean diameters of agarose beads.

Another polymer, the poly-acrylamide-co-acrylic acid, has been used for the preparation of monodisperse hydrogel microspheres. Thanks to its biocompatibility it has been used as a drug device [78, 91]. The average diameter of the microspheres depends on the pore sizes (from 0.33 to 1.70 μm) of SPG membranes used in the emulsification preparation.

In the case of employing nonbiodegradable polymer (see **Table 7**), the dispersed phase is usually made of a monomer or polymer and additives or initiators, while the continuous phase is made of water, stabilizer, and emulsifiers, which are adsorbed on the surface of the droplets to stabilize them. Then, increasing the temperature to above the decomposition temperature of the initiator, the suspension polymerization proceeds to form uniform particles. During the polymerization, the monodispersity is maintained if the emulsification and polymerization conditions are adequate.

Several types of monomers have been employed for the preparation of microparticles, starting from monomers such as methacrylates (methylmethacrylate, butyl acrylate, cyclohexyl acrylate, etc.) [83, 86], poly(methacrylic acid-*co*-methyl methacrylate) copolymers (Eudragit) [95], polyimide (PIP) [83] and polyurethane (PU) pre-polymer [70, 87], styrene and its derivate monomer [74, 79, 82–84, 86], N-isopropylacrylamide (NIPAM) [102], and divinylbenzene (DVB) [97].

Omi *et al.* [83] reported the occlusion of PIP prepolymer (diphenilmethane-4,4′-bis-allylnagiimide, BAN-I-M) into uniform polymeric microparticles via the emulsification technique with SPG membrane. The occlusion of functional material, such

Table 6 Literature data of the previous investigations dealing with the preparation of Biodegradable particles by membrane emulsification.

Method	*Operation procedures*	*Membrane*	*Dp (μm)*	*Dispersed phase*	*Continuous phase*	*Emulsifier (%wt)*	*Pc (kPa) of dispersed phase*	*D_d (μm)*	*Ref*
Direct	Cross flow	Hydrophilic SPG	5.2	PLA (10–15%) in DCM/LOH 11: 1 v/v	Demineralized water	SDS (0.06%) PVA (1%)	7	14.6–38.1	71
Direct	Cross flow	Hydrophobic SPG	4.7	Chitosan (1%) in acetic acid, NaOH (0.9%)	Liquid paraffin petroleum ether 7:5	PO-500 (4%)	13.1	3.9	72
Premix	Stirred batch	Hydrophilic MPG	2.8	PLA (0.12%)+Arlacel 83 (2%) + DCM/toluene (21/79)	Demineralized water	PVA (2%)	-	3–9	75
Direct	Cross–flow	Hydrophilic Ceramic Al_2O_3-TiO_2 Membrane with active ZrO_2	0.1 0.2 0.45	Gelucire (44/14), vitam. (E 3%)	Demineralized water	Tween 20 (0.02%)	600	0.07–0.215	77
Direct	Cross–flow	Hydrophobic SPG	1.7	Poly (acrylamide–co-acid-acrylic)	Cyclohexane	PVA (2%)	-	2.45	78
Direct	Cross–flow	Hydrophilic SPG	0.48 1.95 3.63	PLGA(1.2%), rifampicin (87%), DCM (11.6%)	Deionized water	PVA (2%)	24–28	1.27–9.3	80
Direct	Cross–flow	Hydrophilic MPG	-	Chitosan (1%) in acetic acid, Nacl (0.9%)	Liquid paraffin 58% petroleum ether 42%	PVA PEG	-	4–12	81
Premix	Stirred batch	Hydrophobic SPG polyethylene	10.2 11.8 25.6	Agarose (10%) in water	Liquid paraffin/ petroleum ether 7:5 (v/v)+	PO-500 (4%)	98.07	3–9	88
Premix	Stirred batch	Hydrophobic SPG	10.2	Agarose (10%) in water	Liquid paraffin/ petroleum ether 7:5 (v/v)+	PO-500 (4%)	98.07	10	89
Premix	Stirred batch	Hydrophilic SPG	5.9	PLGA (3–30%) in ethyl acetate (EA) and dimethyl sulfoxide	Deionized water	PVA (1%)	50–250	1–5	92
Premix	-	Hydrophilic SPG	-	PLA in DCM	Deionized water+ methanol	PVA (1%)	-	1	94

(*Continued*)

Table 6 (Continued)

Method	*Operation procedures*	*Membrane*	*Dp (μm)*	*Dispersed phase*	*Continuous phase*	*Emulsifier (%wt)*	*Pc (kPa) of dispersed phase*	*D_d (μm)*	*Ref*
Premix	Stirred batch	Hydrophilic SPG	1.00 1.95 2.60 3.63 5.25	PLGA (8.3%), sunsoft 818H (1.67%), rifampicin in DCM	Distilled water	PVA (1%), PEG (0.017%)	8.83–39.23	2.5–11.3	96
Direct	Stirred batch	Hydrophilic SPG	1.00 1.95 2.60 3.63	PLGA (5%) and rifampicin (0.5%) in DCM	Distilled water	PVA (2%) PEG (0.026%)	1.96–2.94	3–8	101
		V VHP hydrophobic	0.1					20–100	
Premix	Stirred batch	PVDF hydrophilic	0.1	(PLGA) in methylene chloride, adriamycin, daumoncin	Demineralized water	-	-	40–100	85
		Al_2O_3 hydrophilic ceramic	0.03					8–110	

Table 7 Literature data of the previous investigations dealing with the preparation of No-Biodegradable particles by membrane emulsification

Method	*Operation procedures*	*Membrane*	*D_D (μm)*	*Dispersed phase*	*Continuous phase*	*Emulsifier (%wt)*	*P_{TM} (kPa) of dispersed phase*	*D_d (μm)*	*Ref*
Direct	Cross flow	Hydrophilic SPG	1.42 5.25 9.5	PU WP300 (20–40%) in xylene	Deionized water	SDS (0.03%) PVP (10–40%) MST-1(0.3%)	-	5–18	70
Direct	Cross flow	Hydrophilic SPG	2.5	Benzene/xylene (2:1v/v); tereptaoil dichloruro (TDC)	Deionized water	SDS (0.5%) PVA (0.5%)	-	7.9	73
Direct	Cross flow	Hydrophilic SPG	1.6	Stytene (87.3%) ADVN (0.5%); DMAEMA (2.3%) hexadecane (10%)	Deionized water	PVP (0.4%) SDS (0.03%)		7.7÷113	74
Direct	Stirred cell	Hydrophiic metallic	100	Paraffin wax	Deionized water	Tween 20(2%) Carbomer (0.01–0.25%)	-	79–259	76
Direct	Cross flow	Hydrophilic SPG	-	Acetoxystyrene (58%), divinylbenzene (2%), benzoylperoxide (1.2%), in xylene (25%), dodecane (12%)	Deionized water	PVA (2%) SDS (0.7%) Na_2SO_4(0.3%)		1–2	79
Direct	Cross flow	Hydrophilic SPG	5.2	PST/PMMA (2%) in DCM, LOH (16%)	Deionized water	SDS (0.03%) PVA (1%)	5–7	10	82
Direct	Cross flow	Hydrophilic SPG	1.4	BANI-M (30%), styrene (18%) Butyl acrylate (30%) 2EHA (12.5%), LOH (5%), ADVN (3.8%)	Deionized water	SDS (0.04%) PVA (0.6%)	20–30	6.3	83
Direct	Cross flow	Metallic membrane	100–150	Styrene (27.5%), DVB (27.5%), 4-methyl-2-pentanol (44%)	Deionized water	PVA (0.1%), NaCl (5.6%)	-	150–270	84
Direct	Cross flow	Hydrophilic SPG membrane	2.9	Styrene (76%) Butyl acrylate (18%) Carbon black (2.8%) Benzoy eroxide (BPO), (2.8%)	Deionized water	SDS (0.2%) PVA (1.6%)	30	5.8	86
Direct	Cross flow	Hydrophilic SPG membrane	5.2	PU (45%) Vynil monomer (56%) ADVN (3.5%) in Xylene (40%)	Deionized water	SDS (0.9%) MST-1 (1.3%) Na_2SO_4 (1%), $NaNO_2$ 1%	-	8–20	87
Direct	Cross flow	Hydrophilic SPG membrane		Eudragit (1%), NaOH (1.2%) in water	Water, HCl (0.12%)	PVA (0.5%)	300	2–20	95
Direct	Cross flow	Hydrophilic SPG membrane	5.2	DVB, benzoyl peroxide (BPO), hydroquinone (HQ)	Deionised water	SDS, PVA, NA_2SO_4	-	4–14	97
Direct	Stirred batch	Hydrophilic SPG membrane	4.8	NIPAM, N, No-methylenebisacrylamide (MBA), ammonium persulfate (APS), water	Kerosene, 2.2-dimethoxy-2-phenylacetophenone	–	1.5–3	10–20	102

as the PI pre-polymer (PIP) in uniform polymer particles, can find promising applications in sophisticated electronic devices such as adhesive spacers of liquid-crystal panel boards (after a minor screening process), and adhesives or insulators for microtip circuits. The dispersed phase consisted of styrene and various acrylates, a water-insoluble reagent (lauryl alcohol, LOH), and initiator (2,29-azobis-2,4-dimethyl valeronitrile, ADVN). The water continuous phase contained small amount of polyvinyl alcohol (PVA) and SDS as stabilizing pair. The dispersed phase was pressured through the ceramic hydrophilic SPG membranes. Uniform polymeric microparticles with a maximum occluding of 28.4 wt.% of PIP was obtained. The PIP inclusion was improved when the crosslinking agent (ethyleneglycol dimethacrylate, EGDMA) was employed. Furthermore, the use of methylmethacrylate (MMA) and other acrylates was able to occlude almost 100% of PIP without the presence of EGDMA. The particles produced had a diameter of 6–12 μm.

Another interesting pre-polymer is the PU, which can be used in various elastomer formulations, paints, adhesives for polymers and glass, artificial leather, as well as in biomedical and cosmetic sectors. Yuyuma *et al.* [70] reported the possibility of producing PU spheres starting from 20/40% of PU pre-polymer solution in xylene. The PU droplets were dispersed in water using SPG hydrophilic membranes of different pore size (1.5–9.5 μm). The PU droplets were polymerized and the final solid PU particles with different dimensions (5 and 18 μm) were obtained after solvent evaporation. Ma *et al.* [87] also reported the formation of uniform PU microspheres hybridized with a vinyl polymer (VP), polyacrylate, or polystyrene (PST). The PU/xylene mixture dissolved in the monomer (sometimes containing a crosslinker) was pressed through the hydrophilic SPG membrane into the continuous phase containing a stabilizer to form uniform droplets. Then, the prepolymer was chain-extended by adding a chain-extender solution in the aqueous phase. The droplets were left for chain extension at room temperature for some hours with di- and triamines by suspension polymerization at 70 °C for 24 h. Solid and spherical PU–VP hybrid particles with an average diameter of 20 μm, a smooth surface, and a higher destructive strength were obtained.

Ma *et al.* [82] prepared microcapsules with uniform distribution of PST–poly(methyl methacrylate) (PMMA) by using SPG hydrophilic membranes. The PST, PMMA, and co-surfactant (LOH) dissolved in dichloromethane (DCM) were used as a dispersed phase, while the aqueous phase containing PVA and sodium lauryl sulfate (SDS) was the continuous phase. The P_{cr} decreased with increasing LOH amount because of preferential partition of LOH on the surface of the droplets in the initial stage of emulsification. The droplets were polymerized at 70 °C and the obtained microcapsules have a diameter ranging from 6 to 10 μm, 6 times larger than the membrane pore size of 1.4 μm.

Recently, monodisperse carbon cryogel (MCC) microspheres have also been produced via SPG ME using a phenol-formaldheyde (PF) solution as an inexpensive carbon precursor, followed by freeze-drying and carbonization in an inert atmosphere [93]. The effect of the initial pH of the PF solution on the porous structure of PF-CC monolith was examined. As a result, PF-MCC microspheres with developed mesoporosity could be synthesized. The pore volume and specific surface area of the PF-MCC microspheres as well the size diameter (0.5–1.6 μm) were confirmed to be comparable to those of the resorcinol (RF)-MCC microspheres which were synthesized from a relatively expensive resorcinol solution, which is usually employed as raw material of MCC particles. The developed porous structure and inexpensive raw materials make PF-MCC microspheres more practical than RF-MCC microspheres.

In other works, Figoli and co-workers [98–100] reported the preparation of polymeric particles combining the phase-inversion technique with the membrane process. A model membrane, a monopore polyethylene film, was used to prove the concept of making in a single step: first, the polymeric drop in an organic media (emulsion) and, then immediately after, its solidification (particle formation) by entering in contact with the coagulation phase (water/alcohol). The particle formation unit is shown in **Figure 6**. Modified polyetheretherketone (PEEKWC) and polyvinylidene fluoride (PVDF) particles, with and without catalyst (ammonium molybdate tetrahydrate $(NH_4)_6Mo7O_{24}{\cdot}4H_2O$), of different size (300–800 μm) and morphology (asymmetric with a porous or dense layer) have been prepared. In particular, PEEKWC and PVDF catalytic microcapsules were used as heterogeneous catalyst and interphase contactor. The reaction studied was the oxidation of benzyl alcohols to benzaldehydes with hydrogen peroxide acting as oxidizing agent. The results showed that the catalytic polymeric microcapsules strongly improved

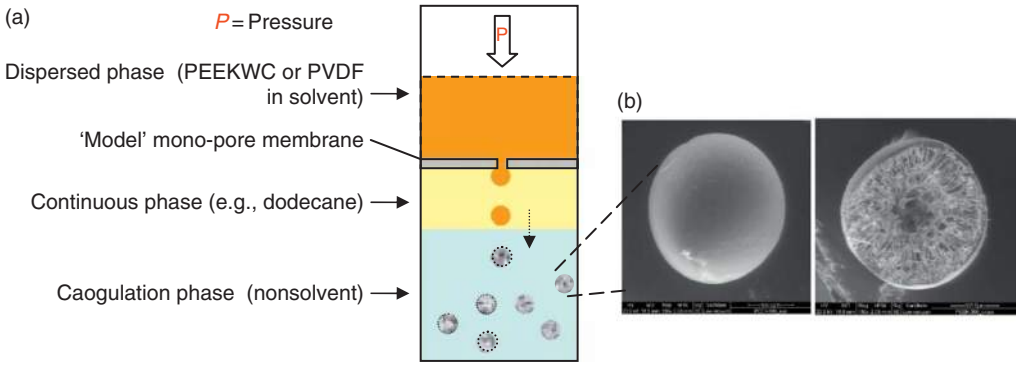


Figure 6 (a) Scheme of modified particle formation unit. (b) Surface and cross section of polyetheretherketone (PEEKWC) particles.

the interactions between hydrophilic (catalytic complexes) and hydrophobic species (alcohol) due to the particular polymeric microenvironment.

4.03.9 Patents in ME

In this section, the results of an analysis of patents on ME (**Table 8**) are discussed.

The first patent on ME goes back to 1990 (JP2095433). Inventors of the technology were Nakajima Tadao and Shimizu Masataka of the Miyazaki Pref. Gov., Japan. The invention showed the possibility to prepare an emulsion with uniform particles through the use of a microporous membrane with uniform pore diameter. The droplet size and size distribution are controlled by appropriate choice of the process conditions and membrane pore-size distribution. This method produces emulsions by a drop-by-drop mechanism, that is, the dispersed phase is added drop by drop through porous membranes to the continuous phase. Emulsions with uniform droplet size are produced in mild operation conditions and simple apparatus. Various materials can be emulsified with remarkably improving the physical characteristics.

In 1992, different patents have been published concerning simple and multiple emulsions, spread, spherical silica gel and polymers production by means of stirred ME or cross flow ME. In 1993, a new patent (JP5220382) analyzed the production of monodisperse simple and multiple emulsions by ME introducing an accurate analysis of the operational parameters and the characteristics of the used materials. The simple apparatus and a simple operating procedure with a reduced consumption of energy are very advantageous from the economical viewpoint. Therefore, more specifically, the invention is very useful in the production of various end products which require emulsions as base ingredients, such as the production of foods with improved texture. Other products benefiting from uniform emulsions include medicines, cosmetics, pigments, functional plastic particles, functional inorganic material particles, raw materials for fine ceramics, as well as in solvent extraction.

4.03.9.1 ME in Food Industry

In food industry, many patents have been applied by the Japanese Morinaga Milk Industry (JP4323224, JP6007085, US5279847, JP7087887, US5417995, and EP0672351). These patents respond to the request of the food industry to prepare simple (W/O and O/W) and double (W/O/W and O/W/O) emulsions having low-fat content and excellent flavor without requiring a stabilizer and a gelling agent as components. These patents relate to methods for producing emulsions, low-fat spread, and multiple emulsion type spread having good taste easily, with excellent stability and preservative properties on a level never achieved by any conventional methods.

The increasing attention in food field toward the preparation of products preserving properties of natural components in terms of taste and fragrance has determined the realization of a patent (EP0737425) from the Japanese chemical company Asahi Denka Kogyo KK. The inventors of this invention have extensively investigated the emulsified structural of natural fresh cream. As a result, they have found that the incorporation of an emulsifying agent and specific proteins affords an ideal O/W type emulsion endowed with enhanced properties and characteristics, both of natural fresh cream and of vegetable cream. The invention

Table 8 List of patents developed in membrane emulsification

Publication date	*Title*	*Publication number*	*Inventor*	*Applicant*
06–04–1990	Production of emulsion	JP2095433	Nakajima Tadao; Shimizu Masataka	Miyazaki Pref Gov
10–08–1992	Production of emulsion and spherical silica Gel	JP4219131	Ito Mutsuhiro; Fujisaki Minoru; Nakatani Kazuhiko; Yamazaki Mitsuhito; Arimura Masayuki	Fuji Davison Chemical
14–09–1992	Production of polymer bead	JP4258601	Hashizume Kiyoko	Chtsu Tire & Rubber Co Ltd
14–09–1992	Production of double emulsified spread and its production	JP4258251	Oronogi Siugeo; Kumazawa Renzo; Toyama Kazuyoshi; Kato Makoto; Sano Yjzo; Takahashi Kiyotaka; Fujimoto Masahisa	Morinaga Milk Industry Co Ltd
12–11–1992	Production of mododisperse organic polymer beads	JP4323224	Yamagoshi Tomio; Fujisaki Minoru; Iyo Mutsuhiro; Yamazaki Murahito	Fuji Davison Chemical
27–07–1993	Production of Emulsion	JP5184895	Otsuka Yukio	Sekisui Fine Chemical Co Ltd
31–08–1993	Monodisperse Single and Double emulsion and its production	JP5220382	Nakajima Tadao; Shimizu Masataka; Kukizaki Masahito	Miyazaki Pref Gov
11–01–1994	Production of fine polymer particle and fine polymer particle produced thereby	JP6001854	Hasegawa Jun; Haneda Hidekazu	Nippon Zeon Co
18–01–1994	Doubly emulsified spread and its production	JP6007085	Tomita Mamoru; Toyama Kazuyoshi; Kato Makoto; Asano Yuzo; Takahashi Kiyotaka; Fujimoto Masahisa	Morinaga Milk Industry Co Ltd
18–01–1994	Methods for producing emulsions, low-fat spread and oil-in-water-in-oil type spread	US5279847	Okonogi Shigeo (JP); Kato Ryo (JP); Asano Yuzo(JP); Yuguchi Hiroya (JP); Kumazawa Renzo (JP); Sotoyama Kazuyoshi (JP); Takahashi Kiyotaka (JP); Fujimoto Masahisa (JP)	Morinaga Milk Industry Co Ltd (JP)
22–02–1994	Production of aqueous copolymer resin dispersion	JP6049104	Yamamoto Akihito; Yoshino Fumio	Dainippon Ink & Chemicals
24–05–1994	Production of monodisperse fine spherical particle	JP6142505	Hirayama Chuichi; Ihara Hirotaka; Iwatsuki Makoto	Hirayama Chuichi; Ihara Hirotaka; Ajinomoto KK
26–07–1994	Stable multiple emulsions comprising interfacial gelatinous layer flavor encapsulating multiple emulsions and low/no-fat food products comprising the same	US5332595	Caonkar Anilkumar G (US)	Gen Foods inc (US)
23–08–1994	Production of emulsion	JP6233923	Saka Sadanori; Kitahara Michio; Nakada Satoru	Nonogawa Shoji YK; Fuji Shirishia Kagaku KK
15–11–1994	Emulsifying method and device	JP6315617	Nakajima Tadao; Shimizu Masataka; Inasaki Yoshihiko; Fjimoto Kenit	Miyazaki Pref Gov; Kiyomoto Tekko kk

(*Continued*)

Table 8 (Continued)

Publication date	*Title*	*Publication number*	*Inventor*	*Applicant*
04–04–1995	Mixed emulsified spread and its preparation	JP7087887	Tomita Mamoru; Toyama Kazuyoshi; Kato Makoto; Asano Yuzo; Takahashi Kiyotaka	Morinaga Milk Industry Co Ltd
25–04–1995	Production of emulsion	JP7108164	Saka Sadanori; Katahara Michio; Yamazaki Mitsuhito	Nonogawa Shoji YK; Fuji Stlysia Chem Ltd
23–05–1995	Spread and a method for production of said spread	US5417995	Tomita Mamoru (JP); Sotoyama Kazuyoshi (JP); Kato Ryo (JP); Asano Yuzo (JP); Takahashi Kiyotaka (JP)	Morinaga Milk Industry Co Ltd (JP)
20–09–1995	Method for producing emulsions	EP0672351	Okonogi Shigeo (JP); Kato Ryo (JP); Yuguchi Hiroya (JP); Asano Yuzo (JP)	Morinaga Milk Industry Co Ltd (JP)
05–12–1995	Method for preparing oil-in-water emulsion of edible fatty oil	JP7313056	Yamano Yoshimasa; Aitani Shoichi; Hosoya Yasuto	Nisshin Oil Mills Ltd
16–10–1996	Oil-in-water emulsion containing lysophospholipo-proteins	EP0737425	Okutomi Yasuo (JP); Shimada Toshihiro (JP)	Asahi Denka Kogyo KK (JP)
05–08–1997	Preparation of emulsion and polymer fine particle	JP9201526	Mukai Katsunori; Hisada Tak Takashi; Naito Masanori	Sekisu Fine Chemical Co Ltd
04–09–1997	Processes for producing emulsified fat composition	WO9731708	Suzuki Kanichi (JP)	Kanegafuchi Chemical Ind (JP); Suzuki Kanichi (JP)
09–10–1997	Dispersion of immiscible phases	WO9736674	Williams Richard Andrew (GB); Wheeler Derek Alfred (GB); Morley Neil Christopher (GB)	Disperse Tech Ltd (GB); Williams Richard Andrew (GB); Wheeler Derek Alfred (GB); Morley Neil Christopher (GB)
17–02–1998	Production of emulsion	JP10043577	Mukai Katsunori; Hisada Takashi	Sekisui Fine Chemical Co Ltd
04–08–1998	Sustained release emulsion preparation of medicine and its production	JP10203962	Nakajima Tadao; Shimizu Masataka; Komatsu Yoshinori; Kato Naoki	Miyazaki Pref Gov; S P G Techno KK; Meiji Milk Prod Co Ltd
07–09–1999	Emulsifying method of photographic hydrophobic substance, emulsified material and silver halide photographic censitive material	JP11242317	Endo Kiyoshi	Konishiroku Photo Ind
07–12–1999	Membrane emulsifiying device	JP11333271	Taniguchi Toru	Reika Kogyo KK
20–04–2000	Stable oil-in-water emulsion, method for preparing same and use in cosmetics and dermatology	WO0021491	Roulier Veronique (FR); Quemin Eric (FR)	Oreal (FR); Roulier Veronique (FR); Quemin eric (FR)
28–06–2001	Rotating membrane	WO0145830	Williams Richard (GB)	Univ Leeds (GB); Williams Richard (GB)

(*Continued*)

Table 8 (Continued)

Publication date	*Title*	*Publication number*	*Inventor*	*Applicant*
03–07–2001	Polyphase emulsion	JP2001179077	Goto Masashi; Maekawa Akio; Nakajima Tadao; Shimizu Masataka	Sunstar Inc; Miyazaki Prefecture
04–12–2002	Device and process for making emulsions	EP1262225	Schliessmann Ursula Dipl-ing (DE); Stroh Norbert Dipl-Ing (DE)	Fraunhofer Ges Forschung (DE)
28–11–2003	Method for forming emulsion and method for forming resin particles	JP2003335804	Hayashi Shinichi; Kojima Eyoji	Sony Chemicals
15–01–2004	S/O suspension s/o/w emulsion, and their manufacturing method	JP2004008837	Nakajima Tadao; Shimizu Masataka; Kukizaki Masahito	Miyazaki Prefecture
15–04–2004	Production method of emulsion	JP2004113933	Kobi Yoshiki	Kuraray Co
05–08–2004	Uniform emulsion by membrane emulsification	US2004152788	Wu Huey Shen (US); CGA Takahiro (JP); Omi Shinzo (JP); Yamazaki Naohiro (JP)	
31–12–2004	Process for producing inorganic spheres having uniform particle sizes and apparatus therefor	KR20040111082	Tatematsu Shin; Yamada Kazuhiko; Yamada Kenji	Asahi Glass Co Ltd
03–02–2005	Method and apparatus for manufacturing inorganic spherical body	JP2005028358	Yamada Kenji; Tatematsu Shin; Yamada Kazuhiko	Asahi Glass Co Ltd
03–02–2005	Emulsion production device	JP2005028254	Nagahama Toru; Yoshino Tomoaki	Taisho Pharma Co Ltd
03–02–2005	Method of producing emulsion	JP2005028255	Yoshino Tomoaki; Nagahama Toru	Taisho Pharma Co Ltd
20–04–2005	Chitose microsphere and microcapsule with uniform size and its preparation method	CN1607033	Ma Guanghui (CN); Su Zhiguo (CN); Wang Lianyan (CN)	Inst of Process Engineering CH (CN)
14–07–2005	Device and method of preparing emulsion	JP2005186026	Nakajima Noboru; Fujiwara Mitsuteru	SPG Techno KK
13–10–2005	Disposable membrane module for preparing emulsion	JP2005279326	Nakajima Noboru; Fujiwara Mepsuteru; Maeda Daigo	SPG Techno KK
11–05–2006	Method for preparing mircosphere	US2006096715	Suzuki Takehiko (JP); Matsukawa Yasuhisa (JP); Suzuki Akira (JP)	Tanabe Seiyaku Co
07–06–2006	Process for producing a fine emulsion from a coarse emulsion	EP1666130	Danner Thomas Dr (DE); Voss Hartwig Dr (DE); Bauder Andreas (DE); Viereck Sonja (DE)	Basf AG (DE)
15–06–2006	Method for controlling droplet size of an emulsion when mixing two immiscible fluids	US2006128815	Clare Hugh J (GB); Pearson Christopher A (GB); Shanks Ian A (GB)	
13–07–2006	Method for producing emulsion fuel and apparatus for producing the same and apparatus for modifying fuel	JP2006182890	Nakajima Noboru; Fujiwara Mitsuteru; Maeda Daigo; Watanabe Koji	SPG Techno KK

(*Continued*)

Table 8 (Continued)

Publication date	*Title*	*Publication number*	*Inventor*	*Applicant*
31–08–2006	Process for preparation an aqueous addition-polymer dispersion	WO2006089939	Gaschler Wolfgang (DE); Danner Thomas (DE); Bauder Andreas (DE); Funkhauser Steffen (DE); Hamers Christoph (DE)	Basf AG (DE); Gaschler Wolfgang (DE); Danner Thomas (DE); Bauder Andreas (DE); Funkhauser Steffen (DE); Hamers Christoph (DE)
19–10–2006	Microsieve membrane for emulsification and lithographic method of making the same	WO2006110035	Sanchez-De Viues Stefan (NL)	Fluxxion B V (NL) Senchez-De Vries Stefan (NL)
07–12–2006	Method of producing metal particle	JP2006328471	Ishikawa Yuchi; Son Hitonori	KRI Inc
21–12–2006	Method for producing emulsion composition	JP2006341252	Fujimoto Minamino Tatsuo; Akagi Hidekuni; Iwasaki Yoshihiko; Shimizu Masataka; Nakajima Tadao	Kiyomoto Ikon & Machinery Work, Miyazaki Prefecture
28–12–2006	Method for preparing emulsion using porous body and its apparatus	JP2006346565	Nakajima Noboru; IV Ashita Kazuhiro; Fujiwara Mitsuteru; Maeda Daigo	SPG Techno KK
17–01–2007	Preparation of emulsion for decreasing liquid-drop diameter continuouslly and gradually by porous film	CN1895763	Li Na (CN)	XI AN Comm Univ (CN)
24–05–2007	Emulsification process and emulsification apparatus	JP2007125535	Fujimoto Kenji; Iwasaki Yoshihiko; Shimizu Masataka; Torigoe Niyoshi	Kiyomoto Iron & Machinery Work; Shimizu Masataka; Torigoe Kiyoshi; Miyazaki Prefecture
26–09–2007	Nanometer micro-capsules haying the same size for carrying medicine and the method of preparing the same	CN101040849	Ma Guanghui Song (CN)	Chinese Acad Inst Process Eng (CN)
01–11–2007	Method for producing multiple emulsions that are stable in storage	US2007253986	Stange Claf (DE); Mutter Martina (DE); Osward Tanja (DE); Schmitz Mark (DE)	Bayer Technology Services GMBH (DE)
28–05–2008	An apparatus and method for generating emulsions	GB2444035	Kosvintsey Serguei Rudolfovich (GB); Holdich Richard Graham (GB); Cumming Tain William (GB)	Micropore Technologies Ltd (GB)
19–03–2009	Porous membrane process for production of the same, and process for production of inorganic spheres	WO2009034769	Matsubara Toshiya [JP]; Katayama Hajime [JP]; Yamada Kenji [JP]; Tamitsuji Ghikaya [JP]	AGC SI Tech Co Ltd[JP]; Matsubara Toshiya [JP]; Katayama Hajime [JP]; Yamada Kenji [JP]; Tamitsuji Chikaya [JP]
06–04–2009	Producing method for mono-dispersed cross-linked corpuscle of large-caliber by membrane emulsification tehniques	KR20090033576	Park DD Yeon [KR]; Kim Byoung Yon [KR]; Chun Moon Seok [KR]	LG Chemical Ltd [KR]

(*Continued*)

Table 8 (Continued)

Publication date	*Title*	*Publication number*	*Inventor*	*Applicant*
13–08–2009	Membrane emulsification method, method for producing the same and method for producing polymer fine particle and composite particle by using the method	JP2009178698	Masuda Hideki; Yagishita Takashi; Fujimura Ryoko; Nishio Kazuyuki	Kanagawa Kagaku Guutsu Akad; Japan Science & Tech Agency
22–10–2009	Manufacturing method of a membrane and a membrane thereof, for emulsification	US2009264550	Rayner Marilyn [SE]	

shows that the ME process can be also used for preparing emulsions containing shear-sensitive ingredients (such as proteins), preserving their property, producing excellent fresh cream in palatability.

4.03.9.2 ME in Other Fields

The Japanese firm Kanegafuchi Chemical Industrial Co. Ltd. proposed the premix ME process for the preparation of emulsions having high content of dispersed phase (water or oil) difficult to prepare with conventional methodologies (WO9731708). The application of ME processes has been extended to various fields such as pharmaceutical and cosmetic products (JP11242317 and WO0021491) or in the chemical industry (JP2006182890 and WO2006110035).

4.03.9.3 Improvements on Plant and Devices

There are various patents concerning the optimization of ME processes focusing on either apparatuses or device optimization to promote the use of this technology on a productive scale. In 1994, Nakajima *et al.* (JP6315617) prepared a stirred-ME plant for small volumes of dispersed and continuous phases. In 2005, in response to the request of specific applications requiring sterile conditions, Nakajima *et al.* (JP2005279326) proposed a disposable membranes module that permitted to operate under conditions of sterility as well as reducing the production time. Williams *et al.* proposed (1) a plant and method to produce dispersed systems using a ceramic or metallic membrane (WO9736674) and (2) an apparatus for the ME endowed with a rotating membrane (WO0145830).

4.03.9.4 Worldwide Applications of ME

The analysis carried out evidenced that Japan is the principal country in which patents on ME have been developed (more than 60%; **Figure 7**), followed by Unites States with 13%. The data clearly show a lower number of studies in the ME field in the European countries. European companies that promoted patent on ME include Micropore Technologies (UK), Fraunhofer ges forschung, and BASF AG (Germany).

Figure 8 illustrates the behavior of patents on ME per year published from 1990 to December 2009.

The distribution shows two peaks, one in the early 1990s, when the technique was introduced, and one in more recent times (2006), in which the greatest part of the published patents concerned the application of the ME process (food, photo, cosmetics, pharmaceutical, and chemistry). Patents published in the early 1990s primarily concerned the possibility of ME technology to prepare dispersed systems as alternative to the conventional mechanical methodologies. Subsequently, with the acquisition of a great amount of information about the ME methodology (such as the properties and parameters influence), new application fields have been explored (pharmaceutical, photographic, and fuels). Major attention has been oriented to improve the process efficiency and product quality; in particular, research efforts have been devoted to optimize both plant and devices.

The analysis carried out evidenced that the field in which ME technology has been most applied is the food sector followed by the chemical one (**Figure 9**).

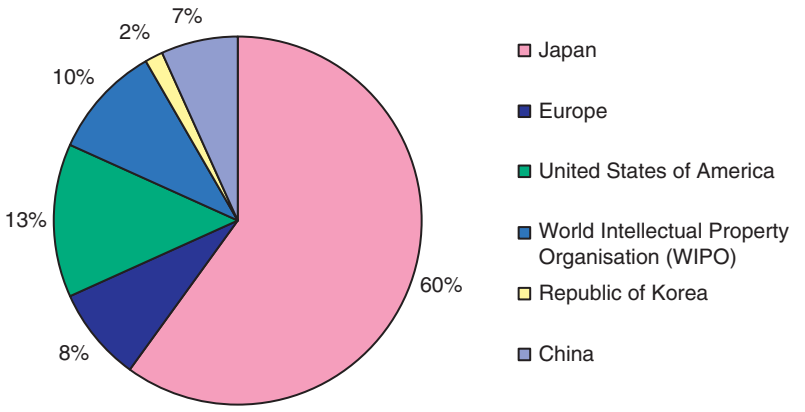


Figure 7 Country in which patents on membrane emulsification have been developed.

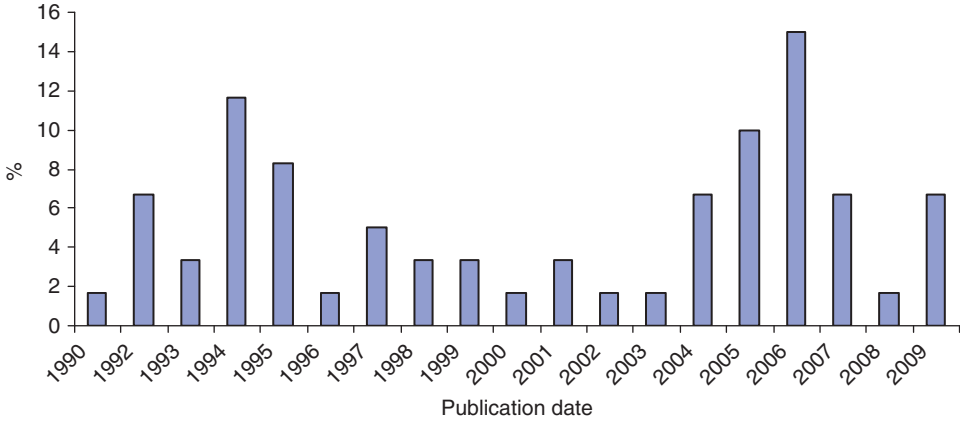


Figure 8 The behavior of patents on membrane emulsification per year published from 1990 to December 2009.

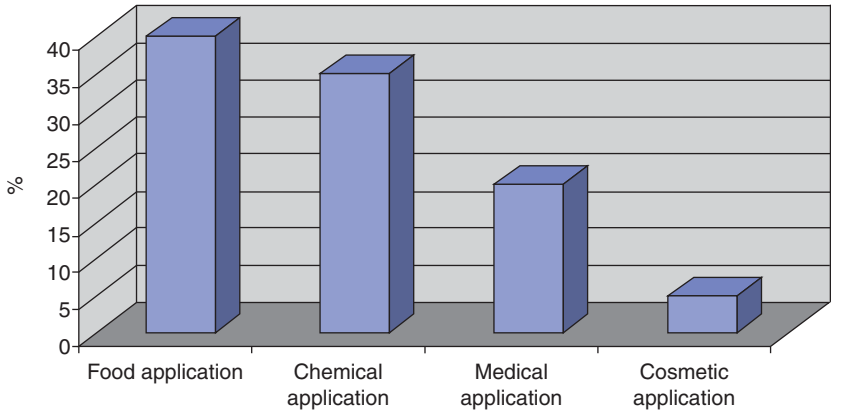


Figure 9 Main industrial applications of membrane emulsification process.

4.03.10 Conclusions and Perspectives

The ME introduced in 1990 has received in the initial years a strong impulse shown by an increasing number of patent published in that period. It is, however, more recently that the potentialities of such technology have led to a higher number of applications in various fields. Productive plant for niche applications shows the advantages of the technology. The benefits of ME process for the emulsion field include low shear properties, especially for the preparation of double emulsions or emulsions containing shear-sensitive ingredients, and to control microstructured fabrication of fine particles. The limitations of ME process include low dispersed phase flux and fouling phenomena. However, its full exploitation at the industrial level is still not achieved. In particular, membranes specifically designed for emulsification process are required in order to intensify emulsification process and to meet the demanding requirements for size-controlled emulsions for specific applications.

References

[1] Schultz, S., Wagner, G., Urban, K., Ulrich, J. *Chem. Eng. Technol.* **2004**, *27*, 361–368.
[2] Nakashima, T., Shimizu, M. *Key Eng. Mater.* **1991**, *61/62*, 513–516.
[3] Suzuki, K., Shuto, I., Hagura, Y. *Food Sci. Technol. Int.* **1996**, *2*, 43–47.
[4] Kawakatsu, T., Kikuchi, Y., Nakashima, M. *J. Am. Oil Chem. Soc.* **1997**, *74*, 317–321.
[5] Schubert, H., Engel, R., Kempa, L. *IUFoST World Congress 13th World Congress of Food Science and Technology*, IUFoST, Nantes, France, 17–21 September 2006.
[6] Giorno, L., De Luca, G., Figoli, A., Piacentini, E., Drioli E. *Membrane Operations: Innovative Separations and Transformations*; Wiley: Weinheim, 2009; Chapter 21, pp 463–497.
[7] Katoh, R., Asano, Y., Furuya, A., Sotoyama, K., Tomita, M. *J. Membr. Sci.* **1996**, *113*, 131–135.
[8] Williams, R. A., Peng, S. J., Wheeler, D. A., Morley, N. C., Taylor, D., Whalley, M. *Chem. Eng. Res. Des.* **1998**, *76*, 902–910.
[9] Schröder, V., Schubert, H. *Spec. Publ. R. Soc. Chem.* **1999**, *227*, 70–80.
[10] Engler, J., Wiesner, M. R. *Water Res.* **2000**, *34*, 557–565.
[11] Choi, C. K., Park, J. Y., Park, W. C., Kim, J. J. *J. Membr. Sci.* **1999**, *157*, 177–187.
[12] Vladisavljevic, G. T., Williams, R. A. *J. Colloid Interface Sci.* **2006**, *299*, 396–402.
[13] Zhu, J., Barrow, D. *J. Membr. Sci.* **2005**, *261*, 136–144.
[14] Sugiura, S., Nakajima, M., Iwamoto, S., Seki, M. *Langmuir* **2001**, *17*, 5562–5566.
[15] Kobayashi, I., Nakajima, M., Chun, K., Kikuchi, Y., Fujita, H. *AIChE J.* **2002**, *48*, 1639–1644.
[16] Sugiura, S., Nakajima, N., Kumazawa, N., Iwamoto, S., Seki, M. *J. Phys. Chem. B* **2002**, *106*, 9405–9409.
[17] Schröder, V., Behrend, O., Schubert, H. *J. Colloid Interface Sci.* **1998**, *202*, 334–340.
[18] Christov, N. C., Ganchev, D. N., Vassileva, N. D., Denkov, N. D., Danov, K. D., Kralchevsky, P. A. *Colloids Surf. A* **2002**, *209*, 83–104.
[19] Yasuno, M., Nakajima, M., Iwamoto, S. *et al. J. Membr. Sci.* **2002**, *210*, 29–37.
[20] Kukizaki, M. *J. Membr. Sci.* **2009**, *327*, 234–243.
[21] Kukizaki, M., Goto, M. *J. Chem. Eng. Jpn.* **2009**, *42*, 520–530.
[22] Kosvintsev, S. R., Gasparin, G., Holdich, R. G. *J. Membr. Sci.* **2008**, *313*, 182–189.
[23] Vladisavljevic, G. T., Williams, R. A. *Adv. Colloid Interface Sci.* **2005**, *113*, 1–20.
[24] Scherze, I., Marzilger, K., Muschiolik, G. *Colloids Surf. B* **1999**, *12*, 213–221.
[25] Katoh, R., Asano, Y., Furuya, A., Sotoyama, K., Tomita, M. *J. Membr. Sci.* **1996**, *113*, 131–135.
[26] Vladisavljevi, G. T., Tesch, S., Schubert, H. *Chem. Eng. Process.* **2002**, *41*, 231–238.
[27] Giorno, L., Mazzei, R., Oriolo, M., Davoli, M., Orioli, E. *J. Colloid Interface Sci.* **2005**, *287*, 612–623.
[28] Yasuno, M., Nakajima, M., Iwamoto, S. *et al. J. Membr. Sci.* **2002**, *210*, 29–37.
[29] Vladisavljevic, G. T., Schubert, H. *Desalination* **2002**, *144*, 167–172.
[30] Gijsbersten-Abrahamse, A. J., van der Padt, A., Boom, R. M. *3ième Congrès Mondial de l'Emulsion Lyon*, France, 2002; vols. 24–27.
[31] Yuan, Q., Aryanti, N., Gutirrez, G., Williams, R. A. *Ind. Eng. Chem. Res.* **2009**, *48*, 8872–8880.
[32] Trentin, A., Ferrando, M., López, F., Güella, C. *Desalination* **2009**, *245*, 388–395.
[33] D'oria, C., Charcosset, C., Barresi, A. A., Fessi, H. *Colloids Surf. A* **2009**, *338*, 114–118.
[34] Vladisavljevic, G. T., Schubert, H. *J. Membr. Sci.* **2003**, *225*, 15–23.
[35] Schröder, V., Schubert, H. *Colloid Surf.* **1999**, *152*, 103–109.
[36] Schröder, V., Beherend, O., Schubert, H. *J. Colloid Interface Sci.* **1998**, *202*, 334–340.
[37] Joscelyne, S. M., Trägårdh, G. *J. Food Eng.* **1999**, *39*, 59–64.
[38] Mine, Y., Shimizu, M., Nakashima, T. *Colloids Surf. B: Biointerfaces* **1996**, *6*, 261–268.
[39] Berot, S., Giraudet, S., Riaublanc, A., Anton, M., Popineau, Y. *Trans. IChemE* **2003**, *81*, 1077–1082.
[40] Asano, Y., Sotoyama, K. *Food Chem.* **1999**, *66*, 327–331.
[41] Ribeiro, H. S., Rico, L. G., Badolato, G. G., Schubert, H. *J. Food Sci.* **2005**, *70*, 117–123.
[42] Giorno, L., Piacentini, E., Mazzei, R., Drioli, E. *J. Membr. Sci.* **2008**, *317*, 19–25.
[43] Kawakatsu, T., Tragardh, G., Tragardh, C., Nakajima, M., Oda, N., Yonemoto, T. *Colloid Surf. A* **2001**, *179*, 29–37.
[44] Vladisavljevic, G. T., Tesch, S., Schubert, H. *Chem. Eng. Process.* **2002**, *41*, 231–238.
[45] Liu, H. J., Nakajima, M., Kimura, T. *J. Am. Oil Chem. Soc.* **2004**, *81*, 705–711.
[46] Mine, Y., Shimizu, M., Nakashima, T. *Colloid Surf. B* **1996**, *6*, 261–268.
[47] Hatate, Y., Uemura, Y., Ijichi, K., Kato, Y., Hano, T. *J. Chem. Eng. Jpn.* **1995**, *28*, 656–659.
[48] Maciejewska, M., Osypiuk, J., Gawdzik, B. *J. Polym. Sci. Polym. Chem.* **2005**, *43*, 3049–3058.
[49] Omi, S., Kaneka, K., Nakayama, A., *et al. J. Appl. Polym. Sci.* **1997**, *65*, 2655–2664.

[50] Wang, L. Y., Ma, G. H., Su, Z. G. *J. Control. Release* **2005**, *106*, 62–75.
[51] Sugiura, S., Nakajima, M., Ushijima, H., Ushijima, K., Yamamoto, K., Seki, M. *J. Chem. Eng. Jpn.* **2001**, *34*, 757–765.
[52] Suzuki, K., Fujiki, I., Hagura, Y. *Food Sci. Technol. Int. Tokyo* **1998**, *4*, 164–167.
[53] Kandori, K., Kishi, K., Ishikawa, T. *Colloids Surf.* **1991**, *55*, 73–78.
[54] Cheng, C. J., Chu, L. Y., Xie, R. *J. Colloid Interface Sci.* **2006**, *300*, 375–382.
[55] Cheng, C. J., Chu, L. Y., Xie, R., Wang, X. W. *Chem. Eng. Technol.* **2008**, *31*, 377–383.
[56] Vladisavljević, G. T., Tesch, S., Schubert, H. *Chem. Eng. Process.* **2002**, *41*, 231–238.
[57] Geerken, M. J., Lammertink, R. G. H., Wessling, M. *J. Colloid Interface Sci.* **2007**, *312*, 460–469.
[58] Mine, Y., Shimizu, M., Nakashima, T. *Colloids Surf. B* **1996**, *6*, 261–268.
[59] Kazuhiko, K., Kazuko, K., Tatsuo, I. *Colloids Surf.* **1991**, *61*, 269–279.
[60] Stillwell, M. T., Holdich, R. G., Kosvintsev, S. R., Gasparini, G., Cumming, I. W. *Ind. Eng. Chem. Res.* **2007**, *6*, 965–972.
[61] Schadler, V., Windhab, E. J. *Desalination* **2006**, *189*, 130–135.
[62] Okochi, H., Nakano, M. *Chem. Pharm. Bull.* **1997**, *45*, 1323–1326.
[63] Higashi, S., Iwata, K., Tamura, S. *Cancer* **1995**, *75*, 1245–1254.
[64] Higashi, S., Maeda, Y., Kai, M., *et al. Hepato-Gastroenterology* **1996**, *43*, 1427–1430.
[65] Higashi, S., Setoguchi, T. *Adv. Drug Delivery Rev.* **2000**, *45*, 57–64.
[66] Nakashima, T., Shimizu, M., Kukizaki, M. *Adv. Drug Delivery Rev.* **2000**, *45*, 47–56.
[67] Shima, M., Kobayashi, Y., Fujii, T., *et al. Food Hydrocoll.* **2004**, *18*, 61–70.
[68] Vladisavljevic, G. T., Shimizu, M., Nakashima, T. *J. Membr. Sci.* **2004**, *244*, 97–106.
[69] Thies, C. In *Microencapsulation Methods and Industrial Applications*; Benita, S., Ed.; Marcel Dekker: New York, 1996; Vol. 17, pp 1–21.
[70] Yuyama, H., Yamamoto, K., Shirafuji, K., Nagai, M., Ma, G. H., Omi, S. *J. Appl. Polym. Sci.* **2000**, *77*, 2237–2245.
[71] Ma, G.-H., Nagai, M., Omi, S. *Colloids Surf. A: Physiochem. Eng. Aspects* **1999**, *153*, 383–394.
[72] Wang, L.-Y., Ma, G.-H., Su, Z.-G. *J. Control. Release* **2005**, *106*, 62–75.
[73] Chu, L.-H., Xie, R., Zhu, J.-H., Chen, W. M., Yamaguchi, T., Nakao, S. *J. Colloid Interface Sci.* **2003**, *265*, 187–196.
[74] Ma, G.-H., Su, G.-Z., Omi, S., Sundberg, D., Stubbs, J. *J. Colloid Interface Sci.* **2003**, *266*, 282–294.
[75] Liu, R., Ma, G.-H., Wan, Y.-H., Su, Z.-G. *Colloids Surf. B: Biointerfaces* **2005**, *45*, 144–153.
[76] Vladisavljevic, G. T., Williams, R. A. *J. Colloid Interface Sci.* **2006**, *299*, 396–402.
[77] Charcosset, C., El-Harati, A., Fessi, H. *J. Control. Release* **2005**, *108*, 112–120.
[78] Nagashima, S., Koide, M., Ando, S., Makino, K., Tsukamoto, T., Ohshima, T. *Colloids Surf. A: Phisiochem. Eng. Aspects* **1999**, *153*, 221–227.
[79] Westover, D., Seitz, W. R., Lavine, B. K. *Microchem. J.* **2003**, *74*, 121–129.
[80] Ito, F., Makino, K. *Colloids Surf. B: Biointerfaces* **2004**, *39*, 17–21.
[81] Wang, L.-Y., Gu, Y.-H., Zhou, O.-Z., Ma, G.-H., Wan, Y.-H., Su, Z.-G. *Colloids Surf. B: Biointerfaces* **2006**, *50*, 126–135.
[82] Ma, G.-H., Nagai, M., Omi, S. *J. Colloid Interface Sci.* **1999**, *214*, 264–282.
[83] Omi, S., Matsuda, A., Imamura, K., Nagai, M., Ma, G.-H. *Colloids Surf. A: Physiochem. Eng. Aspects* **1999**, *153*, 373–381.
[84] Dowding, P. J., Goodwin, J. W., Vincent, B. *Colloids Surf. A: Phisiochem. Eng. Aspects* **2001**, *180*, 301–309.
[85] Costa, M. S., Cardoso, M. M. *Desalination* **2006**, *200*, 498–500.
[86] Ha, Y. K., Song, H. S., Lee, H. J., Kim, J. H. *Colloids Surf. A: Phisiochem. Eng. Aspects* **1999**, *162*, 289–293.
[87] Ma, G.-H., An, C.-J., Yuyama, H., Su, Z.-G., Omi, S. *J. Appl. Polym. Sci.* **2003**, *89*, 163–178.
[88] Zhou, Q.-Z., Ma, G.-H., Su, Z.-G. *J. Membr. Sci.* **2009**, *316*, 694–700.
[89] Zhou, Q.-Z., Wang, L. Y., Ma, G.-H., Su, Z.-G. *J. Membr. Sci.* **2008**, *322*, 98–104.
[90] Zhou, Q.-Z., Wang, L. Y., Ma, G.-H., Su, Z.-G. *J. Colloid Interface Sci.* **2007**, *311*, 118–127.
[91] Fuchigami, T., Toki, M., Nakanishi, K. *J. Sol–Gel Sci. Technol.* **2000**, *19*, 337–341.
[92] Doan, T. V. P., Olivier, J. C. *Int. J. Pharm.* **2009**, *382*, 61–66.
[93] Yamamoto, T., Ohmori, T., Kim, Y. H. *Carbon* **2010**, *48*, 912–928.
[94] Sawalha, H., Purwanti, N., Rinzema, A., Schröen, K., Boom, R. *J. Membr. Sci.* **2008**, *310*, 484–493.
[95] Sheibat-Othman, N., Burne, T., Charcosset, C., Fessi, H. *Colloids Surf. A: Physicochem. Eng. Aspects* **2008**, *315*, 13–22.
[96] Ito, F., Fujimori, H., Honnami, H., *et al. Colloids Surf. B: Biointerfaces* **2008**, *67*, 20–25.
[97] Hao, D.-X., Gong, F.-L., Wei, W., Hu, G.-H., Ma, G.-H., Su, Z.-G. *J. Colloid Interface Sci.* **2008**, *323*, 52–59.
[98] Figoli, A., De Luca, G., Longavita, E., Drioli, E. *Sep. Sci. Technol.* **2007**, *42*(13), 2809–2827.
[99] Buonomenna, M. G., Figoli, A., Spezzano, I., Drioli, E. *Catal. Commun.* **2008**, *9*(13), 2209–2212.
[100] Buonomenna, M. G., Figoli, A., Spezzano, I., Morelli, R., Drioli, E. *J. Phys. Chem. B* **2008**, *112*, 36.
[101] Ito, F., Fujimori, H., Honnami, H., *et al. Colloids Surf. B: Biointerfaces* **2008**, *66*, 65–70.
[102] Cheng, C.-J., Chu, L.-Y., Zhang, J., Zhou, M.-Yu, Xie R. *Desalination* **2008**, *234*, 184–194.

Biographical Sketches

Emma Piacentini is a researcher contractor at the Institute on Membrane Technology, ITM-CNR (Italy). She works in the field of membrane emulsification technology and membrane bioreactor.

Lidietta Giorno is a membrane biotechnologist with background in biological science, chemical technologies, and new materials. Her research experiences include membrane bioengineering, biocatalytic membrane reactors, integrated membrane systems for bioseparations and bioconversions, downstream processing based on molecular separation, membrane chirotechnology, and membrane emulsifier. She has been involved in membrane science and engineering research and development for almost 20 years.

She is a director of the Institute on Membrane Technology of the National Research Council of Italy, ITM-CNR and is involved in research cooperations at European and international level. She worked abroad in the USA at Sepracor Inc. (1992); in The Netherlands at ATO-DLO (1994); and in France, at The University of Compiegne (1997 and 2000). She is a visiting professor at Tianjin University of Science and Technology, China, since 2008.

Lidietta Giorno is a co-author of three books and some 70 peer reviewed scientific papers in international journals. She is an editorial board member of scientific journals, a member of the referee pool of scientific journals and research agencies, and a member of international committees and several scientific societies.

She has served on the European Membrane Society Council for two mandates and is currently the president of the EMS Council and editor of the *EMS Membrane Newsletter*.

Alberto Figoli is researcher at the Institute on Membrane Technology (ITM-CNR). His research includes the membrane preparation and characterization, membrane process for capsule preparation, and study on pervaporation and food-packaging application. He is the author of about 40 publications, including book chapters, and the author of a US patent on novel membrane preparation.

Professor Enrico Drioli has been working in Membrane Science and Membrane Engineering for many years even when a student in chemistry at the University of Naples. He is a full professor at the Department of Chemical Engineering and Materials at the University of Calabria where he founded, in 1993, the Institute of Membrane Technology of the Italian Research Council. He served there as a director until December 2008. He also served as dean of the School of Engineering of the University of Calabria during the years 1982-85.

He received various award and honors: Doctorate Honoris Causa from University of Paul Sabatier of Toulouse (France) (8 July 2009); International Cooperation Honor Award on September 2005 given by the Membrane Industry Association of China (MIAC) for his special dedication to the International Cooperation between China and Europe in the field of membrane and science technology; guest professor in the Environment and Safety Engineering Department at the Jiangsu Polytechnic University, China (since June 2005); Honorary Member of the A. V. Topchiev Institute of Petrochemical Synthesis at the Russian Academy of Sciences, Moscow (since 1999); Doctorate Honoris Causa in Chemistry and Chemical Technology from Russian Academy of Science (February 1992); Honorary Professor at the China Northwest University in Xi'an, Shaanxi, People's Republic of China (September 1991); President of the European Society of Membrane Science and Technology (known today as the European Membrane Society) (1982–98); Honorary President of the European Membrane Society (since 1999); Member of the International Scientific Advisory Committee of the Grand Water Research Institute at Technion–Israel Institute of Technology, Israel (since 2004); Member and Moderator of the Research Advisory Council of the Middle East Desalination Research Center Oman, Muscat (since May 1997); Member of the International Advisory Board of the State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences (since 2007); Founding member of the European Federation on Regenerative Medicine (since 2006); Expert in the panels of the OECD project 'Nanotechnology and clean water' (www.oecd.org/sti/nano).

His scientific activity has been mainly in: Membrane Science and Engineering; Membranes in Artificial Organs; Integrated Membrane Processes; Membrane Preparation and Transport Phenomena in Membranes; Membrane Distillation and Membrane Contactors; and Catalytic Membrane and Catalytic Membrane Reactors.

He is the author of more than 530 scientific papers, and 10 scientific books and holds 18 patents in the field of Membrane Science and Technology.

Drioli is the Member of the Advisory Boards of: *Journal of Membrane Science* – Elsevier, and *Polish Journal of Chemical Technology*. In addition, he is the member of the International Advisory Board of *Journal of Water Supply*: Research and Technology – AQUA. He is also the senior advisor to *Chinese Journal of Membrane Science and Technology* (China), and *Technology of Water Treatment Journal*.

Drioli is the member of the editorial boards for *Chemical Engineering and Processing* Elsevier: *Desalination* –Elsevier; *Chemical Engineering and Technology Journal* – Wiley-VCH; *Industrial & Engineering Chemistry Research* (from January 2002 to 2006)–American Chemical Society; *Separation Science and Technology* – M. Dekker; *Clean Technologies and Environmental Policy* – Springer-Verlag; *Water Treatment* – China Ocean Press (China); *Russian Journal of Physical Chemistry* – MAIK Nauka, Interperiodica Publ. (Russia); and *Journal of Separation and Purification Technology* – Childwall University Press (China).

4.04 Liquid Membranes

M E Vilt and W S W Ho, The Ohio State University, Columbus, OH, USA

N N Li, NL Chemical Technology, Inc., Mount Prospect, IL, USA

Nomenclature

- c_f concentration of target species in the aqueous feed solution, mg l^{-1} (g m^{-3} or ppm)
- c_s concentration of target species in the aqueous strip solution, mg l^{-1} (g m^{-3} or ppm)
- j flux of target species through the supported liquid membrane, g $(s\,m^2)^{-1}$
- k_a mass transfer coefficient for the aqueous feed solution, m s^{-1}
- k_{as} mass transfer coefficient for the aqueous strip solution, m s^{-1}
- k_e mass transfer coefficient due to the complexation/extraction reaction, m s^{-1}
- k_m mass transfer coefficient for the membrane phase, m s^{-1}
- k_s mass transfer coefficient due to the decomplexation/stripping reaction, m s^{-1}
- K_o overall mass transfer coefficient, m s^{-1}
- m_f distribution coefficient of the target species between the organic membrane phase and the aqueous feed solution
- m_s distribution coefficient of the target species between the organic membrane phase and the aqueous strip solution

4.04.1 Introduction

4.04.1.1 Historical Development

Li invented a liquid membrane process for the separation of hydrocarbons in 1968 [1]. The process used liquid surfactant membranes operating in a drop column. Droplets of a feed solution containing hydrocarbons were injected into an aqueous solution containing surfactants. A coating around the feed droplet resulted and a liquid membrane was formed. The coated droplet then rose through a solvent phase where selective mass transport occurred through the liquid membrane. The oil drops coalesce at the top of the column, allowing the water and surfactant to return to the aqueous phase. Li's initial process led to the development of the double emulsion method or emulsion liquid membrane (ELM), which is used to separate hydrocarbon solutions as well as metal ions from their aqueous solutions. For facilitated transport, Li incorporates a chemical reaction inside the emulsion droplets as well as in the liquid membranes. He classifies these as two types of facilitated transport as described later in Sections 4.04.3.1.1 and 4.04.3.1.2 [2–4].

Supported liquid membranes (SLMs) for separation of ions from aqueous solutions were demonstrated by Cussler [5] in 1971 using an organic-containing solid support. The solid support was filter paper soaked in organic solution and was used to separate sodium chloride from aqueous solutions. A microporous polypropylene (PP) solid support containing a carrier agent was investigated for copper separation by Baker *et al.* [6] in 1977 and Lee *et al.* [7] in 1978. Hollow fiber supports were first reported in 1980 by Babcock *et al.* [8]. Instability and loss of carrier agents have been a serious issue for SLMs and led to the development of supported liquid membranes with strip dispersion by Ho [9].

4.04.1.2 Emulsion Liquid Membranes

An ELM is formed when a stable emulsion containing two immiscible phases is dispersed in a continuous external phase. The transport of a target species in the external phase occurs through the liquid membrane phase of the emulsion into the internal phase by one of two facilitated transport mechanisms. ELMs have been investigated for a variety of applications, which will be described in more detail later.

4.04.1.3 Supported Liquid Membranes

When a porous support contains a liquid membrane solution and is placed between a feed and receiving solution, an SLM is formed. Supports can be in a flat

sheet or hollow fiber configuration. Applications for SLMs have primarily focused on metal separation from aqueous solutions. Industrial use of SLMs has been hindered by the issue of instability, which occurs from the gradual loss of liquid membrane solution from the pores of the solid support.

4.04.1.4 SLMs with Strip Dispersion

SLM with strip dispersion is a recently developed liquid membrane process and a promising solution to the issue of SLM instability. An aqueous feed solution contacts an organic liquid membrane solution, which is embedded in the pores of a support. The organic liquid membrane solution is a continuous phase extending out from the porous support, ensuring a constant supply of liquid membrane solution. Within the continuous organic solution a strip solution is dispersed by mechanical mixing. Laboratory and pilot plant studies have demonstrated long stability and efficient removal and recovery of metal species from aqueous solutions.

4.04.2 Emulsion Liquid Membranes

4.04.2.1 General Description

An ELM can be considered as a double emulsion consisting of three phases: the external, membrane, and internal phases. Li developed two types of facilitated transport mechanisms to describe the mass transport and separation in ELM [2, 10].

4.04.2.1.1 Emulsion liquid membrane system

An ELM is a three-phase system and can consist of water/oil/water (W/O/W) or oil/water/oil (O/W/O) phases. In either system, the liquid membrane is the phase separating the like phases. For a W/O/W system, the oil phase separating the two aqueous phases is the liquid membrane phase [11]. The ELM process can be described in four steps, which are shown in **Figure 1** [12].

The first step in forming an ELM is the formation of an emulsion between two immiscible phases. This is typically done with the use of surfactants and high-speed agitation. Emulsion droplets range from 1–3 μm in diameter, thus providing good stability [11]. Second, the emulsion is dispersed in a third continuous phase with constant agitation. Once dispersed in the continuous phase, globules of the emulsion of a diameter of 100–2000 μm form [11]. The mixing rate in the dispersion step is an important operating parameter. If dispersing speed is too fast, emulsion breakage can occur, and if too slow, large globules can form, reducing the mass transfer area. During this second step of the ELM process, mass transfer from the external phase to the internal phase occurs by one of the two facilitated transport mechanisms. After the desired separation, the emulsion and the continuous phase are separated in a settling step. The final step in the ELM process involves breaking the emulsion, whereby the internal phase is then recovered and the membrane phase can be reused. The emulsion is usually broken by the use of an electric field [13].

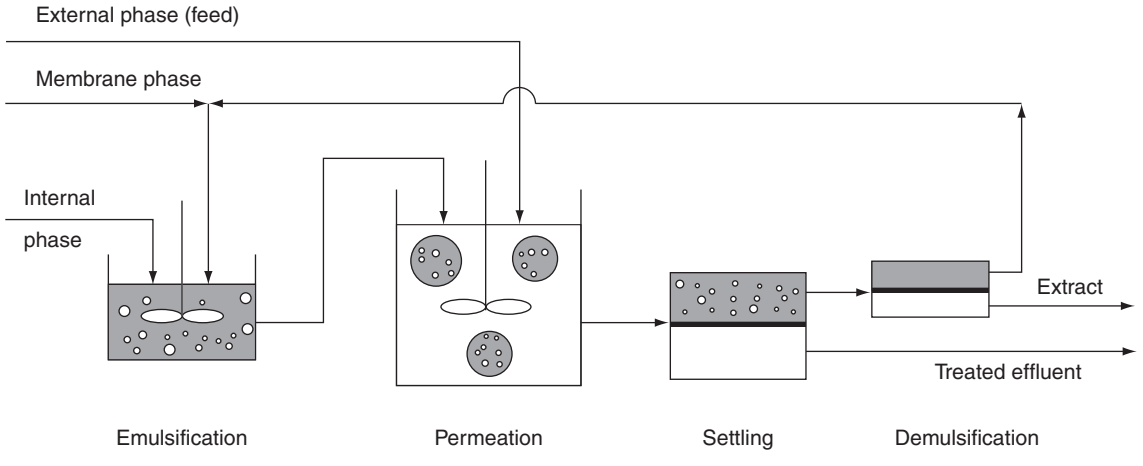


Figure 1 Emulsion Liquid Membrane Process. From Correia, P. F. M. M., de Carvalho, J. M. R. *J. Membr. Sci.* **2000**, *179*, 175–183.

4.04.2.1.2 Type 1 facilitation

Type 1 facilitation involves diffusion of a species in the external phase, through the membrane phase, to the internal phase. Once in the internal phase, a chemical reaction occurs, prohibiting the reaction product's diffusion back through the membrane. The reaction maintains a low solute concentration in the internal phase, providing a high driving force. Phenol removal from wastewater is an example of an ELM with type 1 facilitation. Phenol in the external aqueous phase diffuses through the oil membrane phase and reacts with NaOH in the internal phase. This results in the formation of sodium phenolate, which is not soluble in the membrane oil phase and so is retained in the internal aqueous phase [11].

4.04.2.1.3 Type 2 facilitation

Carrier-facilitated transport is another name for type 2 facilitation [3, 14, 15]. A mobile carrier compound in the liquid membrane phase transfers the target species from the feed solution to the strip solution. A good example of this mechanism is the transport of copper as shown in **Figure 2** [16].

The extractant HA (shown in the dimer form $(HA)_2$) reacts with Cu^{2+} at the interface of the feed solution with the liquid membrane to form a copper-extractant complex, $CuA_2(HA)_2$ [16]. The complex diffuses through the liquid membrane to the interface of the liquid membrane and the strip solution. At this interface, a decomplexation/stripping reaction occurs with a strong acid present in the strip solution. The Cu^{2+} is stripped into the strip solution, and the extractant is regenerated. The extraction and stripping reactions for the copper example are given in Equations (1) and (2), respectively:

$$Cu^{2+} + 2(HA)_2 \rightarrow CuA_2(HA)_2 + 2H^+ \quad (1)$$

$$CuA_2(HA)_2 + 2H^+ \rightarrow Cu^{2+} + 2(HA)_2 \quad (2)$$

The copper extraction process with ELMs has been developed extensively and reported in more detail in this article [3, 14, 15].

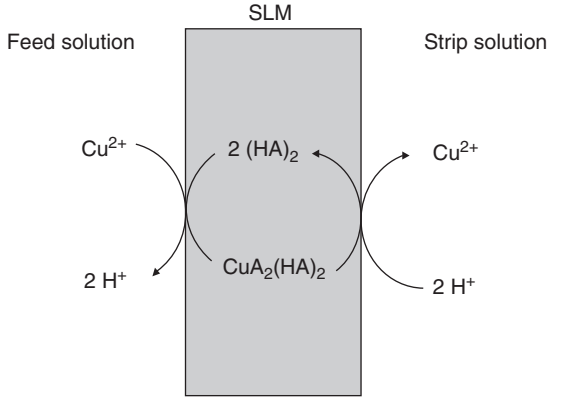


Figure 2 Carrier-facilitated transport mechanism for copper. From Ho, W. S. W. *Ann. N. Y. Acad. Sci.* **2003**, *984*, 97–122.

4.04.2.2 Theory

Several models have been developed to describe type 1 and type 2 facilitation.

4.04.2.2.1 Diffusion-type mass transfer models for type 1 facilitation

The spherical shell approach and the emulsion globule approach are the two methods that have been used to describe type 1 facilitation. Models using the spherical shell approach have many shortcomings, which have been addressed by the emulsion globule approach [17]. The current state-of-the-art model for type 1 facilitation, the advancing front model, was developed by Ho *et al.* [18] and was based on the emulsion globule approach [19]. The model assumes that the reaction of solute with the internal phase reagent is instantaneous and irreversible at a reaction front. Over time, this reaction front advances toward the globule center as the internal reagent is consumed [17]. The zero order solution is valid in most cases and can be implemented easily. The advancing front model has been modified to include an external phase mass transfer resistance [20, 21]. Kim *et al.* [22] included an additional mass transfer resistance from a membrane phase layer at the interface of the internal phase. Yan *et al.* [23] presented a model in which the first-order reaction is irreversible, but not instantaneous, and accounted for mass transfer in the external phase.

Unlike the models described above, the reversibility of the internal phase reaction was first reported by Teramoto *et al.* [24] and Bunge and Noble [25]. Chan and Lee [26] and Borwankar *et al.* [27] considered the leakage of the internal phase into the external phase. Bhowal and Datta [28] took into account membrane breakage and its effect on pH of the external phase. Monte Carlo simulation was used by Bandyopadhyaya *et al.* [29] to account for globule–globule interactions.

4.04.2.2.2 Carrier-facilitated transport models for type 2 facilitation

As with type 1 facilitation, models developed from the spherical shell approach have shortcomings which can be addressed by the emulsion globule approach. Teramoto *et al.* [30] presented the first model that accounted for a carrier in the membrane phase. This model included the external phase mass transfer resistance and accounted for a peripheral thin membrane layer of the emulsion globule as additional mass transfer resistance. The model also accounted for membrane leakage. A similar model was developed by Kataoka *et al.* [31, 32]; however, this model did not account for membrane leakage. Both models have complicated equations with a large number of parameters that must be evaluated. A model that simplified the system of equations and had fewer parameters was developed by Lorbach *et al.* [33] and was applied to copper extraction. This model was further simplified by Lorbach and Marr [34] with the common facilitated transport assumption that the free-carrier and metal-carrier complex have the same diffusivity. The pH of the external phase was assumed to be constant, and mass transfer resistance in the peripheral thin membrane was eliminated. The resulting model has become the state-of-the-art model for carrier facilitated transport for ELMs [19]. The Lorbach and Marr model was extended by Ortner *et al.* [35] to describe ELMs in a countercurrent column. A large number of nonlinear equations resulted and were solved numerically.

Yan [36] developed a simplified model describing batch extraction. An irreversible first-order reaction between the solute and the carrier was used by assuming a constant carrier concentration at the interface. By using a large excess of internal reagent, an irreversible first-order stripping reaction between the solute–carrier complex and the internal reagent was assumed. A perturbation solution was obtained in which the zero-order, or steady-state solution, described extraction in ELMs well.

The Lorbach and Marr model was modified by Reis and Carvalho [37] to account for a changing pH of the external phase. This led to more accurate reaction rate constants. Biscaia Junior *et al.* [38] developed a model, which accounted for swelling and breakage of the emulsion globules.

4.04.2.3 Applications

Removal of zinc from wastewater in the viscose fiber industry, phenol removal, cyanide removal, the recovery of nickel from electroplating solutions, extraction of copper from leach solution, treatment of wastewater, biochemical processing, biomedical encapsulation and release, and use as a well control fluid are the main applications for ELMs.

4.04.2.3.1 Removal of zinc from wastewater in the viscose fiber industry

The first commercial plant for zinc removal from wastewater in the viscose fiber industry was put into operation in 1986 by Lenzing AG in Austria [39–41]. The selective separation of zinc over calcium from the wastewater stream containing 400–600 ppm zinc, 5–8 g l^{-1} H_2SO_4, 25 g l^{-1} Na_2SO_4, and other additives was demonstrated with the extractant di(2-ethylhexyl) dithiophosphoric acid (DTPA). DTPA is rarely used in solvent extraction due to high cost and slow stripping kinetics. However, in the case of ELMs, DTPA is preferred over di(2-ethylhexyl) thiophosphoric acid (MTPA). This is due to enhanced stability at low pH and because the slow stripping kinetics are overcome by the large interfacial area of the ELM [39]. The pilot plant for zinc removal had an average separation efficiency of 99.5% with a wastewater capacity of 75 m^3 h^{-1}. The receiving phase of 2.5 M H_2SO_4 was concentrated to 60 g l^{-1} of zinc and, after further concentration by evaporation, can be reused in the process stream. This process has also been used commercially in Germany and the Netherlands [39]. Zinc containing wastewater from a viscose fiber plant has been treated with an ELM process in China since 1995 and is described by Wang *et al.* [42]. The process recovers 95% of the zinc for reuse. The voltage required during emulsion splitting was reduced by decreasing the amount of surfactant and increasing the volume ratio of the membrane phase to the internal aqueous phase. Exxon developed a copper extraction process, which is similar to other metal extraction processes by liquid membranes [3, 14].

4.04.2.3.2 Removal of phenols

Early work in the removal of phenol from wastewater paved the way for commercialization [18, 43–52]. Zhang *et al.* [53, 54] have reported on phenol removal at the Nanchung Plastic Factory in Guangzhou, China. The emulsion consisted of a liquid membrane phase of 3.5 wt.% LMS-2, 6.7 wt.% liquid paraffin in kerosene, with 5 wt.% NaOH as the internal phase. By the use of ELMs, the waste stream with a phenol concentration of 1000 mg l^{-1} was reduced to 0.5 mg l^{-1} with an extraction efficiency of 99.95%.

The surfactant LMS-2 was developed for the project and resulted in a very stable ELM.

Nanoti *et al.* [55] reported the use of ELMs with a hollow fiber contactor for the removal of phenol from highly concentrated solutions (3500–5000 ppm). The problems of emulsion leakage and swelling, which are typical for external solutions with high phenolic concentrations, were not observed. Park and Chung [56] compared emulsification by mechanical stirring and ultrasonic homogenization. Higher phenol removal was achieved with the latter. The selective removal and recovery of phenol from phenolic resin plant effluents containing formaldehyde was exhibited by Correia *et al.* [57].

A novel ELM process for the removal of phenol and substituted phenols was presented by Park *et al.* [58]. The process first converts the liquid membrane phase into a non-Newtonian form by the addition of high-molecular-weight polymers. Under low shear rate conditions, an increase in viscosity is observed, which helps stabilize the emulsion without a decrease in phenol diffusion. Emulsion breakage is further minimized by dispersion in a Taylor–Couette flow field using a Taylor vortex column.

Experimental and modeling studies applying ELMs for the extraction of 2-chlorophenol were reported by Correia and de Carvalho [12, 59]. An ELM process for the removal of nitrophenols from real wastewater with an extraction efficiency of 99.9% was demonstrated by Luan and Plaisier [60]. An initial total nitrophenol concentration of 6700 mg l^{-1} in wastewater solutions was reduced to 2 mg l^{-1} in the optimized process, which also removed nitrobenzene with high efficiency.

Phenol removal from highly concentrated waste solutions (7000–47 000 mg l^{-1}) using *N,N*-di(1-methylheptyl) acetamide (N_{503}) as a carrier has been demonstrated by Wan *et al.* [61]. The two-stage ELM process was used to treat four types of industrial phenolic wastewaters and met the target concentration of 0.5 mgl^{-1} phenol in the effluent.

Reis *et al.* [62] studied removal and recovery of phenol with the carrier Cyanex 923 (mixture of phosphine oxides) with ELMs and nondispersive solvent extraction with hollow fibers. Removal and recovery of phenol for the ELM process were slightly less than the extraction process and were 98% and 91%, respectively. The extraction of the polyphenols, 2-(4-hydroxyphenyl)ethanol [63] and 4-hydroxycinnamic acid [64], has also been recently studied by Reis *et al.*

4.04.2.3.3 Cyanide removal

An ELM process was commercialized for cyanide removal from gold processing wastewater at the Huang-Hua Mountain Gold Plant, near Tianjin, China [19, 65, 66]. Jin and Zhang [65] describe an application that reduces the cyanide concentration from 130 to 0.5 mg l^{-1}, with an extraction efficiency of 99.6%. The plant was installed with little capital investment, and it led to pollution control and productivity increase [66].

4.04.2.3.4 Recovery of nickel from electroplating solutions

A system for the recovery of nickel from electroplating waste solutions was described by Draxler and Marr [40, 67]. An ELM composed of 5 wt.% DTPA as a carrier, 3 wt.% ECA 11522 Polyamine as a surfactant, and 92 wt.% of the paraffin, Shellsol T, achieved a nickel extraction efficiency of 99.8%. The electroplating solution had an initial nickel concentration of 400–6000 mg l^{-1}, which was reduced to 1 mg l^{-1}. Nickel recovery from a simulated Watts electroplating rinse solution was investigated by Juang and Jiang [68]. Hoffmann *et al.* [69] compared Cyanex 301 (di-*iso*-octyldithiophosphinic acid) and D2EHPA (di(2-ethylhexyl) phosphoric acid) as carriers, and found that Cyanex 301 was a better extractant for nickel extraction, but suffered from increased swelling.

4.04.2.3.5 Wastewater treatment

The standard ELM processes for the removal of heavy metals (Zn, Cd, Cu, and Pb) from wastewaters in metallurgical and incineration plants using the carrier MTPA were developed by Marr and Draxler [39]. A liquid membrane phase composed of 5 wt.% MTPA and 3 wt.% ECA 11522 Polyamine dissolved in the diluent Shellsol T was used in this process. In a pilot plant operation, heavy metals were removed with 99% efficiency to achieve concentrations of 0.2 mg l^{-1} Zn^{2+}, 0.02 mg l^{-1} Cd^{2+}, 0.007 mg l^{-1} Cu^{2+}, and 0.01 mg l^{-1} Pb^{2+} in the treated stream. The process for incineration of plant waste involves the removal of mercury, which is accomplished by ion-exchange resins in the first step of the process. The wastewater is then treated with an ELM process in which stripping with sulfuric and hydrochloric acid is needed to regenerate the carrier.

A 9-day continuous field test that processed 5579 gallons of feed solution with an ELM process for the recovery of Cu from mine solutions was reported by

Wright *et al* [70]. No major equipment or mechanical failures were experienced, and the emulsion composition was optimized to allow for mild demulsifying conditions. Chakravarti *et al.* [71] compared the carriers LIX 622 (5-dodecylsalicylaldoxime) and LIX 84 (2-hydroxy-5-nonylacetophenone) in an ELM process for the removal of Cu from simulated wastewater. Copper removal from residual mine water using the carrier LIX-860 (5-nonilsalicylaldoxime) was demonstrated by Valenzuela *et al.* [72]. Hu and Wiencek [73] reported the use of hollow fiber modules for an ELM system for copper removal from aqueous solutions. Valenzuela *et al.* [74] recently investigated the removal of zinc from acidic mine drainage with the carrier D2EHPA.

The removal of lead from storage battery industrial wastewater was studied by Guerel *et al.* [75]. After a pH adjustment from 1.4 to 4.0, lead was reduced from 4.2 to 0.071 ppm. Bourenane *et al.* [76] removed cobalt and lead from simulated wastewater with efficiencies of 99% and 94%, respectively, using an ELM system containing the carrier D2EHPA. Optimization of operating parameters for lead removal was investigated by Sabry *et al.* [77] and resulted in 99% efficiency of lead removal from synthetic wastewater containing 400–1000 mg l^{-1} of lead.

Li *et al.* [78] demonstrated removal of chromium from electroplating effluent. The initial chromium concentration of 184 mg l^{-1} was reduced to below 0.5 mg l^{-1} in ELMs containing the tertiary amine, N7301, the surfactants monosuccimide, L113A, and bissuccimide, L113B. Compared to Span 80, the surfactants L113A and L113B were able to form more stable emulsions, leading to increased chromium removal over time. The carriers Aliquat 336 (trioctylmethylammonium chloride) and tri-*n*-octylamine (TOA) were studied by Chakraborty *et al.* [79] for the removal of chromium from dilute aqueous solutions. A mixture of Aliquat 336 and TOA resulted in maximum chromium extraction compared to a single carrier containing organic phase. This slight synergistic effect may be attributed to the formation of a mixed ligand complex [79]. Banerjea *et al.* [80] presented experimental and modeling results for the extraction of chromium from acidic solutions with the carrier Aliquat 336. Bhowal *et al.* [81] developed a model for chromium extraction by ELMs with Aliquat 336 in which the equilibrium of sodium hydroxide and the chloride form of Aliquat 336 is considered.

Breembroek *et al.* [82] proposed design guidelines for an ELM pilot plant consisting of a rotating disk contactor column for cadium removal from wastewater. The resulting design of the ELM process was based on rules for solvent extraction columns, and achieved the target of 95% cadmium removal. ELMs, SLMs, and nondispersive solvent extraction (NDSX) were compared as liquid membrane processes for cadmium removal from wet phosphoric acid by Urtiaga *et al.* [83]. The ELM process had slower cadium removal compared to the NDSX process. The presence of surfactant in the liquid membrane phase reduced extraction kinetics. Diffusion of cadium in the acid solution was also reduced in the ELM process due to the slow stirring that was needed to maintain emulsion stability. Cadium removal from dilute acidic aqueous solutions using the carrier D2EHPA was studied by Basualto *et al.* [84].

The removal and recovery of nuclear waste has been investigated using ELM processes. Removal and recovery of plutonium from simulated waste solutions with the carrier 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) was demonstrated by Kedari *et al.* [85]. Extraction of plutonium was 98% from simulated waste solution containing Cs-137, Ce-144, Ru-103, and Ru-106 and only 84% when uranium was added to the same solution. El-Said *et al.* [86] compared experimental and modeling results for Cs-137 extraction using the crown ether, 18C6, as a carrier. Uranium removal and recovery from acidic waste solutions using the carrier tri-*n*-octylphosphine oxide (TOPO) was studied by Kulkarni *et al.* [87, 88] and El-Reefy *et al.* [89, 90]. Complete extraction of uranium from Gattar G II sulfate leach liquor (1200 mg l^{-1} of U) was reported by El Sayed [91] with the carrier Aliquat 336. Yang *et al.* [92] synthesized three different N-alkylcaprolactams for use as carriers in an ELM process for uranium extraction. A two-stage process was proposed and was found to be effective for uranium removal when the initial uranium feed concentration was 1.1 mM or less. El-Hazek and El Sayed [93] proposed an ELM process for uranium extraction from phosphoric acid solutions. The ELM was composed of a liquid membrane phase containing D2EHPA and TOPO dissolved in kerosene with the surfactant Span 80 and 0.5 M citric acid as the internal phase.

Treatment of distillery effluent for the removal of acetic acid was reported by Kumaresan *et al.* [94] using both batch and continuous processes. Initial biological oxygen demand and chemical oxygen

demand concentrations of 3500 and 68 000 ppm were reduced to 94 and 900 ppm, respectively.

The removal of ammonia from wastewater has been investigated extensively [95–105]. Ammonia removal with ELMs involves type 1 facilitation, where ammonia reacts with sulfuric or phosphoric acid forming an ammonium salt in the internal phase. The ELM process is advantageous over other ammonia removal processes, but suffers from the recovery of an ammonium salt instead of the preferred ammonium hydroxide [39]. Despite this major disadvantage, a 4-ton d^{-1} capacity pilot plant in China demonstrated ammonia removal from wastewater generated in a metal production plant [106]. Devulapalli and Jones [107] achieved 99.5% removal of aniline from wastewater with an ELM containing a liquid-membrane phase of Span 80 and kerosene with an internal phase of HCl. 2-propanol was used during the demulsifying process and led to 98% recovery of the liquid membrane phase, which was then reused.

4.04.2.3.6 Biochemical processing

Biochemical processing applications with ELMs include the separation of amino acids (L-phenylalanine), biochemicals (lactic acid), and antibiotics (penicillin G), from fermentation broths. Thien *et al.* [108] studied the separation of L-phenylalanine using the quaternary ammonium salt, Aliquat 336, as a carrier. Solute hydrophobicity of amino acids was found to have a strong correlation with initial flux. This study also addressed the issue of system optimization to provide sufficient driving force (concentration of the counter ion, Cl^-) while minimizing emulsion swelling. The use of the anion extractant, D2EHPA, for recovery of L-phenylalanine was reported by Itoh *et al.* [109]. An optimized ELM system for the recovery of L-phenylalanine using D2EHPA was presented by Hong *et al.* [110]. Hong and Yang [111] extended this work and developed a continuous ELM process. With a fermentation solution at a pH of 2.5 and an initial L-phenylalanine concentration of 36 g l^{-1}, a concentrated internal solution of 170 g l^{-1} can be obtained. Juang and Wang [112] investigated the separation of L-phenylalanine from aspartic acid with the carrier D2EHPA. The separation of D-phenylalanine from racemic D,L-phenylalanine solutions was reported by Pickering and Chaudhuri [113].

Removal of lactic, acetic, propionic, and acrylic acids was studied by O'Brien and Senske [114]. They developed an ELM process for the selective recovery of acrylic acid from propionic acid and acetic acid containing fermentation broths. The carrier Alamine 336 (tri-octyl/decyl amine) was reported for lactic acid extraction by Chaudhuri and Pyle [115]. This work was extended by Scholler *et al.* [116] in which the extraction of lactic acid from an actual fermentation broth was demonstrated. Extraction efficiencies for the aqueous solution (simulated fermentation broth) were almost double those of the actual fermentation broth. Reisinger and Marr extracted lactic acid with the carrier, Amberlite LA-2 (*N*-lauryl-*N*-trialkylmethylamine) [117, 118]. TOPO, tri-*n*-butyl phosphate (TBP), TOA, and dioctylamine were compared as carriers for lactic acid recovery from fermentation broths by Hano *et al.* [119]. Yuanli *et al.* [120] developed a model to describe the swelling of ELMs during lactic acid extraction with the carriers TMP and TOA. The resulting model agreed well with experimental data. Citric acid extraction from fermentation broths with the carrier Alamine 336 was first studied by Boey *et al.* [121]. A tertiary amine carrier was used in modeling and experimental studies by Stoica-Guzun *et al.* [122] for citric acid extraction. Recent studies on citric acid extraction with the carriers Alamine 336 [123] and Aliquat 336 [124] have been reported.

The recovery and bioconversion of penicillin G with an ELM system was reported by Scheper *et al.* [125]. Penicillin G was extracted through a membrane phase of Span 80 and Amberlite LA-2 in kerosene to an internal phase containing the enzyme penicillin acylase, which converted penicillin G into the products phenylacetic acid and 6-aminopenicillinic acid. Hano *et al.* [126] recovered penicillin G with di-*n*-octylamine as a carrier, ECA 4360J (Exxon) as a surfactant (it should be noted that Li used ECA 4360 extensively in his work on liquid membranes, because it resulted in stable emulsions), with a mixed solvent of kerosene and *n*-butyl acetate, and an internal phase of Na_2CO_3. The group of Lee *et al.* [127–130] addressed the issue of penicillin G decomposition due to the high pH of the internal phase containing Na_2CO_3. An extraction efficiency of 95% was reported with a concentration of the internal phase 9 times the original penicillin G concentration in the external phase, with the extractant Amberlite-LA 2 [127]. The efficiency of penicillin G extraction with membrane phases containing a dilute polymer solution to improve emulsion stability was

reported by Lee [131]. ELMs with the carrier Aliquat 336 for the recovery of the cephalosporin antibiotics Cephalexin and Cephalosporin-C were reported by Sahoo and Dutta [132] and Sahoo *et al.* [133], respectively. Detailed review articles on extraction of biochemicals with liquid membrane processes are available [134–137].

4.04.2.3.7 Encapsulation applications – well control fluid and slow release of drugs

A well control fluid for preventing well blowout and sealing loss zones in oil and gas wells has been commercially available from Exxon since 1985 [138]. The control fluid is a pumpable water-in-oil emulsion containing clay particles and water droplets separately in the oil phase [11]. When the emulsion is subjected to high shear that ruptures the oil film, the clay particles come in contact with the water, resulting in tremendous swelling of the clay particles and finally a viscous high-strength paste.

ELMs have been demonstrated as effective delivery mechanisms for the slow and prolonged release of drugs in various biomedical applications [4]. In order for the W/O/W ELM systems to be administered intravenously, emulsion droplets for drug delivery applications must be under 0.1 μm [139]. The additional restriction of small droplet size, along with the condition of membrane stability, has led to the development of a variety of emulsification techniques for ELM formation for drug-delivery applications. The major emulsification techniques are the traditional double emulsion method, phase inversion, cross-flow membrane emulsification, pre-mix membrane emulsification, and microchannel emulsification [139]. Li and his associates also used liquid membranes for oral intake of encapsulated medicine and enzymes for removing toxin materials in the intestines (an oral form of artificial kidney) [4]. Emulsification procedures for drug delivery ELMs were recently reviewed by van der Graaf *et al.* [140]. Numerous applications exist for the slow release of drugs with ELMs. Applications such as prolonged drug release, taste masking of bitter drugs, and topical drug application have been recently reviewed by a number of authors [4, 139–145].

4.04.2.3.8 Other applications

ELMs have been investigated for the separation of hydrocarbons and hydrometallurgical extraction applications [11]; recent advances in these areas will be discussed. An O/W/O ELM system was investigated by Chakraborty and Bart [146] for the separation of toluene from a mixture of toluene and *n*-heptane. Addition of silver ions in the aqueous phase increased toluene extraction, but decreased membrane stability, which was addressed by the addition of ethylene glycol, to act as a membrane stabilizer.

Ribeiro *et al.* [147] studied the selective separation of cobalt from cobalt and nickel containing synthetic leaching liquor. The ELM system was composed of the carrier, Cyanex 302 (bis(2,4,4-trimethylpentyl) monothiophosphinic acid), Escaid 110 (Exxon) as a diluent, and the surfactant produced by Exxon, ECA 4360. A selectivity of 494 was obtained at an optimal external solution pH of 4.1. Tri-alkyl-amine hydrochloride was investigated as a carrier for the recovery of cobalt from a cobalt and nickel waste stream by Fang *et al.* [148]. According to a study by Kulkarni *et al.* [149], methane sulfonic acid is a better stripping agent in an ELM system for nickel extraction with the carrier D2EHPA compared to the traditional stripping solutions of HCl, H_2SO_4, and HNO_3.

The group of Sengupta *et al.* [150–152] has recently reported several works on copper extraction with ELMs. The carrier LIX 984N-C (equi-volume mixture of LIX 860N-IC (5-nonyl salicylaldoxime) and LIX 84I-C (2-hydroxy-5-nonyl-acetophenone-oxime)) achieved superior copper removal at low pH and high copper concentrations compared to predominantly ketoxime extractants such as LIX 84 or LIX 84-I (2-hydroxy-5-nonyl-acetophenone oxime) [150, 151]. The extractant LIX 84-I was effective for copper extraction in ammoniacal-ammonium sulfate solutions at a pH range of 8.1–9.0 [152]. Gameiro *et al.* [153] recently compared LIX 84-I and LIX 54 for copper removal from ammoniacal aqueous solutions. Both extractants demonstrated over 99% removal and over 90% recovery from feed solutions containing 300 mg l^{-1} of copper. In an effort to improve ELM stability, the use of polyethylene glycol as a surfactant that extracts and emulsifies was studied by Uddin and Kathiresan [154]. The extraction of copper, nickel, and cobalt from aqueous solutions was investigated, and the selectivity of the metals was reported as Cu > Co > Ni.

In 2008, an analysis of operating parameters of an ELM process using a hollow fiber contactor for zinc recovery was presented by Fouad and Bart [155]. Mass transfer resistances from the organic boundary layer, the interfacial reaction, and the aqueous boundary layer all affected the extraction of zinc in a hollow fiber contactor. Prasadh *et al.* [156] optimized stable emulsion formation using

computational fluid dynamics. Optimized parameters were then used in the recovery of zinc and copper from synthetic and electroplating effluents with the carrier D2EHPA. Zinc removal and recovery from dilute acidic effluents was studied by Valenzuela *et al.* [157] with an ELM process employing the alkylphosphonic compound, PC-88A, as a carrier. Selective removal and recovery of gallium from zinc plant waste was conducted by Kumbasar and Tutkun [158]. Gallium was extracted with 99% efficiency and concentrated by a factor of 10.

An ELM containing the biodegradable surfactant LK-80 (complex mixture of esters and polyesters of 33 high-molecular-weight alcohols and 36 fatty acids), methyl *iso*-butyl ketone as a carrier, and liquid paraffin as a diluent was applied for gold extraction by Kargari *et al.* [159, 160]. A reaction- and diffusion-controlled mass transfer model was developed, and it accurately described gold extraction from chloride solutions [160]. Othman *et al.* [161] successfully separated silver from liquid photographic waste solutions using the carrier Cyanex 302.

Singh and Argekar [162] showed over 99% recovery of molybdenum from spent catalyst, ferrous scrap, and low-grade molybdenite concentrate solutions. The recovery of molybdenum from dilute solutions was also investigated. The ELM system consisted of tris(2-ethylhexyl) phosphate in toluene as the liquid membrane phase and an internal stripping phase of 1.8 M Na_2CO_3. This process was able to concentrate molybdenum by a factor of 15 from a dilute feed concentration of 66–1000 ppm in the recovered internal phase. Molybdenum recovery from dilute solutions with the carrier Aliquat 336 was presented by Kulkarni and Mahajani [163]. The simultaneous extraction of chromium and molybdenum with the carrier Alamine 336 was investigated by Chakraborty *et al.* [164] with both experimental and modeling results described.

Kageyama *et al.* [165] demonstrated the use of ELMs for analytical applications. The removal of Fe^{3+} from an aqueous solution containing trace amounts of heavy metals was desired, due to iron matrix interference during metal analysis by graphite-furnace atomic absorption spectrometry (GFAAS). The aqueous solution was emulsified with an organic solution containing the surfactant Span-80, toluene, and *n*-heptane. The emulsion was slowly dispersed in an external phase containing HCl, ammonium sulfate, and 8-quinolinol. The iron was transported from the internal phase through the liquid membrane to the external solution where it was complexed with 8-quinolinol. More than 90% of the iron in the internal phase was removed, which was enough to allow for successful trace metal analysis of Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Pb^{2+} by GFAAS. A similar method was applied by Matsumiya *et al.* [166] for the selective removal of copper from solutions for trace heavy metal analysis by GRAAS.

4.04.3 Supported Liquid Membranes

4.04.3.1 General Description

The term SLM is generally used to describe a separation process in which a solid porous support containing a liquid membrane phase is placed between a feed and receiving solution, which are both immiscible in the membrane phase. Immobilized liquid membrane is another term that has been also used to describe the same process.

4.04.3.1.1 Traditional supported liquid membranes

Traditional supported liquid membranes have an organic liquid membrane solution embedded in the pores of a polymeric support. The liquid membrane solution is immiscible with aqueous solutions and contains a carrier dissolved in organic solvent and sometimes a modifier. The modifier may be added to avoid the formation of a third phase or to enhance the selectivity of a target species. The target species in the feed solution can be transported through the liquid membrane by means of carrier-facilitated transport. Transport occurs when the support containing the liquid membrane is placed between two aqueous phases, which act as the feed and the stripping solutions. The two general configurations used for SLMs are the flat sheet SLM (FSSLM) and the hollow fiber SLM (HFSLM). The small amount of organic liquid membrane solution used is at first an advantage of the SLMs; however, gradual loss of the organic solution eventually leads to instability.

4.04.3.1.2 Facilitated transport mechanisms

Transport of species with SLMs typically occurs by type 2 facilitation or carrier-facilitated transport with the following steps [167]:

1. target species diffusion from the bulk phase across the aqueous boundary layer to the membrane interface;

2. formation of carrier-target species complex;
3. diffusion of the complexed carrier across the membrane;
4. the release of the target species at the strip interface and regeneration of the carrier;
5. the diffusion of the released target species from the membrane-strip interface to the bulk strip phase; and
6. the return of the carrier across the membrane. Carrier-facilitated transport can be further classified into coupled cotransport and coupled counter transport [168]. When a neutral or basic carrier is used in the SLM process, cotransport takes place [167]. In cotransport, counter ions along with the target species in the feed solution form a carrier complex in the liquid membrane phase and are both transferred to the strip solution. Counter transport occurs when an acidic carrier loses a proton to the feed solution during the formation of the target species-carrier complex. The carrier is regenerated when the target species is released into the strip solution while simultaneously gaining a proton from the strip solution. Additional steps, specific to the transport mechanism, can also be included for:
7. diffusion of co- or counter-species across the aqueous boundary layer; and
8. carrier complexation with co- or counter-species.

4.04.3.2 Theory: Carrier-Facilitated Transport Models

Numerous studies developing mathematical models for the elucidation of transport mechanisms in SLMs have been conducted. These models have both addressed the FSSLM and HFSLM configurations for a variety of conditions. Detailed comparisons of SLM models have been presented by Noble and Way [169] and de Gyves and Rodriguez de San Miguel [167].

The majority of models developed to describe carrier-facilitated transport through FSSLMs assume ideal steady-state conditions and a linear concentration gradient throughout the membrane [170–182]. Models describing unsteady-state transport in FSSLM using Fick's second law have been developed more recently [183–186]. A simplified model developed by Danesi *et al.* [182] describing metal transport through FSSLMs has been successfully applied to a number of experimental systems [187].

Recently, a dimensionless correlation for mass transfer in an FSSLM was proposed by Mohammadi *et al.* [188]. The correlation, which considers equilibrium, diffusion parameters, and properties of the membrane, had a 19.23% average deviation when compared to 325 experimental data points.

Danesi [189, 190] developed a simplified model for HFSLMs in both single pass and recycle modes of operation. The model assumes that the radial and axial concentration gradients are linear. This leads to a simple, but only approximate, solution for the two limiting cases of low and high metal concentrations in the feed solution. Steady-state continuity mass conservation equations and conditions were considered by Kim and Stroeve [191–193] in developing models describing HFSLMs. Their resulting models account for solute mass transfer in axial and radial directions in the HFSLM. Urtiaga and Irabien [194] compared solutions obtained from film theory and continuity approaches for HFSLMs. The film theory approach resulted in a correlation for mass transfer predictions that was valid when the value of the Peclet number was greater than 40. At Peclet numbers less than 40, continuity mass conservation and related boundary conditions must be used. Jeong *et al.* [195] considered the diffusion resistance of hydrogen ions in a model, which was applied to the selective separation of cobalt from cobalt and nickel sulfate solutions. The kinetics of extraction and stripping for copper transport in a HFSLM were included in a numerical model by Valenzuela *et al.* [196].

The big carrousel mechanism assumes the carrier diffuses into a thin aqueous reaction layer where carrier complexation with the target species takes place [197]. This mechanism was used by Yang and Kocherginsky [197] to model copper removal from ammoniacal wastewater in HFSLMs.

4.04.3.3 Applications

Major applications for SLMs include the removal and recovery of metals, removal and recovery of antibiotics and other biochemicals, and the treatment of nuclear waste. SLMs offer advantages over other separation processes for a wide variety of applications, but have seen little commercial success due to long-term stability issues.

4.04.3.3.1 Removal and recovery of metals

SLMs have been applied for the removal and recovery of metals from metal processing wastewater, dilute aqueous solutions, and other industrial waste streams. A major review of metal ion separations was conducted by de Gyves and Rodriguez de San Miguel [167] in 1999. SLM systems for removal/recovery of

selected metals from 1999 to 2008 are shown in **Table 1** [198–260].

SLMs have also been studied for the recovery of the following metals (not listed in **Table 1**): aluminum [261, 262], gold [171, 263–270], palladium [271–276], platinum [277, 278], molybdenum [279–281], lithium [282–284], arsenic [285–287], silver [288], and rhodium [289].

4.04.3.3.2 Removal and recovery of antibiotics and other biochemicals

Penicillin G (benzylpenicillin) was first transported through an SLM by Marchese *et al.* [290] using a flat sheet polytetrafluoroethylene (PTFE) support. Polypropylene hollow fibers were used as a support for the extraction of penicillin G and penicillin V with subsequent enzymic hydrolysis to 6-aminopenicillanic acid by Tsikas *et al.* [291]. The most common carrier used in penicillin extraction studies has been the secondary amine, Amberlite LA-2. Compared to Adogen 464 (1-methyltrioctylammonium chloride), Amberlite LA-2 (*N*-lauryl-*N*-trialkylmethylamine) demonstrated superior stability in long-term studies [291]. Lee *et al.* [292] used Amberlite LA-2 in 1-decanol as the membrane phase with a PP flat sheet support. This work was extended to show the strong transport competition between penicillin G and phenylacetic acid when both are in the feed solution [293]. The mechanism and rates of transport of penicillin G through an SLM containing Amberlite LA-2 were investigated by Juang *et al.* [294]. The hexafluorophosphates of 1-*n*-butyl-, 1-*n*-hexyl- and 1-*n*-octyl-3-methyl imidazolium, and trioctylmethylammonium chloride (TOMAC) were used as ionic liquids in a polyvinylidene fluoride (PVDF) SLM in a study by Matsumoto *et al.* [295]. The ionic liquids in this study did not improve extraction or stripping compared to conventional solvent extraction with butyl acetate. Cephalosporin C extraction through a PP SLM containing the carrier Aliquat 336 was reported by Ghosh *et al.* [296]. The extraction of macrolide compounds from analytical samples for high-performance liquid chromatography (HPLC) testing has also been investigated [297].

The recovery of citric acid from a fermentation broth with a PP support has been demonstrated by Friesen *et al.* [298]. Citric acid extraction with the carrier Alamine 336 (tri-octyl/decyl amine) was studied with the solvents heptane and xylene, in which heptane led to instability [299]. Juang and Chen [300] compared TOA and TOA salts, and concluded that all the TOA salts studied increased citric acid transport, with the citrate salt having the highest enhancement. An SLM system subjected to a thermal gradient was proposed by Rockman *et al.* [301]. The extraction of citric and maleic acid from kiwi fruit juice has been carried out by Schaefer and Hossain [302]. Extraction from mixed aqueous solutions containing citric and lactic acids has been reported by Sirman *et al.* [303] and Juang *et al.* [304].

The recovery of lactic acid and ethyl lactate with liquid polyorganosiloxanes functionalized with amine, ether, ester, and alkyl organo-functional groups was reported by Yahaya *et al.* [305]. Lactic acid transport was poor, but ethyl lactate transport with ether and amine-functionalized polyorganosiloxane was achieved with a stable operation of 100 h. Lactic acid permeation using a PVDF support loaded with tri-*n*-octylamine was studied by Juang *et al.* [306]. The authors indentified the interfacial reaction and membrane diffusion as the rate-controlling steps in the SLM process. Lactic acid extraction with the carriers trialkyl phosphine oxide [307] and Alamine 336 [308] has also been investigated. Enantiomer separation of D,L-lactic acid mixtures has been investigated [309–311]. Hadik *et al.* [309, 310] demonstrated the enantioseparation with the chiral selector *N*-3,5-dinitrobenzoyl-l-alanine octyl ester, while a modified carbonate form of Aliquat 336 was demonstrated by Yang and Chung [311]. Various organic acids were extracted by Shen *et al.* [312] using tri-*n*-octylphosphine oxide. An SLM process to produce high-purity aconitic acid from cane molasses solutions containing oxalic, maleic, and citric acids was proposed by McMurray and Griffin [313].

Various crown ethers were studied as carriers for the extraction of phenylalanine hydrochloride by Bryjak *et al.* [314]. The extractant D2EHPA has been investigated for phenylalanine separation in a spiral channel SLM by Kertesz *et al.* [315] and a hollow fiber support by Choi *et al.* [316]. The competitive transport of phenylalanine with competing species when Aliquat 336 is used as a carrier has been reported [317–320]. Stability of 150 h with an SLM containing Aliquat 336 was demonstrated by Molinari *et al.* [320] while operating at an elevated temperature of 70 °C, which greatly increased flux.

Enantioseparation of D,L-phenylalanine has been studied with a variety of SLM systems [321–325]. Various carriers derived from phosphoric and phosphonic acids were synthesized for enantioseparation by Drygiel *et al.* [324]. An SLM process containing encapsulated enzymes in the organic solvent was proposed by Miyako *et al.* [325] for the optical resolution of amino acids. In the first step of the process, L-phenylalanine was enantioselectively esterified by

Table 1 Selected SLM systems for removal/recovery of metals from 1999 to 2008[a]

Target metal ions	*Configuration*	*Feed*	*Strip*	*Carrier/diluent*	*Refs*
Bi(III)	FSSLM	2 M H_2SO_4/0.5 M HCl	DI water	Cyanex 921/kerosene	[198]
Bi(III)	FSSLM	0.1 M HCl	2.5 M HNO_3	Cyanex 301/4-chloroacetophenon	[199]
Cd(II)	FSSLM	0.1–5 M HCl	DI water	Cyanex 923/Solvesso 100 (Exxon)	[200]
Cd(II)	FSSLM	0.1 M HCl, 0.4 M NaCl	0.50 M CH_3COONH_4	TOA/xylene	[201]
Cd(II)	FSSLM	0.1 M HCl, 0.4 M NaCl	0.50 M CH_3COONH_4	N235/xylene	[202]
Cd(II)	FSSLM	orthophosphoric acid	4 M HCl	Cyanex 302/kerosene	[83]
Cd(II)	FSSLM	3 M NaCl	0.04 M EDTA, 1 M NaCl	TBP/cyclohexane	[203]
Cd(II)	HFSLM	pH = 5 by acetate buffer	pH = 1.8	D2EHPA/kerosene	[204]
Cd(II)	FSSLM	pH = 3–6, sulfate	0.9 M H_2SO_4	D2EHPA/kerosene	[205]
Cd(II)	FSSLM	2.7 M HCl, 1 M H_3PO_4	DI water	Cyanex 923/xylene	[172]
Cd(II), Pb(II)	FSSLM	pH = 8.5, 0.1 M NaCl	pH = 3, 0.1 M NaCl	Kelex 100/kerosene	[206]
Cd(II), Zn(II)	FSSLM	HCl–CH_3COONa buffer	1.26 M H_2SO_3	D2EHPA/kerosene	[207]
Cd(II), Zn(II)	FSSLM	Cl^-, NO^{3-}, SO_4^{2-}, SCN^-, ClO^{3-}, $CH3COO^-$	1.26 M H_2SO_4	TOPS-99/kerosene	[208]
Cd(II), Zn(II)	FSSLM	pH = 2–5, sulfate	0.5 M H_2SO_4	D2EHPA, PC 88A/kerosene	[209]
Cd(II), Zn(II)	FSSLM	0.1 M HCl	0.01 M HCl	Aliquat 336/kerosene, *n*-decanol	[210]
Cd(II), Pb(II), Zn(II), Ag(I)	FSSLM	pH = 8 by TEA and Tricine	pH = 3 by HNO_3 or HCl	Lasalocid A/NPOE	[211]
Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II)	FSSLM	pH = 3 by HNO_3	2 M HNO_3	TOPO, D2EHPA, DOPPA/kerosene, DOTDDA/dihexylether	[212]
Co(II)	FSSLM	acetate buffer	0.1 M H_2SO_4	Cyanex 272/kerosene	[213]
Co(II)	FSSLM	0.1–1 M HCl	NaOH	TEA/cyclohexanone	[214]
Co(II)	HFSLM	pH = 5	0.1 M HCl	D2EHPA/kerosene	[215]
Co(II), Li(I)	FSSLM	pH = 4.00–6.75, acetate buffer	0.1 M H_2SO_4	Cyanex 272/kerosene	[216]
Co(II), Mn(II)	FSSLM	pH = 2.5–6.5, sulfate	0.5 M H_2SO_4	D2EHPA/Exxsol D100	[217]
Co(II), Ni(II)	HFSLM	pH = 4–6	H_2SO_4	D2EHPA/kerosene	[218]
Co(II), Ni(II)	HFSLM	pH = 6	1.5 M H_2SO_4	D2EHPA/kerosene	[195]
Co(II), Ni(II)	HFSLM	pH = 3–6	1.5 M H_2SO_4	HEH(EHP)/kerosene	[219]
Co(II), Ni(II)	FSSLM	pH = 1–6, sulfate	1 M H_2SO_4	D2EHPA, Cyanex 272, 301, 302/kerosene	[220]
Cu(II)	HFSLM	ammoniacal wastewater	2 M H_2SO_4	LIX 54/kerosene	[221, 222]

(*Continued*)

Table 1 (Continued)

Target metal ions	*Configuration*	*Feed*	*Strip*	*Carrier/diluent*	*Refs*
Cu(II)	FSSLM/ HFSLM	ammoniacal wastewater	2 M H_2SO_4	LIX 54, LIX 84/kerosene	[223]
Cu(II)	FSSLM	Ni^{2+}, Zn^{2+}, Mn^{2+}	pH = 2.2–3	2H5DBA/kerosene	[224, 225]
Cu(II)	FSSLM	pH = 3.5, sulfate	pH = 1.5	D2EHPA/*n*-decane	[226]
Cu(II)	FSSLM	Cu^{+2}, Zn^{+2}, Co^{+2}, Cd^{+2}, Ni^{+2}	2.3 M H_2SO_4	LIX 984/kerosene	[174]
Cu(II)	FSSLM	pH = 1–3	1.8 M H_2SO_4	Acorga M5640/Iberfluid	[227, 228]
Cu(II)	FSSLM	Ca^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}	pH = 1.0, 1% HNO_3	LIX 84/kerosene	[229]
Cu(II)	HFSLM	pH = 2.8–3.2, mine water	2–4 M H_2SO_4	LIX 860/Kermac 500-T	[196, 230]
Cu(II)	FSSLM	0.1–0.5 M $(NH_4)_2CO_3$	1.8 M H_2SO_4	LIX 973N/Iberfluid	[170]
Cu(II)	FSSLM	pH = 1–3	1.8 M H_2SO_4	MOC-55 TD/Iberfluid	[231]
Cu(II)	HFSLM	pH = 1.5–3	1.5 M H_2SO_4	PC 88A, LIX 84/kerosene	[232]
Cu(II), Fe(III)	FSSLM	pH = 2, sulfate	0.5 M H_3PO_4	D2EHPA/1-decanol	[233]
Cu(II), Zn(II)	FSSLM	pH = 1.5–5	0.9 M H_2SO_4	D2EHPA/kerosene	[234]
Cu(II), Zn(II), Co(II), Ni(II)	FSSLM	synthetic leach liquor	0.9 M H_2SO_4	LIX 84, D2EHPA, Cyanex 272/kerosene	[235]
Cu(II), Zn(II)	FSSLM	Cl^-, NO^{3-}, SO_4^{-2}, ClO_3^-, CH_3COO^-		D2EHPA/kerosene	[236]
Cu(II), Cr(VI), Zn(II)	FSSLM/ HFSLM	pH = 2.5	2 M H_2SO_4	LIX 984N/kerosene	[237]
Cu(II), Ag(I)	FSSLM	acidic thiourea medium	DI water	DB18C6/chloroform	[238]
Cu(II), Ag(I)	FSSLM	acidic thiourea medium	pH= 0–2, HNO_3	D2EHPA/chloroform	[239]
Cu(II), Ag(I), Zn(II)	FSSLM	nitrate	DI water	DB18C6, DA18C6/chloroform	[240]
Cu(II), Ag(I), Zn(II)	FSSLM	nitrate	DI water	DB18C6/chloroform	[241]
Cu(II), Ag(I), Zn(II)	FSSLM	nitrate	DI water	macrobicyclic polyethers/chloroform	[242]
Cr(III)	FSSLM/ HFSLM	pH = 5.5, MES buffer	pH = 0, HNO_3	Lasalocid A/NPOE	[243]
Cr(III)	FSSLM	1.5 M Na_2SO_4	1.5 M H_2SO_4	TEA/cyclohexanone	[244]
Cr(VI)	FSSLM	0.5 M HCl	hydrazine sulfate	Cyanex 923/cumene	[245]
Cr(VI)	FSSLM	0.1 M HCl	0.1 M NaOH	TOA/toluene	[246]
Cr(VI)	FSSLM	pH = 1–5	0.5 M NaOH	TBP	[247]
Cr(VI)	FSSLM	0.5 M HCl	0.5 M NaCl	Cyanex 923/xylene	[173]
Cr(VI)	FSSLM	pH = 3.5–5.6, Cr^{3+}	2 M NaCl	Aliquat 336/NPOE, THF	[248]
Cr(VI)	FSSLM	pH = 3	0.1–2.0 M NaOH	Aliquat 336/toluene	[249]
Fe(III)	FSSLM	0.2 M HCl	6 M HCl	Acylisoxazolones/xylene	[250]
Fe(III), Cu(II), Ni(II)	FSSLM	pH = 2, 1 M NaCl	0.01 and 2 M HCl	Alamine 336, LIX 84/kerosene	[251]
Hg(II)	FSSLM	1 M HCl	0.11 M NaSCN	Cyanex 471X/kerosene	[252]

Hg(II), Ag(I)	FSSLM	0.001 M picric acid	0.04 M $Na_2S_2O_3$, 0.025 M EDTA	PhenS2O, TT12C4/NPOE	[253]
Hg(II), As(III)	HFSLM	HCl	NaOH	TOA/toluene	[254]
Ni(II)	FSSLM/ HFSLM	nickel bath rinse solutions	1.5 M H_2SO_4	LIX 860, Cyanex 302/kerosene	[255]
Ni(II)	FSSLM	pH = 2–5	0.25–1.0 M H_2SO_4	Acorga M5640/Exxsol D100	[256]
Zn(II)	FSSLM	Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, Fe^{3+}, Cr^{3+}	0.014 M L-Cysteine	DC18C6/NPOE	[257]
Zn(II)	FSSLM	pH = 2.5, Fe^{3+}, Ca^{2+}, Mn^{2+}	3.5 M HCl	D2EHPA/kerosene	[175]
Zn(II)	FSSLM	pH = 0.5–3.0, Fe^{3+}, Ca^{2+}, Mn^{2+}	0.5–3.5 M HCl	D2EHPA/kerosene	[258]
Zn(II)	FSSLM	sulfate, Co^{2+}	0.5 M H_2SO_4	D2EHPA/Exxsol D100	[259]
Zn(II)	FSSLM	1 M HCl	1 M NaCl	Cyanex 923/Solvesso 100 (Exxon)	[260]

[a] 2H5DBA = 2-hydroxy-5-dodecylbenzaldehyde. Acorga M5640 = 2-hydroxy-5-nonylbenzaldehyde oxime. Alamine 336 = tri(octyl/decyl) amine. Aliquat 336 = tricaprylmethylammonium chloride. Cyanex 272 = bis(2,4,4-trimethylpentyl)phosphinic acid. Cyanex 301 = di-*iso*-octyldithiophosphinic acid. Cyanex 302 = bis(2,4,4-trimethylpentyl)thiophosphinic acid. Cyanex 471X = tri-*iso*-butylphosphine sulfide. Cyanex 921 = tri-*n*-octylphosphine oxide. Cyanex 923 = phosphine oxides mixture. D2EHPA = di(2-ethylhexyl) phosphoric acid. DA18C6 = diaza-18-crown-6. DB18C6 = dibenzo-18-crown-6. DC18C6 = dicyclohexano-18-crown-6. DOPPA = di[*p*-(1,1,3,3-tetramethylbutyl)phenyl] phosphoric acid. DOTDDA = 1,12-(4,9-dioxatrisdecanyl) diphosphonic acid. HEH (EHP) = (2-ethylhexyl)phosphonic acid mono-2-ethylhexyl ester. LIX 54 = 1-phenyldecanone-1,3-diones. LIX 84 = 2-hydroxy-5-nonylacetophenone. LIX 860 = 5-dodoecylsalicylaldoxime. LIX 973N = mixture of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime. LIX 984N = mixture of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonyl-acetophenone oxime. MOC-55 TD = 5-dodecylsalicylaldoxime. N235 = tricapryl amine. NPOE = *o*-nitrophenyl octyl ether. PC-88A = 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester. PhenS2O = mixed aza-thioether crown containing a 1,10-phenanthroline sub-unit. TBP = tri-*n*-butyl phosphate. TEA = triethanolamine. THF = tetrahydrofuran. TOA = tri-*n*-octylamine. TOPO = trioctylphosphine oxide. TT12C4 = tetrathia-12-crown-4.

a protease complex resulting in L-phenylalanine ethyl ester, which then diffused through the membrane phase. In the receiving phase, an α-chymotrypsin-complex-catalyzed ester hydrolysis to reproduce the initial L-phenylalanine. SLMs have also been studied for the separation of tryptophan [319, 324, 326–329], L-valine [330], dipeptides [329, 331], and other amino acids [322, 324].

4.04.3.3.3 Nuclear waste processing

SLMs have been investigated for the removal of the radioactive materials, uranium, plutonium, americium, strontium, cesium, cerium, and europium, from nuclear waste streams. As detailed reviews on radioactive actinides (U, Pu, and Am) are available [332, 333], this work focuses on recent developments. The selective extraction of uranium(VI) from acidic waste containing Am and Pu by flat-sheet and hollow-fiber SLMs was investigated by Sawant *et al.* [334]. The carrier employed was Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) and the most effective stripping agent was found to be 0.9 M oxalic acid. Alamine 336 was applied as an extractant for uranium transport from HCl solutions by Lakshmi *et al.* [335]. The extraction of the anionic complexes $UO_2C1_3^-$ and $UO_2C1_4^{2-}$ were unexpectedly higher in aromatic diluents (toluene) compared to polar diluents (chloroform) likely due to the hydrogen-bonding possibilities of the latter. With a feed solution concentration of 6 M HCl, Alamine 336 had the lowest amount of acid transported to the strip solution compared to other amine carriers studied for uranium extraction. Uranyl ion transport from HCl medium with Aliquat 336 was reported by Mohapatra *et al.* [336]. The selective separation of uranium from other fission products was achieved, and a transport mechanism was proposed.

The separation of [233]U from irradiated thorium with the carrier di(2-ethylhexyl) *iso*-butyramide (D2EHIBA) was investigated by Shailesh *et al.* [337]. A linear increase in uranium transport was reported with increasing D2EHIBA concentration up to 1.5 M, suggesting no aggregation between the ligand molecules. This study also exhibited selective uranium transport from a feed solution containing a high Th concentration and the presence of other metal ions, such as Cs(I), Sr(II), Fe(III), and Eu(III). PTFE was used as a support in FSSLMs containing 1 M D2EHIBA in *n*-dodecane and was found to be stable for 9 days. Tributyl phosphate diluted in kerosene was used in a HFSLM by Ramakul *et al.* [338] for the separation of uranium from thorium in nitric acid solutions. Extraction and stripping was reported to be highly dependent on the concentration of nitric acid in the feed.

Singh *et al.* [339] studied the separation of uranium from a phosphoric acid medium employing the carrier TOPO, the solvent *n*-dodecane, and ammonium carbonate in the receiving phase. Very low uranium transport was reported when using a pure phosphoric acid medium, possibly due to a strong uranium-phosphoric acid complex not extractable by the carrier. The addition of 2 M nitric acid to the feed solution dramatically increased uranium transport. Uranium recovery of over 90% was achieved using a feed solution of low phosphoric acid (0.001 M) and high nitric acid (2.0 M) concentrations. Selective uranium recovery from thorium with a HFSLM was reported by Ura *et al.* [340]. Using the extractant tributyl phosphate, the rate-controlling step of uranium transport was found to be the diffusion of the uranium–carrier complex through the liquid membrane.

Selective plutonium separation from nitrate solutions with a PP FSSLM containing the carrier tri-*iso*-amyl phosphate (TAP) was reported by Shukla *et al.* [341]. From a feed solution containing 1 mg l^{-1} Pu and 4 M HNO_3, over 90% Pu extraction, was achieved. The FSSLM system used a liquid membrane solution composed of 0.8 M TAP in dodecane and a stripping phase of either 0.5 M sodium carbonate or 0.5 M ascorbic acid.

The carrier 2-ethylhexyl 2-ethylhexylphosphonic acid (KSM-17, equivalent to PC-88A), dissolved in dodecane, and supported on PP flat sheets, was demonstrated by Kedari *et al.* [342] for the recovery of plutonium from waste solutions. Plutonium recovery of over 90% was reported when applying various acidic feed conditions. High selectivity for plutonium was demonstrated when several metal ions were present in the feed solution.

Sawant *et al.* [343] studied both FSSLM and HFSLM configurations for the recovery of plutonium from nitrate solutions with the carrier Cyanex-923. A HFSLM, with PP hollow fibers containing the carrier TBP in dodecane, was studied by Rathore *et al.* [344] for the selective recovery of plutonium from acidic waste containing various fission products. With the optimal stripping solution of 0.1 M $NH_2OH{\cdot}HCl$ in 0.3 M HNO_3, plutonium recovery was ~70%. Rathore *et al.* [345] extended this work for the removal and recovery of plutonium and uranium from nuclear process waste.

The removal of neptunium, plutonium, and americium with polyphosphine polyoxides has been demonstrated by Cristau *et al.* [346]. Ramanujam *et al.* [347] reported an SLM process for actinide removal using the carrier octylphenyl-*N,N′*-di-*iso*-butylcarbamoylmethyl phosphine oxide (CMPO) and a stripping solution consisting of a mixture of citric acid, formic acid, and hydrazine hydrate. The process was suggested for the removal of neptunium, americium, and plutonium from a uranium lean waste solution, as uranium was found to limit the transport of americium.

Over 90% recovery of americium was achieved by Mohapatra *et al.* [348] with a FSSLM process, which used a mixture of TOPO and 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) as the carrier. Sriram *et al.* [349] studied the transport of americium with an SLM impregnated with dimethyldibutyltetradecyl-1,3-malonamide (DMDBTDMA) in *n*-dodecane. The selective transport of americium over iron, which was also present in nuclear waste, was demonstrated, but stability of the SLM was quite poor. Sriram and Manchanda [350] investigated various solvents for the extraction of americium with the carrier DMDBTDMA, and reported that dodecane was the ideal solvent based on its performance and its physical properties. The carrier, *N,N,N′,N′*-tetraoctyl-3-oxapentane diamide (TODGA), was studied by Ansari *et al.* [351] for the transport of americium through FSSLMs. During a 20-day continuous test, recovery of americium was consistently 95% or greater, suggesting good stability. Recently, Ansari *et al.* [352] expanded this work and used TODGA for the recovery of actinides and fission products from nitric acid solution and simulated high level waste.

Asfari *et al.* [353] studied various 1,3-calix[4]-crown-bis-crowns as carriers in an SLM for the removal of cesium from nuclear wastewater. Carriers containing six oxygen atoms in the glycol chain were much more selective for cesium over sodium, compared to the other carriers in the study. Decontamination factors greater than 100 were achieved while maintaining a stability of over 50 days. The carriers 1,3-dipropyloxycalix[4]arene crown ether and 1,3-dipropyloxycalix[4]arene dibenzo crown ether were studied for cesium removal by Kim *et al.* [354]. Mohapatra *et al.* [355] investigated cesium removal with SLMs containing the carrier di-*tert*-butyl benzo 18 crown 6 (DTBB18C6) in nitrobenzene and toluene. Cesium was selectively recovered with an efficiency of 80% from a complex mixture of fission products. The optimal conditions were found to be 0.1 M DTBB18C6, in a solvent mixture of 40% toluene and 60% nitrobenzene, 2 M HNO_3 concentration in the feed, and a receiving phase of distilled water. A FSSLM process for cesium transport using the carrier calix[4]-bis-2,3-naphtho-crown-6 (CNC) was reported by Raut *et al.* [356]. With a CNC concentration of 5×10^{-4} M in a solvent mixture of 80% 2-nitrophenyl octyl ether and 20% *n*-dodecane, ~90% transport of cesium was reported.

The removal of strontium from nuclear waste streams with SLMs has been studied extensively over the past 20 years [357–366]. Mohapatra *et al.* [367] recently studied the crown ether di-*tert*-butyl cyclohexano 18 crown 6 (DTBCH18C6) as a carrier in various solvents for the recovery of strontium from nitrate media. The solvent mixture of benzene and octanol in a 1:1 ratio had the highest transport rates, which was attributed to the low viscosity of the benzene. Strontium transport with an SLM containing 4,4'(5')di-*tert*-butyl-cyclohexano-18-crown-6 (DtBuCH18C6) was reported by Rawat *et al.* [368]. Transport of strontium was slow when using a feed solution containing only nitric acid, due to cotransport of the acid, but was increased when the feed solution also contained aluminum nitrate.

Cerium was successfully separated from synthetic low-level radioactive wastewater by Teramoto *et al.* [369]. Cerium recovery of 99.8% was obtained using a FSSLM containing the carrier CMPO, and the modifier TBP dissolved in dodecane. Optimal cerium transport occurred with the addition of sodium citrate to the strip solution combined with low nitric acid concentration and high sodium nitrate concentration in the feed solution. In studies of cerium recovery using a plate-and-frame SLM module with the carrier CMPO, stabilities of only 5 h were observed [370]. To solve this issue of instability, Teramoto *et al.* [362] followed Ho *et al.*'s [371, 372] approach by adding small amounts of organic membrane solution to the strip solution. This method resulted in long-term stability, and is suggested by an acceptable solution to the SLM instability problem when dealing with nuclear wastes. Fu *et al.* [373] compared a commercial PP hollow fiber module and high-density polyethylene hollow fiber membranes that were prepared via thermally induced phase separation for use in HFSLMs for cerium recovery. The prepared hollow fibers had a higher porosity compared to the commercial hollow fibers, which led to higher cerium flux. In another work by Fu *et al.* [374], a model for cerium transport in FSSLMs was proposed.

4.04.3.3.4 Other applications

SLMs have been used for analytical chemistry applications to obtain sample enrichment prior to instrumental analytical testing. Reviews on membrane-based extraction processes, including SLMs, for analytical applications were conducted by Jonsson and Mathiasson [375] and Jakubowska *et al.* [376]. HFSLM systems for trace-metal analysis of solutions containing Cu, Pb, and Cd were demonstrated by Parthasarathy *et al.* [377]. SLMs have been used for a variety of other analytical applications, such as urine testing [378, 379], antibiotic testing in milk and animal food products [297], determination of phenol in blood plasma [380], and testing of herbicides from water samples [381, 382].

The removal of dyes from textile waste streams with SLM processes has been recently demonstrated. Muthuraman and Palanivelu [383] first reported the use of SLMs for the removal of textile dyes using type 1 facilitated mass transport. FSSLMs containing palm, sunflower and coconut oils were effective in removal of the cationic dye, Astacryl Golden Yellow, from aqueous solutions. The extraction of anionic dyes from aqueous solutions with the carrier, tributyl phosphate, was also demonstrated by Muthuraman and Palanivelu [384]. Operating parameters were studied, and optimal conditions were used for dye removal from actual textile effluent. Hajarabeevi *et al.* [385] achieved 94% recovery of the anionic dye, Acid Red 10B, using a FSSLM containing tributyl phosphate.

4.04.3.4 Stability Issue

Even though SLMs have been extensively studied for a variety of applications, their industrial use has been limited due to the lack of long-term stability. The mechanisms for instability will be briefly discussed as well as approaches taken to improve SLM stability. Instability occurs when the liquid membrane phase (carrier and solvent) is displaced from the pores of the polymer support. Kemperman *et al.* [386] discussed that the possible mechanisms for SLM instability are:

- pressure difference across the membrane;
- solubility of the liquid membrane phase in aqueous feed and strip solutions;
- osmotic pressure difference across the membrane;
- emulsification of the liquid membrane phase from lateral shear forces;
- wetting of pores in polymer support by aqueous phases; and
- blocking of membrane pores by water blockage or carrier precipitation.

If a large enough pressure difference across the membrane exists, the liquid membrane phase can be pushed out of the pores of the support. The critical pressure at which this can happen was defined by Zha *et al.* [387] and can be described by the Laplace equation. By keeping the transmembrane pressure below the critical pressure, this instability mechanism can be avoided and hence is not a major cause for instability in most cases. The pore blocking and pore wetting mechanisms are not considered significant in describing SLM instability [386]. Loss of the liquid membrane phase by solubility becomes unlikely when a carrier and organic solvent are used that have low solubility in water [388]. The two major mechanisms of SLM instability that can be considered are emulsification of the liquid membrane phase and the osmotic pressure difference over the membrane [16, 386, 388].

Several methods for improving SLMs stability have been proposed, and include the following:

- Use of room temperature ionic liquids (RTILs) in SLMs [389, 390]. RTILs have many unique properties including low solubility in water and high interfacial tension, which make their use for stable SLMs promising.
- Re-impregnation of the liquid membrane phase in the support [320, 370, 391–395].
- Use of composite supports that have a barrier or stabilization layer. This barrier layer has been formed by applying hydrophilic coatings on hydrophobic supports [396–398], interfacial polymerization [399–401], phase-inversion [402], and plasma polymerization [403].

4.04.4 Supported Liquid Membranes with Strip Dispersion

4.04.4.1 General Description

SLMs with strip dispersion were first reported by Ho *et al.* [9, 404, 405] and attempted to overcome problems of ELMs and SLMs. The key feature of SLMs with strip dispersion is the constant supply of organic membrane solution, which ensures long-term stability.

4.04.4.1.1 Supported liquid membrane with strip dispersion

The SLM with strip dispersion system developed by Ho is shown in **Figure 3**; an enlarged view is shown in **Figure 4** [405]. As shown in these figures, an aqueous strip solution is dispersed in an organic membrane solution by a mixer, and passed on to one side of a membrane support. When a microporous hydrophobic support is used, the organic phase of the dispersion becomes imbedded in the pores of the support, typically hollow-fiber modules, forming a stable SLM. The organic phase extends from the pores to the strip side. Stability is maintained by having a constant supply of organic membrane solution to the pores. An aqueous feed solution is passed on the other side of the membrane support and the target species is extracted into the organic solution by a selective carrier. The target species is then stripped by the aqueous strip solution. For final recovery of the target species, the mixer is turned off or a settler is used for the loaded strip dispersion (not shown) and the dispersion quickly separates.

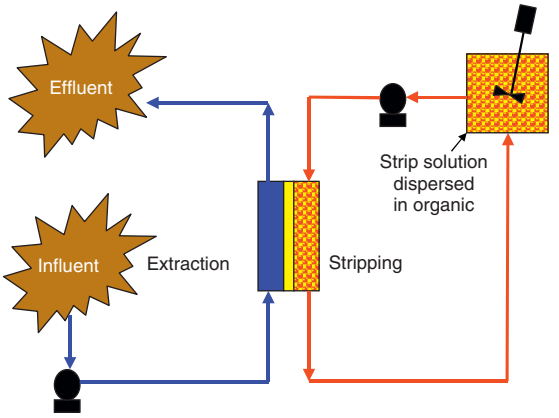


Figure 3 Diagram of the supported liquid membrane with strip dispersion process. From Ho, W. S. W., Wang, B. B. *Ind. Eng. Chem*. Res. **2002**, *41*, 381–388.

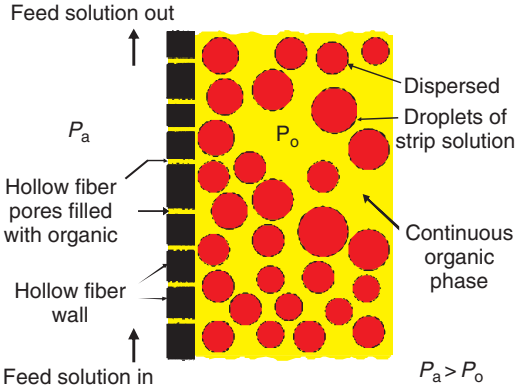


Figure 4 Enlarged view of the supported liquid membrane with strip dispersion. From Ho, W. S. W., Wang, B. B. *Ind. Eng. Chem*. Res. **2002**, *41*, 381–388.

4.04.4.1.2 Facilitated transport mechanisms

Mass transfer in SLMs with strip dispersion occurs with carrier (type 2) facilitated transport, as described in Sections 4.04.3.1.3 and 4.04.4.1.2.

4.04.4.2 Theory

4.04.4.2.1 Carrier-facilitated transport models

Flux through an SLM may be expressed as [405]:

$$j = K_o\left[c_f - \left(\frac{m_s}{m_f}\right)c_s\right] \tag{3}$$

When m_f is much greater than m_s, as when strong acids are used in the aqueous strip solution, the flux can be described by Equation (4):

$$j = K_o c_f \tag{4}$$

The overall mass transfer resistance is described by Equation (5) and consists of the feed-side resistance, the interfacial resistance due to the complexation/extraction reaction, the membrane phase resistance, the interfacial resistance due to the decomplexation/stripping reaction, and the strip side resistance [405]:

$$\frac{1}{K_o} = \frac{1}{K_a} + \frac{1}{m_f K_e} + \frac{1}{m_f K_m} + \frac{1}{m_f K_s} + \frac{1}{(m_f/m_s)K_{as}} \tag{5}$$

4.04.4.2.2 Proton transfer and its influence on feed-side pH

The removal of metals using acidic extractants results in the transfer of protons from the stripping solution to the aqueous feed solution. As discussed in Section 4.04.4.1.2, this can be classified as counter-facilitated transport. Ho *et al.* [406] reported the influence of this proton transfer on the feed solution pH, as a function of distance in a hollow fiber module. When feed pH values are above 3, low module utilization efficiencies occurred due to significant reduction in the feed pH.

4.04.4.3 Applications

Applications for SLMs with strip dispersion are similar to those found for traditional SLMs. Heavy metal removal and recovery has been the focus of current literature. Promising applications in biochemical processing have been demonstrated.

4.04.4.3.1 Chromium removal and recovery

Ho *et al.* [404, 407] demonstrated the removal and recovery of Cr(VI), in the form of chromic acid, using commercial-size hollow-fiber modules. In a two-step process, Cr(VI) was removed from 100 to 0.05 ppm in the acidic feed solution, and concentrated to 200 000 ppm in the aqueous strip solution. The organic membrane solution contained Amberlite LA-2, 1-dodeconol, and PLURONIC L31 in Isopar L. Stripping was achieved with NaOH. Sulfuric acid was found to compete with chromic acid for complexation with the amine carrier at Cr(VI) concentrations less than 100 ppm.

A mathematical model for the removal and recovery of Cr(VI) was optimized by Ortiz *et al.* [408]. The proposed configuration involved a two-step process similar to that described by Ho [404] and consisted of an organic membrane solution that was formed by Alamine 336, 1-dodeconol, and PLURONIC L31 in Isopar L. Optimal operating conditions were reported, and simulations were compared with experimental results.

4.04.4.3.2 Copper removal and recovery

Laboratory and pilot plant studies on the removal and recovery of copper were reported by Ho *et al.* [406, 409]. In pilot plant studies with a 4-in-diameter hollow fiber module using feed solutions from the Berkeley Pit (Bute, Montana, USA), copper in the feed was reduced from 150 ppm to > 0.1 ppm using the carrier LIX 973N. The aqueous strip solution was concentrated to 3700 ppm with no significant contamination from other metals present in the feed. Results from the pilot plant study are shown in **Figure 5** [16].

The recovery of copper catalyst from the wet peroxide oxidation process was reported by Ortiz *et al.* [410, 411]. LIX 622N in kerosene was used as the membrane solution, and was stripped with sulfuric acid. The final aqueous strip solution, containing copper sulfate, was found to be nonecotoxic and suitable for recycling to the oxidation reactor [411]. One hollow fiber module using SLMs with strip dispersion was compared to nondispersive solvent extraction using two modules, one for extraction and the other for stripping.

4.04.4.3.3 Zinc removal and recovery

Ho *et al.* [406, 409] presented laboratory and scale-up results on the removal and recovery of zinc with the carrier Cyanex 301. The feed solution was from the Berkeley Pit (Bute, Montana, USA) and was previously treated for copper removal. After a 4-h run

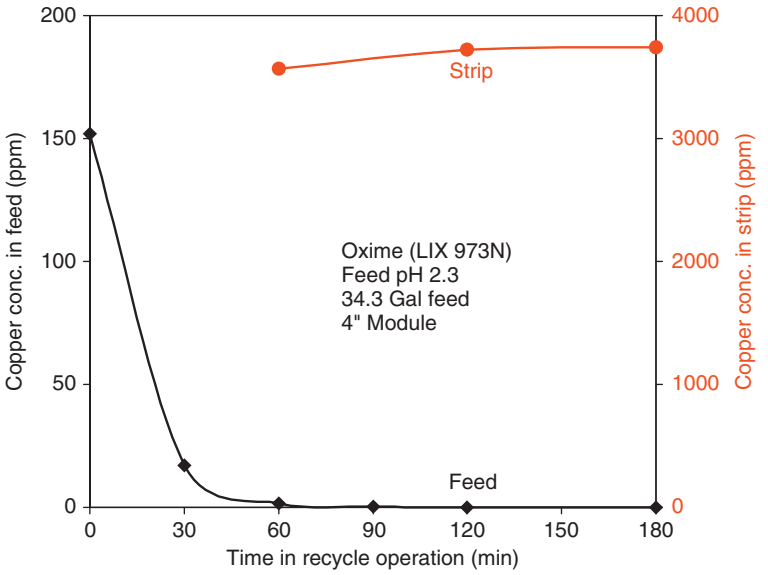


Figure 5 Copper concentrations in feed and strip solutions in the pilot plant study with the SLM with strip dispersion. From Ho, W. S. W. *Ann. N. Y. Acad. Sci.* **2003**, *984*, 97–122.

time in recycle mode, 121 l of feed solution was reduced from 526 to 0.65 ppm, while achieving a strip solution concentration of 20 000 ppm, which is suitable for reuse.

The selective removal and recovery of zinc, from copper containing feed solutions was studied by He *et al.* [412] using a flat-sheet PP support. An optimum pH of 2–2.5 was reported for the separation of zinc from copper, using the carrier D2EHPA in kerosene.

4.04.4.3.4 Cobalt removal and recovery

A system for the removal and recovery of cobalt was reported by Ho [9, 16, 413]. An organic solution containing Cyanex 301, 1-dodecanol, and Isopar L was employed to efficiently recover cobalt at high concentrations. A low feed pH of ~2 was used to avoid proton transfer over the length of the hollow fiber module, as discussed in Section 4.04.5.2.2.

4.04.4.3.5 Strontium removal

New extractants were synthesized for the removal of radioactive strontium, Sr-90 [405]. The extractants were branched alkyl phenylphosphonic acids and were more efficient in strontium removal than the conventional extractant D2EHPA.

4.04.4.3.6 Antibiotic removal and recovery

Ho recovered penicillin G with an efficiency of 93% using the secondary amine, Amberlite LA-2 in Isopar L [16, 414]. With a feed solution concentration of 8840 ppm penicillin G, this antibiotic was concentrated to 41 000 ppm in the aqueous strip solution containing sodium carbonate.

4.04.4.3.7 Other applications

Gold and cadium removal and recovery are other applications which have been reported. The removal and recovery of gold from alkaline cyanide solutions using SLM with strip dispersion has been studied by Sonawane *et al.* [415, 416] using the organic extractant LIX 79 (*N*,*N*-bis(2-ethylhexyl)guanidine) in *n*-heptane. Selectivity of metal cyanide salts was reported as followed [415]: $Au(CN)_2^- > Zn(CN_4^{2-}) > Ag(CN)_2^- > Ni(CN)_4^{2-} > Fe(CN)_6^{2-} > Cu(CN)_4^{3-}$.

The advantages of SLMs with strip dispersion over traditional SLMs are exhibited in the removal and recovery of cadium [417, 418]. In the selective removal of cadium from zinc, the loss of membrane solution was reported to be 0.6–1.4% for SLM with strip dispersion and 12–14% for SLM [417]. The low loss of membrane solution suggests long stability. Increased recovery, higher selectivity, and increased flux were also reported. Similar advantages were reported for the simultaneous removal of cadium and cyanide from simulated electroplating rinse water [418]. An organic solution containing the carriers trialkyl-phosphine oxide (TRPO) and D2EHPA in kerosene removed CN^- and Cd(II) from initial concentrations of 30 and 20 ppm to 0.05 and 0.02 ppm, respectively.

4.04.5 Concluding Remarks/Future Developments

Liquid membrane separation processes can be applied to a variety of processes with outstanding efficiency. The industrial use of liquid membranes has so far been limited, but is expected to grow in the near future. Supported liquid membranes with strip dispersion are characterized with simplicity in operation and stability for a long lifetime. Their potential commercial applications include the removal and recovery of heavy metals and rare earth metals from waste streams and process streams, the recovery of antibiotics and biochemicals from aqueous solutions and fermentation broths, and the use in processing nuclear wastes. In addition, preconcentration for analytical applications is expected to continue and grow.

Acknowledgment

Financial support from the Integrative Graduate Education and Research Traineeship (IGERT) program of the National Science Foundation at the Ohio State University is acknowledged.

References

[1] Li, N. N. Separating Hydrocarbons with Liquid Membranes. US Pat. 3,410,794, 12 November 1968.
[2] Li, N. N. *J. Membr. Sci.* **1978**, *3*, 265–269.
[3] Cahn, R. P., Frankenfeld, J. W., Li, N. N., Naden, D., Subramanian, K. L. Extraction of Metal Ions by Liquid Membrane. In *Recent Developments in Separation Science*; Li, N. N., Ed.; CRC Press: Boca Raton, FL, 1981; Vol. VI, p 51.
[4] Frankenfeld, J. W., Asher, W. J., Li, N. N. Biochemical and Biomedical Separations Using Liquid Membranes. In *Recent Developments in Separation Science*; Li, N. N., Ed.; CRC Press: Boca Raton, FL, 1978; Vol. 4, pp 39–50.
[5] Cussler, E. L. *AIChE J.* **1971**, *7*, 1300–1303.
[6] Baker, R. W., Tuttle, M. E., Kelly, D. J., Lonsdale, H. K. *J. Membr. Sci.* **1977**, *2*, 213–233.

[7] Lee, K.-H., Evans, D. F., Cussler, E. L. *AIChE J.* **1978**, *24*, 860–868.
[8] Babcock, W. C., Baker, R. W., Brooke, J. W., Kelly, D. J., LaChapelle, E. D. *NTIS Report, PB81-179947*, 1980; 40pp.
[9] Ho, W. S. W. Combined Supported Liquid Membrane/ Stripping Dispersion Process for Removal and Recovery of Radionuclides and Metals. US Pat. 6,328,782, 11 December 2001.
[10] Funk, E. W., Li, N. N. Novel Dynamic Membranes – Formation and Process Application. In *Separation Technology*; Li, N. N., Strathmann, H., Eds.; American Institute of Chemical Engineering: New York, 1988; p 155.
[11] Ho, W. S. W., Li, N. N. In *Membrane Handbook*; Ho, W. S. W., Sirkar, K. K., Eds.; Chapman and Hall: New York, NY, 1992; pp 597–610.
[12] Correia, P. F. M. M., de Carvalho, J. M. R. *J. Membr. Sci.* **2000**, *179*, 175–183.
[13] Hsu, E. C., Li, N. N. *Sep. Sci. Technol.* **1985**, *20*, 115–130.
[14] Frankenfeld, J. W., Cahn, R. P., Li, N. N. *Sep. Sci. Technol.* **1981**, *16*, 385–402.
[15] Fuller, E. J., Li, N. N. *J. Membr. Sci.* **1984**, *18*, 251–271.
[16] Ho, W. S. W. *Ann. N. Y. Acad. Sci.* **2003**, *984*, 97–122.
[17] Ho, W. S. W., Li, N. N. In *Membrane Handbook*; Ho, W. S. W., Sirkar, K. K., Eds.; Chapman and Hall: New York, NY, 1992; pp 611–655.
[18] Ho, W. S. W., Hatton, T. A., Lightfoot, E. N., Li, N. N. *AIChE J.* **1982**, *28*, 662–670.
[19] Ho, W. S. W., Li, N. N. *ACS Symp. Ser.* **1996**, *642*, 208–221.
[20] Stroeve, P., Varanasi, P. P. *AIChE J.* **1984**, *30*, 1007–1009.
[21] Fales, J. L., Stroeve, P. *J. Membr. Sci.* **1984**, *21*, 35–53.
[22] Kim, K.-S., Choi, S.-J., Ihm, S.-K. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 167–172.
[23] Yan, N., Shi, Y., Su, Y. F. *Chem. Eng. Sci.* **1992**, *47*, 4365–4371.
[24] Teramoto, M., Takihana, H., Shibutani, M., Yuasa, T., Hara, N. *Sep .Sci. Technol.* **1983**, *18*, 397–419.
[25] Bunge, A. L., Noble, R. D. *J. Membr. Sci.* **1984**, *21*, 55–71.
[26] Chan, C. C., Lee, C. J. *Chem. Eng. Sci.* **1987**, *42*, 83–95.
[27] Borwankar, R. P., Chan, C. C., Wasan, D. T., Kurzeja, R. M., Gu, Z. M., Li, N. N. *AIChE J.* **1988**, *34*, 753–762.
[28] Bhowal, A., Datta, S. *J. Membr. Sci.* **1997**, *135*, 245–250.
[29] Bandyopadhyaya, R., Bhowal, A., Datta, S., Sanyal, S. *Chem. Eng. Sci.* **1998**, *53*, 2799–2807.
[30] Teramoto, M., Sakai, T., Yanagawa, K., Ohsuga, M., Miyake, Y. *Sep. Sci. Technol.* **1983**, *18*, 735–764.
[31] Kataoka, T., Nishiki, T., Kimura, S., Tomioka, Y. *J. Membr. Sci.* **1989**, *46*, 67–80.
[32] Kataoka, T., Nishiki, T., Kimura, S., Tomioka, Y. *Water Treat.* **1990**, *5*, 136–149.
[33] Lorbach, D., Bart, H.-J., Marr, R. *Ger. Chem. Eng.* **1986**, *9*, 321–327.
[34] Lorbach, D., Marr, R. *Chem. Eng. Process.* **1987**, *21*, 83–93.
[35] Ortner, A., Auzinger, D., Wacker, H. J., Bart, H. J. *Process Technol. Proc.* **1991**, *10*, 399–404.
[36] Yan, N. *Chem. Eng. Sci.* **1993**, *48*, 3835–3843.
[37] Reis, M. T. A., Carvalho, J. M. R. *J. Membr. Sci.* **2004**, *237*, 97–107.
[38] Biscaia Junior, E. C., Mansur, M. B., Salum, A., Castro, R. M. Z. *Braz. J. Chem. Eng.* **2001**, *18*, 163–174.
[39] Marr, R. J., Draxler, J. In *Membrane Handbook*; Ho, W. S. W., Sirkar, K. K., Eds.; Chapman and Hall: New York, NY, 1992; pp 701–717.
[40] Draxler, J., Marr, R. *Chem. Eng. Process.* **1986**, *20*, 319–329.
[41] Ruppert, M., Draxler, J., Marr, R. *Sep. Sci. Technol.* **1988**, *23*, 1659–1666.
[42] Wang, S., He, P., Hao, D., Zhu, Y. *Tsinghua Sci. Technol.* **2002**, *7*, 91–94.
[43] Li, N. N., Shrier, A. L. Liquid Membrane Water Treating. In *Recent Developments in Separation Science*; Li, N. N., Ed.; CRC Press: Boca Raton, FL, 1972; Vol. 1, p 163.
[44] Cahn, R. P., Li, N. N. *Sep. Sci.* **1974**, *9*, 505–519.
[45] Matulevicius, E. S., Li, N. N. *Sep. Purif. Methods* **1975**, *4*, 73–96.
[46] Halwachs, W., Flaschel, E., Schugerl, K. *J. Membr. Sci.* **1980**, *6*, 33–44.
[47] Terry, R. E., Li, N. N., Ho, W. S. W. *J. Membr. Sci.* **1982**, *10*, 305–323.
[48] Teramoto, M., Takihana, M., Shibutani, M., Yuasa, T., Hara, N. *Sep. Sci. Technol.* **1983**, *18*, 397–419.
[49] Boyadzhiev, L., Bezenshek, E., Lazarova, Z. *J. Membr. Sci.* **1984**, *21*, 137–144.
[50] Ho, W. S. W., Li, N. N. Modeling of Liquid Membrane Extraction Processes. In *Hydrometallurgical Process Fundamentals*; Bautista, R. G., Ed.; 1984; pp 555–597.
[51] Miao, F.-D., Li, X.-P., Zhang, Y.-Q. *Desalination* **1985**, *56*, 355–366.
[52] Gu, Z. M., Ho, W. S. W., Li, N. N. Emulsion Liquid Membrane: Design Considerations. In *Membrane Handbook*; Ho, W. S. W., Sirkar, K. K., Eds.; Chapman and Hall: New York, NY, 1992; pp 656–700.
[53] Zhang, X.-J., Liu, J.-H., Fan, Q.-J., Lian, Q.-T., Zhang, X.-T., Lu, T.-S. Industrial Application of Liquid Membrane Separation for Phenolic Wastewater Treatment. In *Separation Technology*; Li, N. N., Strathmann, H., Eds.; American Institute of Chemical Engineering: New York, 1988; pp 190–203.
[54] Zhang, X.-J., Liu, J.-H., Lu, T.-S. *Water Treat.* **1987**, *2*, 127–135.
[55] Nanoti, A., Ganguly, S. K., Goswami, A. N., Rawat, B. S. *Ind. Eng. Chem. Res.* **1997**, *36*, 4369–4373.
[56] Park, H.-J., Chung, T.-S. *Korean J. Chem. Eng.* **2003**, *20*, 731–735.
[57] Correia, P. F. M. M., de Carvalho, J. M. R. *J. Membr. Sci.* **2003**, *225*, 41–49.
[58] Park, Y., Skelland, A. H. P., Forney, L. J., Kim, J.-H. *Water Research* **2006**, *40*, 1763–1772.
[59] Correia, P. F. M. M., de Carvalho, J. M. R. *Chem. Eng. Sci.* **2001**, *56*, 5317–5325.
[60] Luan, J., Plaisier, A. *J. Membr. Sci.* **2004**, *229*, 235–239.
[61] Wan, Y. H., Wang, X. D., Zhang, X. J. *J. Membr. Sci.* **1997**, *135*, 263–270.
[62] Reis, M. T. A., de Freitas, O. M. F., Ismael, M. R. C., Carvalho, J. M. R. *J. Membr. Sci.* **2007**, *305*, 313–324.
[63] Reis, M. T. A., de Freitas, O. M. F., Ferreira, L. M., Carvalho, J. M. R. *J. Membr. Sci.* **2006**, *269*, 161–170.
[64] Reis, M. T. A., de Freitas, O. M. F., Ferreira, L. M., Carvalho, J. M. R. *Sep. Sci. Technol.* **2006**, *41*, 841–860.
[65] Jin, M., Zhang, Y. In *Proceedings of the International Congress on Membranes and Membrane Processes*, Chicago, IL, 20–24 August 1990; Vol. I, pp 676–678.
[66] Cahn, R. P., Li, N. N. In *Separation and Purification Technology*; Li, N. N., Calo, J. M., Eds.; Marcel Dekker: New York, 1992; pp 195–212.
[67] Draxler, J., Marr, R. *Chem. Eng. Process.* **1986**, *20*, 319–329.
[68] Juang, R.-S., Jiang, J.-D. *J. Membr. Sci.* **1995**, *100*, 163–170.
[69] Hoffmann, A., Verhaege, M., De Ketelaere, R. F. In *Solvent Extraction for the 21st Century*, *Proceedings of ISEC '99, Barcelona, Spain*, 11–16 July 1999; Cox, M., Hidalgo, M., Valiente, M., Eds.; Society of Chemical Industry: London, UK, 2001.

[70] Wright, J. B., Nilsen, D. N., Hundley, G., Galvan, G. J. *Miner. Eng.* **1995**, *8*, 549–556.
[71] Chakravarti, A. K., Chowdhury, S. B., Mukherjee, D. C. *Colloids Surf. A* **2000**, *166*, 7–25.
[72] Valenzuela, F., Fonseca, C., Basualto, C., Correa, O., Tapia, C., Sapag, J. *Miner. Eng.* **2005**, *18*, 33–40.
[73] Hu, S. B., Wiencek, J. M. *AIChE J.* **1998**, *44*, 570–581.
[74] Valenzuela, F., Cabrera, J., Basualto, C., *et al. Sep. Sci. Technol.* **2007**, *42*, 363–377.
[75] Guerel, L., Altas, L., Bueyuekguengoer, H. *Environ. Eng. Sci.* **2005**, *22*, 411–420.
[76] Bourenane, S., Samar, M. E.-H., Abbaci, A. *Acta Chim. Slovenica* **2003**, *50*, 663–675.
[77] Sabry, R., Hafez, A., Khedr, M., El-Hassanin, A. *Desalination* **2007**, *212*, 165–175.
[78] Li, H., He, X., Liang, Y. *Sep. Sci. Technol.* **2003**, *38*, 1633–1648.
[79] Chakraborty, M., Murthy, Z., Bhattacharya, C., Datta, S. *Sep. Sci. Technol.* **2005**, *40*, 2353–2364.
[80] Banerjea, S., Datta, S., Sanyal, S. K. *Sep. Sci. Technol.* **2000**, *35*, 483–501.
[81] Bhowal, A., Datta, S. *J. Membr. Sci.* **2001**, *188*, 1–8.
[82] Breembroek, G. R. M., Witkamp, G. J., Van Rosmalen, G. M. *Sep. Sci. Technol.* **2000**, *35*, 1539–1571.
[83] Urtiaga, A. M., Alonso, A., Ortiz, I., *et al. J. Membr. Sci.* **2000**, *164*, 229–240.
[84] Basualto, C., Poblete, M., Marchese, J., *et al. J. Braz. Chem. Soc.* **2006**, *7*, 1347–1354.
[85] Kedari, C., Pandit, S., Chowta, S., Jambunathan, U. *Sep. Sci. Technol.* **2005**, *40*, 2509–2526.
[86] El-Said, N., El-Sheref, E., Borai, E. *J. Membr. Sci.* **2003**, *211*, 183–191.
[87] Kulkarni, P. S., Mukhopadhyay, S., Bellary, M. P., Ghosh, S. K. *Hydrometallurgy* **2002**, *64*, 49–58.
[88] Kulkarni, P. S. *Chem. Eng. J.* **2003**, *92*, 209–214.
[89] El-Reefy, S. A., Selim, Y. T., Aly, H. F. *Anal. Sci.* **1997**, *13*, 333–337.
[90] El-Reefy, S. A., Selim, Y. T., Aly, H. F. *J. Radioanal. Nucl. Chem.* **1998**, *228*, 21–25.
[91] El Sayed, M. S. *Hydrometallurgy* **2003**, *68*, 51–56.
[92] Yang, L., Zhang, Z., Guo, Y., Gao, X., Takeuchi, H. *Sep. Purif. Technol.* **2005**, *47*, 88–94.
[93] El-Hazek, N. T., El Sayed, M. S. *J. Radioanal. Nucl. Chem.* **2003**, *257*, 347–352.
[94] Kumaresan, T., Begum, M. S. K. M., Sivashanmugam, P., Anantharaman, N., Sundaram, S. *Chem. Eng. J.* **2003**, *95*, 199–204.
[95] Li, N. N., Shrier, A. L. Liquid Membrane Water Treating. In *Recent Developments in Separation Science*; Li, N. N. Ed.; CRC Press: Boca Raton, FL, 1972; Vol. 1, p 163.
[96] Schiffer, D. K., Choy, E. M., Evans, D. F., Cussler, E. L. *AIChE Symp. Ser.* **1974**, *70*, 150–156.
[97] Maugh, T. H. *Science* **1976**, *193*, 134–150.
[98] Cahn, R. P., Li, N. N., Minday, R. M. *Environ. Sci. Technol.* **1978**, *12*, 1051–1056.
[99] Halwachs, W., Schugerl, K. *Int. Eng. Chem.* **1978**, *20*, 519–528.
[100] Schlosser, S., Kossaczky, E. *J. Membr. Sci.* **1980**, *6*, 83–105.
[101] Downs, H. H., Li, N. N. *J. Sep. Process Technol.* **1981**, *2*, 19–24.
[102] Marr, R. J., Kopp, A. *Int. Chem. Eng.* **1982**, *22*, 44–60.
[103] Frankenfeld, J. W., Li, N. N. In *Handbook of Separation Process Technology*; Rousseau, R. W., Ed.; Wiley: New York, 1987; p 840.
[104] Lee, C. J., Chan, C. C. *Ind. Eng. Chem. Res.* **1990**, *29*, 96–100.
[105] Marr, R. J., Koncar, M. *Chem. Ing. Technol.* **1990**, *62*, 175–182.
[106] Li, K. *Huanjing Kexue Xuebao* **2000**, *20*, 117–121.
[107] Devulapalli, R., Jones, F. *J. Hazard. Mater.* **1999**, *B70*, 157–170.
[108] Thien, M. P., Hatton, T. A., Wang, D. I. C. *Biotechnol. Bioeng.* **1988**, *32*, 604–615.
[109] Itoh, H., Thien, M. P., Hatton, T. A., Wang, D. I. C. *Biotechnol. Bioeng.* **1990**, *35*, 853–860.
[110] Hong, S. A., Choi, H. J., Nam, S. W. *J. Membr. Sci.* **1992**, *70*, 225–235.
[111] Hong, S. A., Yang, J. W. *J. Membr. Sci.* **1994**, *86*, 181–192.
[112] Juang, R.-S., Wang, Y.-Y. *J. Membr. Sci.* **2002**, *207*, 241–252.
[113] Pickering, P. J., Chaudhuri, J. B. *J. Membr. Sci.* **1997**, *127*, 115–130.
[114] O'Brien, D. J., Senske, G. E. *Sep. Sci. Technol.* **1989**, *24*, 617–628.
[115] Chaudhuri, J. B., Pyle, D. L. *Chem. Eng. Sci.* **1992**, *47*, 49–56.
[116] Scholler, C., Chaudhuri, J. B., Pyle, D. L. *Biotechnol. Bioeng.* **1993**, *42*, 50–58.
[117] Reisinger, H., Marr, R. *Bioforum* **1992**, *15*, 234–237.
[118] Reisinger, H., Marr, R. *J. Membr. Sci.* **1993**, *80*, 85–97.
[119] Hano, T., Matsumoto, M., Ohtake, T., Sasaki, K., Hori, F., Kawano, Y. *Process Metall.* **1992**, *7B*, 1887–1892.
[120] Yuanli, J., Fuan, W., Hyun, K. D., Sook, L. M. *J. Membr. Sci.* **2001**, *191*, 215–223.
[121] Boey, S. C., Garcia del Cerro, M. C., Pyle, D. L. *Chem. Eng. Res. Des.* **1987**, *65*, 218–223.
[122] Stoica-Guzun, A., Juncu, G., Floarea, O. *Chem. Eng. Technol.* **1999**, *22*, 65–69.
[123] Yordanov, B., Boyadzhiev, L. *J. Membr. Sci.* **2004**, *238*, 191–197.
[124] Manzak, A., Tutkun, O. *Sep. Sci. Technol.* **2004**, *39*, 2497–2512.
[125] Scheper, T., Likidis, Z., Makryaleas, K., Nowottny, C., Schuegerl, K. *Enzyme Microbio. Technol.* **1987**, *9*, 625–631.
[126] Hano, T., Ohtake, T., Matsumoto, M., Ogawa, S., Hori, F. *J. Chem. Eng. Jpn.* **1990**, *23*, 772–775.
[127] Lee, S. C., Lee, W. K. *J. Chem. Technol. Biotechnol.* **1992**, *55*, 252–261.
[128] Lee, K. H., Lee, S. C., Lee, W. K. *J. Chem. Technol. Biotechnol.* **1994**, *59*, 365–370.
[129] Lee, K. H., Lee, S. C., Lee, W. K. *J. Chem. Technol. Biotechnol.* **1994**, *59*, 371–376.
[130] Mok, Y. S., Lee, S. C., Lee, W. K. *Sep. Sci. Technol.* **1995**, *30*, 399–417.
[131] Lee, S. C. *J. Membr. Sci.* **2004**, *237*, 225–232.
[132] Sahoo, G. C., Dutta, N. N. *J. Membr. Sci.* **1998**, *145*, 15–26.
[133] Sahoo, G. C., Dutta, N. N., Dass, N. N. *J. Membr. Sci.* **1999**, *157*, 251–261.
[134] Schügerl, K. *Adv. Biochem. Eng. Biotechnol.* **2005**, *92*, 1–48.
[135] Schlosser, S., Kertesz, R., Martak, J. *Sep. Sci. Technol.* **2005**, *41*, 237–266.
[136] Dutta, N. N., Sahoo, G. C. *Adv. Biochem. Eng. Biotechnol.* **2002**, *75*, 209–242.
[137] Dutta, N. N., Ghosh, A. C., Mathur, R. K. *Adv. Biochem. Eng. Biotechnol.* **1997**, *56*, 111–145.
[138] Exxo n. *Chem. Eng. News,* **1985**, *December 9*, 28–29 (*The Lamp*, **1985**, *67*, 17).
[139] Okochi, H., Nakano, M. *Adv. Drug Deliv. Rev.* **2000**, *45*, 5–26.
[140] van der Graaf, S., Schroen, C. G. P. H., Boom, R. M. *J. Membr. Sci.* **2005**, *251*, 7–15.
[141] McClements, D. J., Decker, E. A., Weiss, J. *J. Food Sci.* **2007**, *72*, R109–R124.

[142] Khan, A. Y., Talegaonkar, S., Iqbal, Z., Ahmed, F. J., Khar, R. K. *Curr. Drug Deliv.* **2006**, *3*, 429–443.
[143] Nakashima, T., Shimizu, M., Kukizaki, M. *Adv. Drug Deliv. Rev.* **2000**, *45*, 47–56.
[144] Hino, T., Kawashima, Y., Shimabayashi, S. *Adv. Drug Deliv. Rev.* **2000**, *45*, 27–45.
[145] Sinha, V. R., Kumar, A. *Indian J. Pharm. Sci.* **2002**, *64*, 191–199.
[146] Chakraborty, M., Bart, H.-J. *Chem. Eng. Technol.* **2005**, *28*, 1518–1524.
[147] Ribeiro, C. P., Costa, A. O. S., Lopes, I. P. B., Campos, F. F., Ferreira, A. A., Salum, A. *J. Membr. Sci.* **2004**, *241*, 45–54.
[148] Fang, J., Li, M., Xu, Z. *Sep. Sci. Technol.* **2003**, *38*, 3553–3574.
[149] Kulkarni, P. S., Tiwari, K. K., Mahajani, V. V. *Sep. Sci. Technol.* **2001**, *36*, 639–656.
[150] Sengupta, B., Sengupta, R., Subrahmanyam, N. *Hydrometallurgy* **2006**, *81*, 67–73.
[151] Sengupta, B., Sengupta, R., Subrahmanyam, N. *Hydrometallurgy* **2006**, *84*, 43–53.
[152] Sengupta, B., Bhakhar, M. S., Sengupta, R. *Hydrometallurgy* **2007**, *89*, 311–318.
[153] Gameiro, M. L. F., Bento, P., Ismael, M. R. C., Reis, M. T. A., Carvalho, J. M. R. *J. Membr. Sci.* **2007**, *293*, 151–160.
[154] Uddin, M. S., Kathiresan, M. *Sep. Sci. Technol.* **2000**, *19*, 3–9.
[155] Fouad, E. A., Bart, H.-J. *J. Membr. Sci.* **2008**, *307*, 156–168.
[156] Prasadh, K. G., Venkatesan, S., Sheriffa, K. M. M., Anantharaman, B. N. *Chem. Eng. Technol.* **2007**, *30*, 1212–1220.
[157] Valenzuela, F., Auspont, J., Basualto, C., Tapia, C., Sapag, J. *Chem. Eng. Res. Des.* **2005**, *83*, 247–255.
[158] Kumbasar, R. A., Tutkun, O. *Hydrometallurgy* **2004**, *75*, 111–121.
[159] Kargari, A., Kaghazchi, T., Sohrabi, M., Soleimani, M. *J. Membr. Sci.* **2004**, *233*, 1–10.
[160] Kargari, A., Kaghazchi, T., Soleimani, M. *J. Membr. Sci.* **2006**, *279*, 380–388.
[161] Othman, N., Mat, H., Goto, M. *J. Membr. Sci.* **2006**, *282*, 171–177.
[162] Singh, S. P., Argekar, A. P. *Sep. Sci. Technol.* **2003**, *38*, 3747–3760.
[163] Kulkarni, P. S., Mahajani, V. V. *J. Membr. Sci.* **2002**, *201*, 123–135.
[164] Chakraborty, S., Datta, S., Bhattacharya, P., Banerjea, S. *Sep. Sci. Technol.* **2006**, *41*, 771–790.
[165] Kageyama, T., Matsumiya, H., Hiraide, M. *Anal. Bioanal. Chem.* **2004**, *379*, 1083–1087.
[166] Matsumiya, H., Yatsuya, Y., Hiraide, M. *Anal. Bioanal. Chem.* **2006**, *385*, 944–947.
[167] de Gyves, J., Rodriguez de San Miguel, E. *Ind. Eng. Chem. Res.* **1999**, *38*, 2182–2202.
[168] Misra, B. M., Gill, J. S. *ACS Symp. Ser.* **1996**, *642*, 361–375.
[169] Noble, R. D., Way, J. D. *ACS Symp. Ser.* **1987**, *347*, 1–26.
[170] Alguacil, F. J. *Hydrometallurgy* **2001**, *61*, 177–183.
[171] Alguacil, F. J. *Hydrometallurgy* **2002**, *66*, 117–123.
[172] Alguacil, F. J., Navarro, P. *Hydrometallurgy* **2001**, *61*, 137–142.
[173] Alguacil, F. J., Coedo, A. G., Dorado, M. T. *Hydrometallurgy* **2000**, *57*, 51–56.
[174] Ata, O. N. *Hydrometallurgy* **2005**, *77*, 269–277.
[175] Ata, O. N., Colak, S. *Hydrometallurgy* **2005**, *80*, 155–162.
[176] Juang, R.-S. *Ind. Eng. Chem. Res.* **1993**, *32*, 911–916.
[177] Juang, R.-S., Chang, H. L. *Sep. Sci. Technol.* **1996**, *31*, 365–379.
[178] Juang, R.-S., Chen, J.-D., Huan, H.-C. *J. Membr. Sci.* **2000**, *165*, 59–73.
[179] Marchese, J., Campderros, M. E., Acosta, A. *J. Chem. Technol. Biotechnol.* **1993**, *57*, 37–42.
[180] Huang, T. C., Juang, R.-S. *J. Chem. Technol. Biotechnol.* **1988**, *42*, 3–17.
[181] Sastre, A., Madi, A., Cortina, J. L., Miralles, N. *J. Membr. Sci.* **1998**, *139*, 57–65.
[182] Danesi, P. R., Horwitz, E. P., Vandegrift, G. F., Chiarizia, R. *Sep. Sci. Technol.* **1981**, *16*, 201–211.
[183] Hernandez-Cruz, L., Lapidus, G. T., Carrillo–Romo, F. *Hydrometallurgy* **1998**, *48*, 265–276.
[184] Zhang, B., Gozzelino, G., Dai, Y. *J. Membr. Sci.* **2002**, *210*, 103–111.
[185] Benzal, G., Kumar, A., Delshams, A., Sastre, A. M. *Hydrometallurgy* **2004**, *748*, 117–130.
[186] Ata, O. N. *Hydrometallurgy* **2007**, *87*, 148–156.
[187] Alguacil, F. J., Alonso, M., Sastre, A. M., Kumar, A. *Recent Res. Devel. Chem. Eng.* **2003**, *5*, 83–98.
[188] Mohammadi, S., Kaghazchi, T., Kargari, A. *Desalination* **2008**, *219*, 324–334.
[189] Danesi, P. R. *Solv. Extr. Ion Exch.* **1984**, *2*, 115–120.
[190] Danesi, P. R. *J. Membr. Sci.* **1984**, *20*, 231–238.
[191] Kim, J. I., Stroeve, P. *Chem. Eng. Sci.* **1988**, *43*, 247–257.
[192] Kim, J. I., Stroeve, P. *Chem. Eng. Sci.* **1989**, *44*, 1101–1111.
[193] Kim, J. I., Stroeve, P. *J. Membr. Sci.* **1990**, *49*, 37–53.
[194] Urtiaga, A. M., Irabien, J. A. *AIChE J.* **1993**, *39*, 521–525.
[195] Jeong, J., Lee, J.-C., Kim, W. *Sep. Sci. Technol.* **2003**, *38*, 499–517.
[196] Valenzuela, F., Vega, M. A., Yanez, M. F., Basualto, C. *J. Membr. Sci.* **2002**, *204*, 385–400.
[197] Yang, Q., Kocherginsky, N. M. *J. Membr. Sci.* **2007**, *297*, 121–129.
[198] Reyes-Aguilera, J. A., Gonzalez, M. P., Navarro, R., Saucedo, T. I., Avila-Rodriguez, M. *J. Membr. Sci.* **2008**, *310*, 13–19.
[199] Madaeni, S. S., Zand, H. R. K. *Chem. Eng. Technol.* **2005**, *28*, 892–898.
[200] Alonso, M., Lopez-Delgado, A., Sastre, A. M., Alguacil, F. J. *Chem. Eng. J.* **2006**, *118*, 213–219.
[201] He, D., Ma, M. *Hydrometallurgy* **2000**, *56*, 157–170.
[202] He, D., Ma, M. *Sep. Sci. Technol.* **2000**, *35*, 1573–1585.
[203] Nowier, H. G., El-Said, N., Aly, H. F. *J. Membr. Sci.* **2000**, *177*, 41–47.
[204] Marchese, J., Campderros, M. *Desalination* **2004**, *164*, 141–149.
[205] Tripathy, S. S., Sarangi, K., Das, R. P. *Sep. Sci. Technol.* **2002**, *37*, 2897–2911.
[206] Aguilar, J. C., Sanchez-Castellanos, M., Rodriguez de San Miguel, E., de Gyves, J. *J. Membr. Sci.* **2001**, *190*, 107–118.
[207] Swain, B., Sarangi, K., Prasad Das, R. *Sep. Sci. Technol.* **2004**, *39*, 2171–2188.
[208] Swain, B., Sarangi, K., Prasad Das, R. *J. Membr. Sci.* **2006**, *277*, 240–248.
[209] Juang, R.-S., Kao, H.-C., Wu, W.-H. *J. Chem. Technol. Biotechnol.* **2004**, *79*, 140–147.
[210] Juang, R.-S., Kao, H.-C., Wu, W.-H. *J. Membr. Sci.* **2004**, *228*, 169–177.
[211] Canet, L., Ilpide, M., Seta, P. *Sep. Sci. Technol.* **2002**, *37*, 1851–1860.
[212] Belkhouche, N.-E., Didi, M. A., Romero, R., Joensson, J. A. Villemin, D. *J. Membr. Sci.* **2006**, *284*, 398–405.
[213] Swain, B., Jeong, J., Lee, J.-C., Lee, G.-H. *J. Membr. Sci.* **2007**, *288*, 139–148.
[214] Bukhari, N., Chaudry, M., Ashraf Mazhar, M. *J. Membr. Sci.* **2004**, *234*, 157–165.

[215] Prakorn, R., Eakkapit, S., Weerawat, P., Milan, H., Ura, P. *Korean J. Chem. Eng.* **2006**, *23*, 117–123.
[216] Swain, B., Jeong, J., Lee, J.-C., Lee, G.-H. *J. Membr. Sci.* **2007**, *297*, 253–261.
[217] Alguacil, F. J. *Hydrometallurgy* **2002**, *65*, 9–14.
[218] Lee, J.-C., Jeong, J., Chung, K.-S., Kobayashi, M. *Sep. Sci. Technol.* **2004**, *39*, 1519–1533.
[219] Choi, J.-W., Cho, K. S., Oh, B.-K., Youn, I. J., Jeong, J., Park, S., Lee, W. H. *J. Ind. Eng. Chem.* **2001**, *7*, 230–240.
[220] Gega, J., Walkowiak, W., Gajda, B. *Sep. Purif. Technol.* **2001**, *22*, 551–557.
[221] Kocherginsky, N. M., Yang, Q. *Sep. Purif. Technol.* **2007**, *54*, 104–116.
[222] Yang, Q., Kocherginsky, N. M. *J. Membr. Sci.* **2006**, *286*, 301–309.
[223] Yang, Q., Jiang, J., Chung, T.-S., Kocherginsky, N. M. *AIChE J.* **2006**, *52*, 3266–3277.
[224] Molinari, R., Poerio, T., Argurio, P. *J. Membr. Sci.* **2006**, *280*, 470–477.
[225] Molinari, R., Poerio, T., Cassano, R., Picci, N., Argurio, P. *Ind. Eng. Chem. Res.* **2004**, *43*, 623–628.
[226] Molinari, R., Argurio, P., Pirillo, F. *J. Membr. Sci.* **2005**, *256*, 158–168.
[227] Alguacil, F. J., Alonso, M., Sastre, A. M. *Chem. Eng. J.* **2002**, *85*, 265–272.
[228] Alguacil, F. J., Alonso, M. *Environ. Sci. Technol.* **2005**, *39*, 2389–2393.
[229] Cooper, C. A., Lin, Y. S., Gonzalez, M. *J. Membr. Sci.* **2004**, *229*, 11–25.
[230] Valenzuela, F., Basualto, C., Tapia, C., Sapag, J. *J. Membr. Sci.* **1999**, *155*, 163–168.
[231] Alguacil, F. J., Alonso, M., Sastre, A. M. *J. Membr. Sci.* **2001**, *184*, 117–122.
[232] Lee, J.-C., Jeong, J., Park, J. T., Youn, I. J., Chung, H.-S. *Sep. Sci. Technol.* **1999**, *34*, 1689–1701.
[233] Zhang, B., Gozzelino, G. *Colloid Surf. A* **2003**, *215*, 67–76.
[234] Sarangi, K., Das, R. P. *Hydrometallurgy* **2004**, *71*, 335–342.
[235] Parhi, P. K., Sarangi, K. *Sep. Purif. Technol.* **2008**, *59*, 169–174.
[236] Swain, B., Sarangi, K., Das, R. P. *J. Membr. Sci.* **2004**, *243*, 189–194.
[237] Yang, X. J., Fane, A. G., MacNaughton, S. *Water Sci. Technol.* **2001**, *43*, 341–348.
[238] Gherrou, A., Kerdjoudj, H., Molinari, R., Drioli, E. *Desalination* **2001**, *139*, 317–325.
[239] Gherrou, A., Kerdjoudj, H., Molinari, R., Drioli, E. *Sep. Purif. Technol.* **2002**, *28*, 235–244.
[240] Gherrou, A., Kerdjoudj, H., Molinari, R., Drioli, E. *Sep. Sci. Technol.* **2001**, *36*, 2293–2308.
[241] Gherrou, A., Kerdjoudj, H., Molinari, R., Drioli, E. *Sep. Sci. Technol.* **2002**, *37*, 2317–2336.
[242] Arous, O., Gherrou, A., Kerdjoudj, H. *Desalination* **2004**, *161*, 295–303.
[243] Tayeb, R., Zaghbani, A., Tingry, S., Seta, P., Dhahbi, M. *Desalination* **2007**, *204*, 234–240.
[244] Chaudry, M. A., Bukhari, N., Mazhar, M., Abbasi, W. *Sep. Purif. Technol.* **2007**, *55*, 292–299.
[245] Alguacil, F. J., Alonso, M. *Environ. Sci. Technol.* **2003**, *37*, 1043–1047.
[246] Kozlowski, C. A., Walkowiak, W. *J. Membr. Sci.* **2005**, *266*, 143–150.
[247] Venkateswaran, P., Palanivelu, K. *Hydrometallurgy* **2005**, *78*, 107–115.
[248] Choi, D. W., Kim, Y. H. *Korean J. Chem. Eng.* **2005**, *22*, 894–898.
[249] Park, S.-W., Jung, H.-I., Kim, T.-Y., Lee, J.-W. *Sep. Sci. Technol.* **2004**, *39*, 781–797.
[250] Buonomenna, M. G., Molinari, R., Drioli, E. *Desalination* **2002**, *148*, 257–262.
[251] Gill, J. S., Singh, H., Gupta, C. K. *Hydrometallurgy* **2000**, *55*, 113–116.
[252] Bhandare, A. A., Argekar, A. P. *J. Chem. Technol. Biotechnol.* **2002**, *77*, 811–816.
[253] Shamsipur, M., Hashemi, O. R., Lippolis, V. *J. Membr. Sci.* **2006**, *282*, 322–327.
[254] Sangtumrong, S., Ramakul, P., Satayaprasert, C., Pancharoen, U., Lothongkum, A. W. *J. Ind. Eng. Chem.* **2007**, *13*, 751–756.
[255] Van de Voorde, I., Pinoy, L., De Ketelaere, R. F. *J. Membr. Sci.* **2004**, *234*, 11–21.
[256] Alguacil, F. J., Alonso, M., Lopez-Delgado, A. *J. Braz. Chem. Soc.* **2006**, *17*, 839–843.
[257] Shamsipur, M., Azimi, G., Madaeni, S. S. *J. Membr. Sci.* **2000**, *165*, 217–223.
[258] Ata, O. N., Bese, A. V., Colak, S., Donmez, B., Cakici, A. *Chem. Eng. Process.* **2004**, *43*, 895–903.
[259] Alguacil, F. J., Alonso, M. *Sep. Purif. Technol.* **2005**, *41*, 179–184.
[260] Alguacil, F. J., Martinez, S. *J. Chem. Technol. Biotechnol.* **2001**, *76*, 298–302.
[261] Berends, A. M., Witkamp, G. J., Van Rosmalen, G. M. *Sep. Sci. Technol.* **1999**, *34*, 1521–1543.
[262] Berends, A. M., Witkamp, G. J. *Solvent Extr. Ion Exch.* **2001**, *19*, 473–490.
[263] Alguacil, F. J., Alonso, M., Sastre, A. M. *J. Membr. Sci.* **2005**, *252*, 237–244.
[264] Alguacil, F. J. *Solvent Extr. Ion Exch.* **2003**, *21*, 841–852.
[265] Alguacil, F. J., Martin, M. I. *Sep. Sci. Technol.* **2003**, *38*, 2055–2069.
[266] Alguacil, F. J., Alonso, M. *Hydrometallurgy* **2004**, *74*, 157–163.
[267] Kumar, A., Sastre, A. M. *Ind. Eng. Chem. Res.* **2000**, *39*, 146–154.
[268] Sastre, A. M., Madi, A., Alguacil, F. J. *J. Membr. Sci.* **2000**, *166*, 213–219.
[269] Sastre, A. M., Madi, A., Alguacil, F. J. *Hydrometallurgy* **2000**, *54*, 171–184.
[270] Gherrou, A., Kerdjoudj, H. *Desalination* **2002**, *144*, 231–236.
[271] Uheida, A., Zhang, Y., Muhammed, M. *J. Membr. Sci.* **2004**, *241*, 289–295.
[272] Weerawat, P., Nattaphol, V., Ura, P. *Korean J. Chem. Eng.* **2003**, *20*, 1092–1096.
[273] Zaghbani, A., Tayeb, R., Dhahbi, M., *et al. Sep. Purif. Technol.* **2007**, *57*, 374–379.
[274] Fontas, C., Antico, E., Vocanson, F., Lamartine, R., Seta, P. *Desalination* **2006**, *200*, 112–113.
[275] Fontas, C., Salvado, V., Hidalgo, M. *J. Membr. Sci.* **2003**, *223*, 39–48.
[276] Fontas, C., Compano, L., Polo, A., Salvado, V., Hidalgo, M. *Solvent Extr. Ion Exch.* **2001**, *19*, 329–344.
[277] Bhandare, A. A., Argekar, A. P. *J. Membr. Sci.* **2002**, *201*, 233–237.
[278] Fontas, C., Tayeb, R., Tingry, S., Hidalgo, M., Seta, P. *J. Membr. Sci.* **2005**, *263*, 96–102.
[279] Basualto, C., Marchese, J., Valenzuela, F., Acosta, A. *Talanta* **2003**, *59*, 999–1007.
[280] Marchese, J., Valenzuela, F., Basualto, C., Acosta, A. *Hydrometallurgy* **2004**, *72*, 309–317.
[281] Yassine, T. *J. Radioanal. Nucl. Chem.* **2000**, *246*, 665–669.
[282] Bansal, B., Chen, X. D., Hossain, M. M. *Chem. Eng. Process.* **2005**, *44*, 1327–1336.
[283] Ma, P., Chen, X. D., Hossain, M. M. *Sep. Sci. Technol.* **2000**, *35*, 2513–2533.

[284] Bhatnagar, M., Sharma, U. *J. Sci. Islamic Republic Iran* **2003**, *14*, 333–336.
[285] Prapasawat, T., Ramakul, P., Satayaprasert, C., Pancharoen, U., Lothongkum, A. W. *Korean J. Chem. Eng.* **2008**, *25*, 158–163.
[286] Perez, M. E. M., Reyes-Aguilera, J. A., Saucedo, T. I., Gonzalez, M. P., Navarro, R., Avila–Rodriguez, M. *J. Membr. Sci.* **2007**, *302*, 119–126.
[287] Tsai, C.-Y., Chen, Y.-F., Chen, W.-C., Yang, F.-R., Chen, J.-H., Lin, J.-C. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2005**, *A40*, 477–491.
[288] Shamsipur, M., Kazemi, S. Y., Azimi, G., *et al. J. Membr. Sci.* **2003**, *215*, 87–93.
[289] Fontas, C., Palet, C., Salvado, V., Hidalgo, M. *J. Membr. Sci.* **2000**, *178*, 131–139.
[290] Marchese, J., Lopez, J. L., Quinn, J. A. *J. Chem. Technol. Biotechnol.* **1989**, *46*, 149–159.
[291] Tsikas, D., Kaltsidou-Schottelius, E., Brunner, G. *Chemie Ingenieur Technik* **1992**, *64*, 545–548.
[292] Lee, C. J., Yeh, H. J., Yang, W. J., Kang, C. R. *Biotechnol. Bioeng.* **1993**, *42*, 527–534.
[293] Lee, C. J., Yeh, H. J., Yang, W. J., Kang, C. R. *Biotechnol. Bioeng.* **1994**, *43*, 309–313.
[294] Juang, R.-S., Lee, S., Shiau R. *J. Membr. Sci.* **1998**, *146*, 95–104.
[295] Matsumoto, M., Ohtani, T., Kondo, K. *J. Membr. Sci.* **2007**, *289*, 92–96.
[296] Ghosh, A. C., Borthakur, S., Roy, M. K., Dutta, N. N. *Sep. Technol.* **1995**, *5*, 121–126.
[297] Makudali, M. T. A., Nindi, M. M. *Microchim. Acta* **2004**, *148*, 199–214.
[298] Friesen, D. T., Babcock, W. C., Brose, D. J., Chambers, A. R. *J. Membr. Sci.* **1991**, *56*, 127–141.
[299] Sirman, T., Pyle, D. L., Grandison, A. S. In *Separations for Biotechnology*; Pyle, D. L., Ed.; Elsevier: London, 1990; pp 245–254.
[300] Juang, R.-S., Chen, L.-J. *J. Membr. Sci.* **1997**, *123*, 81–87.
[301] Rockman, J. T., Kehat, E., Lavie, R. *AIChE J.* **1997**, *43*, 2376–2380.
[302] Schaefer, A., Hossain, M. M. *Bioprocess Eng.* **1996**, *16*, 25–33.
[303] Sirman, T., Pyle, L., Grandison, A. S. *Biochem. Soc. Trans.* **1991**, *19*, 274–279.
[304] Juang, R.-S., Lee, S.-H., Huang, R.-H. *Sep. Sci. Technol.* **1998**, *33*, 2379–239.
[305] Yahaya, G. O., Brisdon, B. J., England, R. *J. Membr. Sci.* **2000**, *168*, 187–201.
[306] Juang, R.-S., Lee, S.-H., Shiau, R.-C. *J. Membr. Sci.* **1997**, *137*, 231–239.
[307] Zhou, K., Fan, X., Su, Y. *Huadong Huagong Xueyuan Xuebao* **1992**, *18*, 560–565.
[308] Ju, L.-K., Verma, A. *Sep. Sci. Technol.* **1994**, *29*, 2299–2315.
[309] Hadik, P., Szabo, L.-P., Nagy, E. *Desalination* **2002**, *148*, 193–198.
[310] Hadik, P., Szabo, L.-P., Nagy, E., Farkas, Z. *J. Membr. Sci.* **2005**, *251*, 223–232.
[311] Yang, Q., Chung, T.-S. *J. Membr. Sci.* **2007**, *294*, 127–131.
[312] Shen, Y., Groenberg, L., Joensson, J. A. *Anal. Chim. Acta* **1994**, *292*, 31–39.
[313] McMurray, S. H., Griffin, G. J. *J. Chem. Technol. Biotechnol.* **2002**, *77*, 1262–1268.
[314] Bryjak, M., Wieczorek, P., Kafarski, P., Lejczak, B. *J. Membr. Sci.* **1991**, *56*, 167–180.
[315] Kertesz, R., Schlosser, S., Simo, M. *Desalination* **2004**, *163*, 103–117.
[316] Choi, J. W., Cho, K. S., Oh, B. K., Kim, Y. K., Youn, I. J., Lee, W. H. *J. Ind. Eng. Chem.* **2003**, *9*, 294–300.
[317] Adarkar, J. A., Sawant, S. B., Joshi, J. B., Pangarkar, V. G. *Biotechnol. Prog.* **1997**, *13*, 493–496.
[318] Campbell, M. J., Walter, R. P., Singleton, R., Knowles, C. J. *J. Chem. Technol. Biotechnol.* **1994**, *60*, 263–273.
[319] Dzygiel, P., Wieczorek, P., Mathiasson, L., Jonsson, J. A. *Anal. Lett.* **1998**, *31*, 1261–1274.
[320] Molinari, R., De Bartolo, L., Drioli, E. *J. Membr. Sci.* **1992**, *73*, 203–215.
[321] Yamaguchi, T., Nishimura, K., Shinbo, T., Sugiura, M. *Bioelectrochem. Bioenerg.* **1988**, *20*, 109–123.
[322] Bryjak, M., Kozlowski, J., Wieczorek, P., Kafarski, P. *J. Membr. Sci.* **1993**, *85*, 221–228.
[323] Huang, D., Huang, K., Chen, S., Liu, S., Yu, J. *Sep. Sci. Technol.* **2008**, *43*, 259–272.
[324] Dzygiel, P., Wieczorek, P., Jonsson, J. A., Milewska, M., Kafarski, P. *Tetrahedron* **1999**, *55*, 9923–9932.
[325] Miyako, E., Maruyama, T., Kubota, F., Kamiya, N., Goto, M. *Langmuir* **2005**, *21*, 4674–4679.
[326] Woo, I. S., Kang, A. S. *Hwahak Konghak* **1988**, *26*, 435–444.
[327] Wieczorek, P. *J. Membr. Sci.* **1997**, *127*, 87–92.
[328] Wieczorek, P., Joensson, J. A., Mathiasson, L. *Anal. Chim. Acta* **1997**, *346*, 191–197.
[329] Hossain, M. M. *Sep. Purif. Technol.* **2000**, *18*, 71–83.
[330] Deblay, P., Minier, M., Renon, H. *Biotechnol. Bioeng.* **1990**, *35*, 123–131.
[331] Drapala, A., Wieczorek, P. *Desalination* **2002**, *148*, 235–239.
[332] Shukla, J. P., Kumar, A., Singh, R. K., Iyer, R. H. *ACS Symp. Ser.* **1996**, *642*, 391–408.
[333] Mohapatra, P. K., Manchanda, V. K. *Indian J. Chem.* **2003**, *42A*, 2925–2938.
[334] Sawant, S. R., Sonawane, J. V., Venugopalan, A. K., Dey, P. K., Kumar, A., Mathur, J. N. *Ind. J. Chem. Technol.* **2003**, *10*, 531–538.
[335] Lakshmi, D. S., Mohapatra, P. K., Mohan, D., Manchanda, V. K. *Desalination* **2004**, *163*, 13–18.
[336] Mohapatra, P. K., Lakshmi, D. S., Mohan, D., Manchanda, V. K. *Sep. Purif. Technol.* **2006**, *51*, 24–30.
[337] Shailesh, S., Pathak, P. N., Mohapatra, P. K., Manchanda, V. K. *J. Membr. Sci.* **2006**, *272*, 143–151.
[338] Ramakul, P., Prapasawad, T., Pancharoen, U. *J. Chin. Inst. Chem. Eng.* **2007**, *38*, 489–494.
[339] Singh, S. K., Misra, S. K., Sudersanan, M., Dakshinamoorthy, A., Munshi, S. K., Dey, P. K. *Hydrometallurgy* **2007**, *87*, 190–196.
[340] Ura, P., Prakorn, R., Weerawat, P., Milan, H. *J. Ind. Eng. Chem.* **2006**, *12*, 673–681.
[341] Shukla, J. P., Kedari, C. S., Dharmapurikar, G. R. *J. Nucl. Sci. Technol.* **1998**, *35*, 419–424.
[342] Kedari, C. S., Pandit, S. S., Ramanujam, A. *J. Membr. Sci.* **1999**, *156*, 187–196.
[343] Sawant, S. R., Sonawane, J. V., Pabby, A. K., Venugopalan, A. K., Dey, P. K., Venkataramani, B. *Ind. J. Chem. Technol.* **2004**, *11*, 548–554.
[344] Rathore, N. S., Sonawane, J. V., Kumar, A., *et al. J. Membr. Sci.* **2001**, *189*, 119–128.
[345] Rathore, N. S., Sonawane, J. V., Gupta, S. K., *et al. Sep. Sci. Technol.* **2004**, *39*, 1295–1319.
[346] Cristau, H. J., Virieux, D., Dozol, J. F., Rouquette, H. *J. Radioanal. Nucl. Chem.* **1999**, *241*, 543–547.
[347] Ramanujam, A., Dhami, P. S., Gopalakrishnan, V., Dudwadkar, N. L., Chitnis, R. R., Mathur, J. N. *Sep. Sci. Technol.* **1999**, *34*, 1717–1728.
[348] Mohapatra, P. K., Pandey, A. K., Manchanda, V. K. *Radiochimica Acta* **1999**, *84*, 147–152.

[349] Sriram, S., Mohapatra, P. K., Pandey, A. K., Manchanda, V. K., Badheka, L. P. *J. Membr. Sci.* **2000**, *177*, 163–175.
[350] Sriram, S., Manchanda, V. K. *Solvent Extr. Ion Exch.* **2002**, *20*, 97–114.
[351] Ansari, S. A., Mohapatra, P. K., Prabhu, D. R., Manchanda, V. K. *J. Membr. Sci.* **2006**, *282*, 133–141.
[352] Ansari, S. A., Mohapatra, P. K., Prabhu, D. R., Manchanda, V. K. *J. Membr. Sci.* **2007**, *298*, 169–174.
[353] Asfari, Z., Bressot, C., Vicens, J., *et al. ACS Symp. Ser.* **1996**, *642*, 376–390.
[354] Kim, J. K., Kim, J. S., Shul, Y. G., Lee, K. W., Oh, W. Z. *J. Membr. Sci.* **2001**, *187*, 3–11.
[355] Mohapatra, P. K., Lakshmi, D. S., Mohan, D., Manchanda, V. K. *J. Membr. Sci.* **2004**, *232*, 133–139.
[356] Raut, D. R., Mohapatra, P. K., Ansari, S. A., Manchanda, V. K. *J. Membr. Sci.* **2008**, *310*, 229–236.
[357] Buchalter, E. M., Hofman, D. L., Craig, W. M., Birkill, R. S., Smit, J. J. *Chem. Eng. Res. Des.* **1987**, *65*, 381–385.
[358] Ramadan, A., Danesi, P. R. *Solvent Extr. Ion Exch.* **1988**, *6*, 157–166.
[359] Izatt, R. M., Roper, D. K., Bruening, R. L., Lamb, J. D. *J. Membr. Sci.* **1989**, *45*, 73–84.
[360] Lamb, J. D., Bruening, R. L., Linsley, D. A., Smith, C., Izatt, R. M. *Sep. Sci. Technol.* **1990**, *25*, 1407–1419.
[361] Dozol, J. F., Casas, J., Sastre, A. M. *Sep. Sci. Technol.* **1993**, *28*, 2007–2022.
[362] Mikulaj, V., Rajec, P., Svec, A., Mackova, J. *J. Radioanal. Nucl. Chem.* **1993**, *175*, 287–296.
[363] Dozol, J. F., Casas, J., Sastre, A. M. *Sep. Sci. Technol.* **1994**, *29*, 1999–2018.
[364] Mackova, J., Mikulaj, V., Rajec, P. *J. Radioanal. Nucl. Chem.* **1994**, *183*, 85–91.
[365] Chaudry, M. A., Noor, U.-I., Ahmad, I. *J. Radioanal. Nucl. Chem.* **1994**, *185*, 369–385.
[366] Mackova, J., Mikulaj, V. *J. Radioanal. Nucl. Chem.* **1996**, *208*, 111–122.
[367] Mohapatra, P. K., Lakshmi, D. S., Manchanda, V. K. *Desalination* **2006**, *198*, 166–172.
[368] Rawat, N., Mohapatra, P. K., Lakshmi, D. S., Bhattacharyya, A., Manchanda, V. K. *J. Membr. Sci.* **2006**, *275*, 82–88.
[369] Teramoto, M., Fu, S. S., Takatani, K., *et al.Sep. Purif. Technol.* **2000**, *18*, 57–69.
[370] Teramoto, M., Sakaida, Y., Fu, S. S., *et al. Sep. Purif. Technol.* **2000**, *21*, 137–144.
[371] Ho, W. S. W., Poddar, T. K., Pusic, R. Roller, J. Unique Membrane Technology for Removal/Recovery of Metals from Wastewaters and Process Streams. In *American Electroplaters and Surface Finishers Society/EPA Conference for Environmental Excellence*, Lake Buena Vista, FL, USA, 25–27 January; American Electroplaters and Surface Finishers Society: Orlando, FL, 1999.
[372] Ho, W. S. W., Poddar, T. K., Pusic, R., Roller, J. Unique Membrane Technology for Removal/Recovery of Metals from Wastewaters and Process Streams. In *Proceedings of the 1999 International Congress on Membranes and Membrane Processes*, Toronto, Canada, 12–18 June 1999.
[373] Fu, S. S., Mastuyama, H., Teramoto, M. *Sep. Purif. Technol.* **2004**, *36*, 17–22.
[374] Fu, S. S., Teramoto, M., Mastuyama, H. *Sep. Sci. Technol.* **2004**, *39*, 517–538.
[375] Jonsson, J. A., Mathiasson, L. . *J. Chromatogr. A* **2000**, *902*, 205–225.
[376] Jakubowska, N., Polkowska, Z., Namiesnik, J., Przyjazny, A. *Crit. Rev. Anal. Chem.* **2005**, *35*, 217–235.
[377] Parthasarathy, N., Pelletier, M., Buffle, J. *Anal. Chim. Acta* **1997**, *350*, 183–195.
[378] Trocewicz, J. *J. Chromatogr. B* **2004**, *801*, 213–220.
[379] Trocewicz, J., Suprynowicz, Z., Markowicz, J. *J. Chromatogr. B* **1996**, *685*, 129–134.
[380] Norberg, J., Emneus, J., Jonsson, J. A., *et al. J. Chromatogr. B* **1997**, *701*, 39–46.
[381] Megersa, N., Solomon, T., Jonsson, J. A. *J. Chromatogr.* **1999**, *830*, 203–210.
[382] Liu, J.-F., Chao, J.-B., Jiang, G.-B. *Anal. Chim. Acta* **2002**, *455*, 93–101.
[383] Muthuraman, G., Palanivelu, K. *Dyes Pigments* **2006**, *70*, 99–104.
[384] Muthuraman, G., Palanivelu, K. *J. Text. Inst.* **2006**, *97*, 341–347.
[385] Hajarabeevi, N., Bilal, I. M., Amalraj, S., Palanivelu, K. *J. Environ. Sci. Eng.* **2007**, *49*, 33–40.
[386] Kemperman, A. J. B., Bargeman, D., Van Den Boomgaard, T., Strathmann, H. *Sep. Sci. Technol.* **1996**, *31*, 2733–2762.
[387] Zha, F. F., Fane, A. G., Fell, C. J. D., Schofield, R. W. *J. Membr. Sci.* **1992**, *75*, 69–80.
[388] Dreher, T. M., Stevens G. W. *Sep. Sci. Technol.* **1998**, *33*, 835–853.
[389] Fortunato, R., Afonso, C. A. M., Benavente, J., Rodriguez-Castellon, E., Crespo, J. G. *J. Membr. Sci.* **2005**, *256*, 216–223.
[390] de los Rios, A. P., Hernandez-Fernandez, F. J., Tomas-Alonso, F., Palacios, J. M., Gomez, D., Rubio, M., Villora, G. *J. Membr. Sci.* **2007**, *300*, 88–94.
[391] Teramoto, M., Tanimoto, H. *Sep. Sci. Technol.* **1983**, *18*, 871–892.
[392] Nakao, M., Takahashi, K., Takeuchi, H. *J. Chem. Eng. Jpn.* **1987**, *20*, 326–328.
[393] Chiarizia, R., Horwitz, E., Rickert, P., Hodson, K. *Sep. Sci. Technol.* **1990**, *25*, 1571–1586.
[394] Tanigaki, M., Ueda, M., Eguchi, W. *Sep. Sci. Technol.* **1988**, *23*, 1161–1169.
[395] Fujinawa, K., Akiyama, M., Akiba, I., Adachi, H., Imaishi, N., Hozawa, S. *Kagaku Kogaku Ronbunshu* **1989**, *15*, 159–165.
[396] Wijers, M. C., Jin, M., Wessling, M., Strathmann, H. *J. Membr. Sci.* **1998**, *147*, 117–130.
[397] He, T., Versteeg, L. A. M., Mulder, M. H. V., Wessling, M. *J. Membr. Sci.* **2004**, *234*, 1–10.
[398] He, T. *Desalination* **2008**, *225*, 82–94.
[399] Clement, C., Hossain, M. M. *Sep. Sci. Technol.* **1997**, *32*, 2685–2703.
[400] Kemperman, A. J. B., Rolevink, H. H. M., van den Boomgaard, T., Strathmann, H. *J. Membr. Sci.* **1998**, *138*, 43–55.
[401] Wang, Y. C., Thio, Y. S., Doyle, F. M. *J. Membr. Sci.* **1998**, *147*, 109–116.
[402] Yang, Q., Chung, T.-S., Xiao, Y., Wang, K. *Chem. Eng. Sci.* **2007**, *62*, 1721–1729.
[403] Yang, X. J., Fane, A. G., Bi, J., Griesser, H. J. *J. Membr. Sci.* **2000**, *168*, 29–37.
[404] Ho, W. S. W., Poddar, T. K. *Environ. Prog.* **2001**, *20*, 44–52.
[405] Ho, W. S. W., Wang, B. B. *Ind. Eng. Chem.* Res. **2002**, *41*, 381–388.
[406] Ho, W. S. W., Wang, B., Neumuller, T. E., Roller, J. *Environ. Prog.* **2001**, *20*, 117–121.
[407] Ho, W. S. W. Supported Liquid Membrane Process for Chromium Removal and Recovery. US Pat. 6,171,563, 9 January 2001.
[408] Ortiz, I., Fresnedo San Roman, M., Corvalan, S. M., Eliceche, A. M. *Ind. Eng. Chem. Res.* **2003**, *42*, 5891–5899.
[409] Ho, W. S. W., Poddar, T. K., Neumuller, T. E. *J. Chin. Inst. Chem. Eng.* **2002**, *33*, 67–76.
[410] Urtiaga, A., Abellan, M. J., Irabien, J. A., Ortiz, I. *J. Membr. Sci.* **2005**, *257*, 161–170.

[411] Urtiaga, A., Abellan, M. J., Irabien, J. A., Ortiz, I. *Desalination* **2006**, *191*, 79–85.
[412] He, D., Luo, X., Yang, C., Ma, M., Wan, Y. *Desalination* **2006**, *194*, 40–51.
[413] Ho, W. S. W. Combined Supported Liquid Membrane/ Stripping Dispersion Process for Removal and Recovery of Metals. US Pat. 6,350,419, 26 Febuaury 2002.
[414] Ho, W. S. W. Combined Supported Liquid Membrane/ Stripping Dispersion Process for Removal and Recovery of Penicillin and Organic Acids. US Pat. 6,433,163, 3 April 2000.
[415] Sonawane, J. V., Pabby, A. K., Sastre, A. M. *J. Membr. Sci.* **2007**, *300*, 147–155.
[416] Sonawane, J. V., Pabby, A. K., Sastre, A. M. *AIChE J.* **2008**, *54,* 453–463.
[417] Gu, S., Yu, Y., He, D., Ma, M. *Sep. Purif. Technol.* **2006**, *51*, 277–284.
[418] He, D., Gu, S., Ma, M. *J. Membr. Sci.* **2007**, *305*, 36–47.

Biographical Sketches

Michael Edward Vilt is a PhD graduate student at the Ohio State University and is advised by W.S. Winston Ho. His work is focused on recovering antibiotics from fermentation broths using supported liquid membranes with strip dispersion. He received his BS in chemical and environmental engineering from the University of Toledo in 2004.

W.S. Winston Ho, PhD, is University Scholar Professor of chemical and materials engineering at the Ohio State University. Dr. Ho had taught for 10 years; he had over 28 years of industrial R&D experience in membranes and separation processes. He was elected to the National Academy of Engineering, USA, in 2002 in recognition of his distinguished contributions to engineering, including the invention and commercialization of novel separation technologies and the development of new theoretical models for membrane separations. A New Jersey Inventor of the Year (1991), Dr. Ho holds more than 50 US patents, generally with foreign counterparts, in membranes and separation processes. He is the coeditor of *Membrane Handbook*, recipient of the Professional and Scholarly Publishing Award for the most outstanding engineering work in 1993. He received the 2006 Institute Award for Excellence in Industrial Gases Technology and the 2007 Clarence G. Gerhold Award for separations from the American Institute of Chemical Engineers. He obtained his BS degree from National Taiwan University and his MS and PhD degrees from the University of Illinois at Urbana-Champaign, all in Chemical Engineering. His research interests include molecule-based membrane separations, fuel cell membranes, and water purification.

Dr. Norman N. Li, an internationally renowned industrial scientist, has pioneered fundamental chemical engineering separation principles as well as practical applications to industrial processes. A member of the National Academy of Engineering of USA, Dr. Li has had a distinguished career of more than 40 years in the American chemical and petroleum industries. He worked at Exxon, AlliedSignal, UOP, and Honeywell. In 1995, he established NL Chemical Technology, Inc., which develops advanced membranes for water treatment.

Dr. Li is best known for his industrial research in membranes for separation and encapsulation and his invention of liquid membranes. He holds 45 US patents. He has published more than 100 papers, edited 20 books, and given invited lectures at more than 80 universities and industrial laboratories.

Dr. Li has received numerous awards and honors including the prestigious Perkin Medal from the Society of Chemical Industry (2000) – the highest honor in the American chemical industry and was the recipient of the American Institute of Chemical Engineers' (AIChE) Founders Award, which is the highest honor conferred by AIChE. He also received the inaugural Award for Lifetime Achievements from the World Congress of Chemical Engineers (2001) and the American Chemical Society's Award of Separation Science and Technology. Dr. Li has served as president of the North American Membrane Society and the chair of International Congress of Membranes and Membrane Processes.

4.05 Integrated Membrane Operations in Various Industrial Sectors

A Koltuniewicz, Warsaw University of Technology, Warszawa, Poland

4.05.1 Membrane-Based Integrated Systems and Hybrid Processes

Recent achievements in material science, polymer chemistry, and process engineering have opened up new applications for membrane processes. Membranes and membrane-based integrated processes play an important role by creating new prospects for development, reengineering, or retrofitting of industrial processes. Essentially, the modern membrane processes offer practically unlimited selectivity of separation, thereby enabling conservation and the rational use of water and raw materials in various industrial branches. Another attractive feature of the membrane processes is the simplicity of their layout and their modular design that allows for simple expansion and increase of the production capacity.

The rational use of water and proper management of water streams during industrial processes may be attained with membranes by removal of all types of contaminants, for example, suspended solids (microfiltration (MF)), colloids (ultrafiltration (UF)), soluble components (electrodialysis (ED), liquid membrane (LM), supported liquid membrane (SLM), nanofiltration (NF), and reverse osmosis (RO)), volatile organic compounds (VOCs; pervaporation (PV), membrane distillation (MD), and contactors), ions (ED, NF, RO, dialysis (D)), and organic components (PV, MB, contactors, EM, and SLM). Energy production sectors already use water-recycling systems based on MF, MF, and ED on a large scale. The water recovered by this separation can be recycled to the appropriate production stages, which substantially reduces costs. Disposal or

recycling of unavoidable waste streams may be achieved by a variety of membrane separations, which enable the fractionation of wastewaters onto valuable pure materials that can be subsequently reused as resources or valuable by-products [1].

Membrane processes reduce chemical consumption in various operations and also open a new unexploited source of raw materials by recovery, reuse, and recycling of unreacted substrates, and production media such as catalysts, solvents, surfactants, adsorbents, and cooling agents. Diluted metal ions may be recovered from waste streams, mining waters, tailings, leachates, seawater, etc. Diluted organic compounds may be concentrated during PV or MD, which additionally take advantage of and utilize waste heat.

In addition, membranes open up new prospects for energy sources, such as fuel cells and new fuels based on the transesterification of fatty acids with alcohols in membrane reactors. PV enables the enrichment and purification and dewatering of liquid and gaseous fuels. Membranes may also contribute to huge energy savings, thanks to new solutions of energy recovery systems. The substitution of conventional energy-consuming processes by economical membrane alternatives or their combinations, which are called hybrid processes, is especially profitable. The general definition of hybrid which can be used in technology is "something that has two different types of components performing essentially the same function" [2, 3]. Lipnitzki and Field [4] distinguished two different groups of hybrid processes:

1. hybrid processes consisting of processes which are essentially performing the same function such as combination of separation processes and
2. hybrid processes which are composed of two different processes, that is, combination of membranes and reactors.

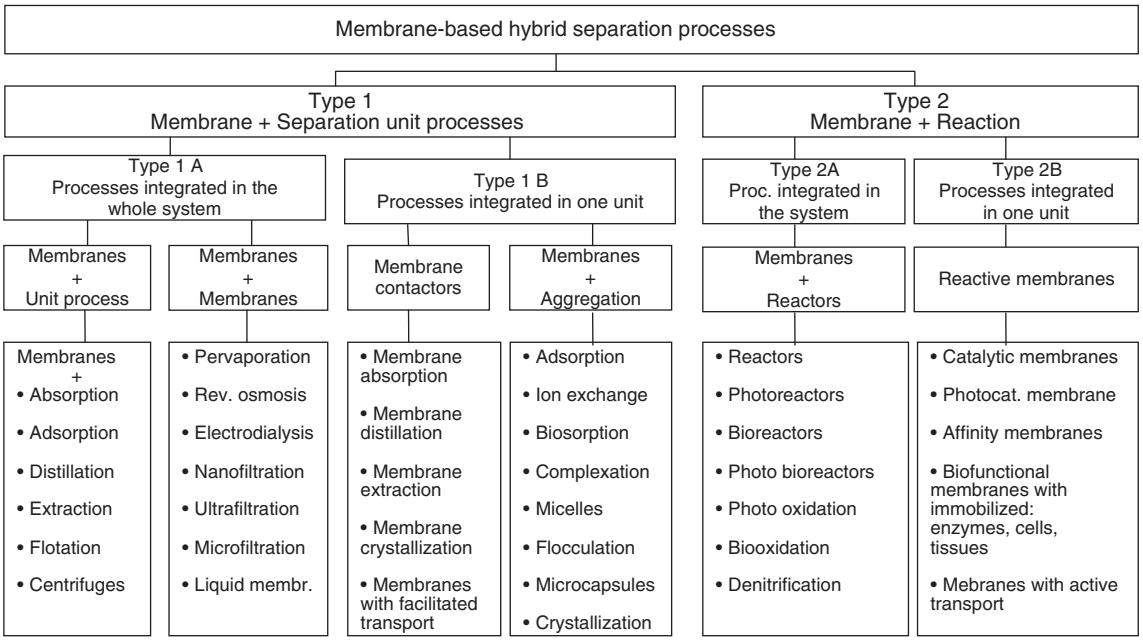
The specific feature of hybrid process is the synergy resulting from this integration, which enhances the process effectiveness. Hybrid processes can be easily optimized because they have higher degrees of freedom, number of parameters, and range of operation. Therefore, integration of some conventional processes with membrane separation technologies permits the rationalization of direct and indirect energy consumption, at the same time improving the product quality and the process capacity and selectivity. The strategy of introducing hybrid processes in the modern technologies is characterized by advanced levels of automation capacity, modularity, and remote control. However, it also includes upgrading and retrofitting of an existing process, thus reducing energy consumption and costs, and could be regarded as a means to form both technically and economically viable technologies.

The general division of the membrane-based separation hybrid processes into the two main types, that is, unit separation process integrated with membrane (type 1, **Figure 1**) and membrane integrated with reaction (type 2, **Figure 1**), is acceptable. However, the degree of this integration is different in a variety of recently elaborated processes and may be enhanced by further subdivision. Particularly, the membrane-based hybrids can be created by integration of the different processes that are performed in the separate units (type A) or by coupling them in one membrane module (type B). Therefore, all membrane-based integrated systems may be classified into the four main specific groups, such as

type 1A – membrane processes combined with conventional unit processes [5] that are performed in the separate units;
type 1B – membrane processes that are integrated with conventional unit processes in one membrane module (membrane contactors and membranes combined with some sort of aggregation of separated substances);
type 2A – membrane processes integrated with reactions that are performed in the separate units; and
type 2B – membrane processes integrated with reactions that are performed in one membrane module (reactive membranes).

4.05.1.1 Membranes with Conventional Unit Processes

The first known hybrid (membrane-based) separation process was a combination of PV and distillation, being published for the dehydration of isopropanol and ethanol mixtures by Binning and James [6] in 1958. It can overcome restrictions encountered using distillation alone, for example, the addition of a solvent, which is removed in subsequent steps, pressure variations, and a high number of trays in the distillation columns. The PV process is integrated into the distillation process to reduce the number of trays by processing a side stream of the distillation column or to split the azeotropes before distillation and also as a polishing step of either the top or the bottom product



A refers to processes integrated in the whole system, B refers to processes integrated in one unit

Figure 1 Membrane-based hybrid processes.

of the distillation column. Distillation/membrane hybrid processes have a potential for energy savings and, under some circumstances, are superior to the single separation processes, especially if high product purities are required. Design methodology for a membrane/distillation column hybrid process has already been evaluated [7–10]. Such systems are used for many applications such as separation of methanol/methyl *tert*-butyl ether (MTBE)/C, mixture [11], aroma concentrate [12], and dewatering of solvents [13]. It was shown that PV can be easily used to break the azeotrope of methanol and 2-methoxy-2-methylbutane (TAME) [14]. Integrated distillation with vapor permeation is used for dehumidification of compressed air [15]. Distillation is also frequently joined with RO in hybrid systems for water desalination, which has been shown to be technically and economically superior to nonintegrated multistage flash distillation (MSF) and RO systems [16] not only by improving the performance and reducing water cost, but also by reducing the cost of materials of construction, equipment, membranes, steam, energy, chemicals, etc. [17]. A hybrid process that combines a vapor permeation process with absorption and stripping process was used for removal of VOCs from gas streams [18, 19], acetone recovery with hybrid comprising PV and absorption column [20], removal of VOCs from groundwater with PV and air stripping [21], and removal of acid gases from natural gas [22]. There are also other hybrids of membranes with unit separation processes, such as systems combining ion-exchange membranes with solvent extraction processes [23]. Membrane-adsorption hybrid system may also be performed solely with adsorptive membranes [24]. Membrane adsorbers are a hybrid synthesis of these two technologies, aiming at combining the selectivity of chromatography resins with the high productivity associated with filtration membranes. Like perfusion beads, membrane adsorbers were developed as an alternative to conventional gel bead chromatography.

4.05.1.2 Membrane Contactors

Membrane contactors [25] form the specific group of hybrids with high level of integration between membranes and such separation processes as distillation, extraction, and absorption or adsorption. In the membrane contactor, these unit processes are performed directly in membrane module where the membrane plays a role of artificial interface between two fluids with mass transfer of separated components between them. This technique is performed by inserting

a microporous membrane wall between the feed phase and a stripping phase. Referring to conventional unit separation processes performed in columns, many advantages of the membrane contactors can be pointed out: there are no overloading, entrainment, weeping, flooding, or emulsification problems, and neither stirring nor mixing is required. One drawback occurs when using a membrane, as it creates additional resistance that hinders diffusion from one phase to another, thus slowing down the separation. In most cases, the large surface area per volume offered by hollow-fiber modules overcomes this disadvantage.

Membrane extraction is used, for example, in lactic acid separation, aromatic acid separation, valeric acid recovery from wastewaters, boric acid separation, acid separation from salts (cadmium from phosphoric acid), the removal of VOCs, benzene–toluene–xylene (BTX), and in detection of trace components such as vitamin E isomers in vegetable oils. MD is applied for ultrapure water (UPW) production, for the separation of VOCs (ethanol, chloroform, and BTX), for the concentration of solutions (acids, bases, and salts), juices etc., and in natural aroma processing. Vacuum membrane distillation (VMD) is based on the use of a microporous hydrophobic membrane for the separation of an aqueous feed solution into a retentate and a permeate by means of the pressure difference induced by the vacuum on the permeate side: the principle is that the liquid stream vaporizes at the membrane surface and the vapor diffuses through the gas phase inside the membrane pores. The driving force of the process corresponds to the partial pressure gradient through the membrane. The conductive heat transfer through the membrane is negligible because of the low pressure on the permeate side [26]. The mass transfer through the membrane pores predominantly takes place according to the Knudsen mechanism, implying that the different molecules move independently of each other [27].

4.05.1.3 Membrane with Aggregation Processes

Membrane with aggregation process involves bonding of the separated species first to some special bonding agent and then separating the aggregates from the stream by membrane separation processes. There are several ways of binding that are used in practice such as adsorption on pulverized adsorbent, biosorption on microorganisms or some biological materials, complexation [28], chelating [29], binding on polymers, coagulation, flocculation, precipitation, crystallization, and micellar solubilization. A very promising way of the binding is to use ion-exchange resins, molecularly imprinted materials, functionalized polymers, etc. It should be noted that several hybrid processes based on aggregation and subsequently the other separation unit processes such as flotation [30–32] or centrifugation [33] must be used.

4.05.1.4 Membrane Reactors

Membrane reactors and membrane bioreactors as well as photoreactors belong to the recent achievements in process engineering. Separation of undesired components may also be carried out throughout their dematerialization by chemical conversion. Combining a membrane with a chemical reaction has been shown to offer advantages in a number of different instances [34], which can be performed in membrane module integrated with reactor or solely in membrane. The catalytic membrane enables an efficient three-phase contact between gaseous phase, liquid phase, and the active surface. The pore size of the catalytic layer can be adjusted in the mesoporous or macroporous range according to the needs of the reaction, with a narrow pore-size distribution. Moreover, the membrane catalyst concept allows a tuning of the reaction rate by adjusting the pressure to suit variable operating situations, that is, different feed concentration, flow rate, and so on [35, 36]. One of potential applications is the use of PV process to drive an equilibrated reaction. Reviews of the literature concerning membrane reactors reveal that a very large fraction of catalytic membrane reactor applications involves reversible reactions, which reach a thermodynamically limited conversion level in a conventional reactor [37–42]. By conducting these reactions in a catalytic membrane, wherein one product can selectively permeate through the membrane and out of the reaction zone, an overall conversion is attained which is much greater than that realized in the conventional reactor [43–54].

The operation of bioreactors [55] with enzymes or whole cells immobilized is used in biotechnology and several research areas. The specially challenging task is the separation of xenobiotic from water and air environment when they are present even in much diluted form. The specific group comprises the

so-called refractory chemicals, which are very resistant to decomposition.

New methods, such as photocatalytic reactions [56], allow in many cases a complete degradation of organic pollutants in very small and harmless species, without using chemicals, avoiding sludge production and its disposal. These processes are based on the electronic excitation of a molecule or solid caused by light absorption (usually ultraviolet (UV) light) [57] that drastically alters its ability to lose or gain electrons and promote decomposition of pollutants to harmless by-products [58–61].

Affinity technologies generally enable the selective binding of molecules based on their individual chemical structure or biological function. Affinity separations rely on the highly specific binding among the counterparts to achieve an efficient separation and purification purpose. The unique principle of affinity separation exploits the specific and reversible binding of a ligand. Ligands [62] are ions, or molecules coordinated to a central atom or molecule in a complex adhesion as an extremely thin layer of molecules (gases, solutes, or liquids) to the surfaces of solid bodies or liquids with which they are in contact. The main advantages of affinity membrane chromatography [63, 64] compared with the classical column chromatography include the higher flow rate, faster binding rate, lower pressure drop, higher productivity, and easier scale-up [65]. Affinity interactions are able to increase separation by selective adsorption [63]. In addition to the affinity mode, using membranes as solid supports also applies to adsorption modes such as ion exchange and hydrophobic interaction/reversed phase.

4.05.2 Industrial Importance of Integrated Membrane Operations

4.05.2.1 Textile Industry

In textile industries, the total water consumption is typically 200–400 l kg^{-1} of fabric and the total volume of wastewater is around 150 million tons/year. Dyeing, washing, scouring, and rinsing operations of the fabrics consume huge amounts of water (**Table 1**). Because of the wide variety of process steps, textile wastewater typically contains a complex mixture of chemicals with large amounts of salt, acid, or alkali, sizing agents, knitting oils, residual dye, and surfactants together with cleaning solvents, such as oxalic acid and auxiliary chemicals. Wet processing of fabrics includes desizing, scouring, bleaching, dyeing or printing, and finishing (heat, mechanical, and chemical finishing).

Desizing is the process of removing size chemicals from textiles, which is one of the industry's largest sources of wastewater pollutants. In this process, large quantities of size that are used in weaving processes are discarded. More than 90% of the size used in textile industry is disposed of in the effluent stream; the remaining 10% is recycled. Desizing processes often contribute up to 50% of the BOD load (BOD, biochemical oxygen demand) in wastewater from wet processing.

Dyeing and rinsing processes for disperse dyeing generate about 100–150 l of wastewater per kilogram of product. Similar processes for reactive and direct dyeing generate even more wastewater, about 125–165 l kg^{-1} of product. Dyes and pigments from printing and dyeing operations are the principal sources of color in textile effluent. Of the 700 000 tons of dyes produced annually

Table 1 The main wastes generated in textile manufacturing

Operation	*Main wastes generated in textile manufacturing*
Slashing/sizing	VOCs BOD; COD; metals; unused starch-based sizes
Desizing	VOCs from glycol ethers BOD from water-soluble packaging waste; fiber sizes; synthetic size; lint; yarn waste; cleaning lubricants; biocides; anti-materials, such as wipes, static compounds rags, and filters; cleaning and maintenance wastes containing solvents
Scouring	VOCs from glycol ethers disinfectants and little or no residual and scouring solvents insecticide residues; waste generated NaOH; detergents, fats; oils; pectin; wax; knitting lubricants; spin finishes; spent solvents
Dyeing	VOCs metals; salt; surfactants; little or no residual COD; sulfide; acidity/alkalinity; spent solvents
Printing	Solvents, acetic acid from suspended solids; urea; little or no residual drying and curing oven solvents; color; metals; waste generated emissions; combustion heat; BOD; foam gases; particulate matter
Finishing	VOCs; contaminants in BOD; COD; suspended fabric scraps and purchased chemicals; solids; toxics; spent trimmings; packaging formaldehyde vapors, solvents waste combustion gases; particulate matter

worldwide, about 10–15% of the dye is disposed of in effluent from dyeing operations. Dyestuffs are highly structured polymers with low biodegradability. There are nearly 3000 different dyes on the commercial market, where more than half of them are azo-compounds, containing at least one azo-, and one or more alkyl-sulfonate reactive groups. Typical reactions of such dyes under alkaline conditions and elevated temperatures are the cleavage of the reactive group and hydrolysis. Both the hydrolyzed form and some of the sulfonated derivatives appear in the wash water, in proportion to the efficiency of the dyeing process. Their concentration in dye baths ranges from 10 to 1000 mg l^{-1}, depending on the strength of the dye and the process in operation. The fabrics absorb 50–70% of the hydrolyzed dye molecules during batch dyeing and the residual dye solution in the tank is diluted by 20–40% upon rinsing. The remainder is discarded in the form of spent dye baths or in wastewater from subsequent textile-washing operations. The average wastewater generation from a dyeing facility is estimated at between 4000 and 8000 m^3 d^{-1}. Dyes may contain metals such as copper, cadmium, chromium, nickel, zinc, and cobalt. In some dyes, these metals are functional (i.e., they form an integral part of the dye molecule); however, in most dyes, metals are simply impurities generated during dye manufacture. The salts in textile wastewater are a potential problem area. Many types of salt are either used as raw materials or produced as by-products of neutralization or other reactions in textile-wet processes. Salt is used mostly to assist the exhaustion of ionic dyes, particularly anionic dyes, such as direct and fiber reactive dyes on cotton. Typical cotton batch dyeing operations use quantities of salt that range from 20% to 80% of the weight of goods dyed, and the usual salt concentration in such wastewater is 2000–3000 ppm. Cotton knit fabrics produced well over 125 kg of salts per ton of fabric and a pH of over 10. The wastewater from this facility contains neutralization salts around 60 ppm. Common salts are sodium chloride and Glauber's salt (sodium sulfate) that constitute the majority of total salt use. Other salts used as raw materials or formed in textile processes include Epsom salt (magnesium chloride), potassium chloride, and others in low concentrations. Regulatory limits imposed on textile facilities and on publicly owned treatment facilities that receive textile wastewater start at 250 ppm. Although the mammalian and aquatic toxicities of these salts are very low, their massive use in certain textile-dyeing processes can produce wastewater with salt levels well above the regulatory limits. Sources of metals found in textile-mill effluents may include fiber, incoming water, dyes, plumbing, and chemical impurities. For example, mercury or other metals may be used as catalysts in the manufacture of certain dyes and may be present as by-products. Metals can be difficult to remove from wastewater.

Finishing processes typically generate wastewater containing natural and synthetic polymers and a range of other potentially toxic substances. Pollution from peroxide bleaching normally is not a major concern. The major pollution issues in the bleaching process are chemical handling, water conservation, and high pH. Hazardous waste generated by textile manufacturers results primarily from the use of solvents in cleaning knitted goods. Solvents may be used in some scouring or equipment cleaning operations; however, more often, scouring processes are aqueous based, and cleaning materials involve mineral spirits or other chemicals. Spent solvents can include tetrachloroethylene and trichloroethylene.

The aquatic toxicity of textile industry wastewater varies considerably among production facilities. Data are available that show that the wastewater of some facilities has high aquatic toxicity, while others show little or no toxicity. The sources of aquatic toxicity can include salt, surfactants, ionic metals and the complex metals therein, toxic organic chemicals, biocides, and toxic anions. Most textile dyes have low aquatic toxicity. On the other hand, surfactants and related compounds, such as detergents, emulsifiers, and dispersants, are used in almost every textile process and can be an important contributor to effluent aquatic toxicity, BOD, and foaming.

Recovery, recycling, and reuse of these materials are excellent ways for facilities to save money and energy, and can be effective tools for minimizing pollutant releases to the environment. By recovering solvents and raw materials, textile mills can reduce raw material costs and can reduce pollution with little modification of existing processes. Water is widely used in the industry for processes ranging from dyeing to preparation and finishing. Raw materials, such as unexhausted dyestuff and additives, can also be recycled. Although not applicable to all processes, in some processes, dye bath reuse can reduce pollution concentrations and effluent volume and generally requires a smaller capital outlay than pretreatment plant construction. It also saves on the

costs of dyes, chemicals, and energy. Dye bath reuse principles can also be applied to bleach baths.

Wet processing consumes a large amount of water from the rinsing of textiles. Preparation and finishing water can also be reused. Implementation of recycling during yarn finishing drastically reduces wastewater pollution, soda (Na_2CO_3), and caustic consumption. The spent rinse water should be processed and concentrated caustic soda may then be reused in mercerizing. Corresponding reductions in hydrochloric acid used to neutralize the effluent can also then be possible.

The following are typical examples of possible water management in the textile industry:

- Direct reuse of noncontaminated process water; for example, cooling water for general factory use.
- Cascading of process water used on a high-quality process to another process requiring only low-quality water; for example, final rinses to first rinse operations; the treatment of wastewater from one source for reuse in another process.
- Closed-loop treatment and recycling of wastewater from a particular source for direct reuse in the process. This is often accompanied by the recovery of process chemicals, by-products, and heat energy; and end-of-line mixed factory effluent treatment and reuse.

Purification treatment to recycle water must have a better performance than for simple discharge according to the limits imposed by legislation. Many processes have been studied to treat textile wastewaters [66, 67]. Conventional methods are biological, physical, and chemical processes of adsorption, filtration, coagulation, flocculation, and sedimentation. However, their application in an industrial plant becomes difficult owing to the operation problems and the costs. Moreover, such conventional methods are insufficient and ineffective for reusing the effluent in the dye/rinse processes, owing to the fact that complete removal of color, suspended/dissolved solids, and refractory chemicals is not possible by these methods, unless accompanied by advanced processes.

Biological treatment by activated sludge provides high efficiency in chemical oxygen demand (COD) removal, but does not eliminate the color of the water and, frequently, operation problems such as bulking appear. The use of flotation instead of sedimentation to separate the treated wastewater from the activated sludge solves this problem, but it increases the depuration costs and it makes the plant operation complicated. Adsorption onto activated carbon followed by chemical coagulation can be used for treating such effluents for colored and refractory materials; however, management of the generated sludge as spent activated carbon and precipitated coagulants requires further treatment and ultimate disposal. Electrochemical methods may be accompanied by chemical coagulation and ion exchange to remove color and turbidity (NTU); to reduce the COD concentration, conductivity, and hardness; and to reduce Fe ions from the dyeing and finishing mill secondary effluents. Ozone treatment improves the biodegradability of recalcitrant effluents and degrades potentially toxic and/or inhibitory pollutants occurring in the same streams. Ozonation also causes a relevant reduction, close to 90%, of all the values of the sum of specific classes of potentially toxic and/or inhibitory pollutants (dyes, halogenated organics, and nonionic surfactants) as confirmed by the lack of any acute toxicity in ozonated samples. Aldehydes are the most likely ozonation by-products. Their total concentration continuously increases during ozonation from 1.2 to 11.8 ppm. Among them, glyoxalin, formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde have been identified by high-performance liquid chromatography (HPLC)-UV analyses. Chemical oxidation by ozone, or a combination of UV radiation and ozone and H_2O_2, and ozonation with electroflocculation [68] have the great interest but their costs are still very high. Hence, the reuse of these effluents can be made possible only via appropriate advanced treatment techniques by which ultimate color removal is accompanied by substantial mineralization, to satisfy the water quality requirements of the process.

Membrane processes have the potential to remove the dyestuff or allow reuse of the auxiliary chemicals used for dyeing or to concentrate the dyestuffs and auxiliaries and produce purified water. The applications of membrane separation processes in textile industries have been described in numerous publications [69–73]. Majority of the reported applications were focused on the recovery of sizing agents from the desizing effluents and on the recovery of the dyeing effluents by MF, UF, NF, and RO.

MF is suitable for removing colloidal dyes from the exhausted dye bath and the subsequent rinses but the auxiliary chemicals pass through the permeate. MF may be used also as a prefiltration step for NF in the treatment of secondary textile wastewater for the direct reuse of polished effluent within the dyeing processes.

UF is effective for the removal of particles and macromolecules and thus UF may be used as a single-step treatment of secondary textile wastewater. The permeate is of such quality as to allow wastewater reuse in the minor processes (rinsing and washing) of the textile industry, but it does not possess the requirements to be reused in delicate processes, such as dyeing light-colored yarns. UF may also be used as pretreatment for the next membrane process of NF or RO working at low operating pressure (which involves low energy costs) and guarantees a constant permeate.

NF allows the separation of low-molecular-weight organic compounds and divalent salts, with an appreciable softening effect. It has been studied as a treatment method of secondary textile effluents. After NF, the permeate is satisfactory and very acceptable for water reuse. NF membranes simplify the treatment to a large extent and easily meet the water quality demands. Moreover, the advantages derived from the application of NF membranes for the removal of dyes from textile effluents include the following: textile dyes are rejected, recovered, and reused; environmental pollution is avoided; and reusable water is produced. During NF high dye rejection value can be achieved, giving a decolorized permeate, suitable for possible reuse or further polishing. In addition to the low pressures used in this process, the low salt rejections are promising for the direct NF of the effluent [74].

RO is suitable for removing all ions and species from dye bath effluents. The permeate produced is usually colorless and total salinity is low. The RO permeate can be directly reused in the dyeing processes as demonstrated by many yarn dyeing tests on an industrial scale, which enables a reduction in the costs (to 50%) and water consumption. The residual organic pollution in terms of COD, color, and surfactants does not interfere with the textile processes. After RO, the effluent is almost completely softened and free of color and surfactants, while maintaining constant quality.

Nevertheless, the main drawbacks of membrane processes are the high cost of the membranes and the possible problems with the disposal of concentrated retentate. Moreover, it should be noted that despite their advantages, membranes are always sensitive to fouling. Careful designing of the pretreatment step (coagulation, sand filtration, and disinfection) is crucial to guarantee good and constant membrane efficiency.

Therefore, membrane separation should be combined with other processes such as biological (active sludge) or oxidative and photo-oxidative ozonation and/or UV adsorption. Integrated systems are very promising, combining the selective and efficient separation of valuable constituents from the water with the destruction of undesired refractory components. Membrane separation processes with oxidation or bioconversion methods are the most promising environmental technologies, indeed being announced by the Environmental Technologies Action Plan (ETAP) for the coming seventh frame program of the EU countries. Good results can also be achieved by a combination of membrane processes with coagulation, precipitation, adsorption, and ion exchange for the recovery and reuse of water from textile effluents.

The separation system based on UF and RO and ozonation for the purification of wastewaters aimed at their reuse has been described by Ciardelli *et al.* [75]. The effluent from dyeing and finishing plants, after activated sludge oxidation, was treated by means of sand filtration, followed by a separation in a UF membrane module. The last separation step, RO with recovery 60% and 95% reduction of salt content and with practical absence of COD and color, therefore can be reused without problems. The quality of water at present used in the textile wet process, drained from wells and in part softened, is worse. Therefore, the permeate produced could be reused in all the production steps, including the most demanding ones concerning water quality such as dyeing with light coloration. Ozonation can be applied successfully for the treatment of the retentate produced by NF of biologically treated textile effluents, reducing the hardness of the filtered solution.

For water recovery, from reactive cotton dyeing the membrane-based integrated systems can be organized as a combination of NF and RO and adsorption. It is advisable to separate the process water into two water types: dye bath for the first rinse and rinse circulating water. The dye bath can be reclaimed by adsorption of the dyestuff and COD on activated carbon, and the reuse of the reclaimed dye bath, including salts. The economic value of the salt content of the dye bath is equal to the cost of reclamation, rendering the solution economically feasible. Recipes for rinsing can be altered to leave out dispersing and complexing agents completely, provided that pretreatment is well performed and that soft water is used for the rinse. The rinse water can be reclaimed by membrane filtration in the NF and RO range and reused for rinsing purposes. Feasibility study on the combination of coagulation and NF to reuse wastewater of a printing, dyeing, and finishing textile industry [76] resulted in COD reduction

below 100 mg l^{-1}. Salt rejection and permeate flux rates were dependent basically on feed pressure.

UF with a flocculation and ozonization integrated system was applied for the treatment of textile wastewaters from a printing, dyeing, and finishing textile plant [77]. In this case, the quality of the effluents is suitable for reuse in all phases of the textile process. In particular, constant UF permeate values were guaranteed.

Secondary effluent coming from a biologically activated sludge plant was treated with sand filtration, MF, and NF. In this case, also the quality of the effluents is suitable for reuse in all phases of the textile process with a limit of 50% recycled water. In both case studies, no significant variations in the hydraulic and mechanical parameters of the membrane processes were detected, indicating the importance of the efficiency of the pretreatment to reduce membrane fouling. Secondary effluent after the biological treatment [78] of textile wastewater was also treated with NF and ozonation for its reuse in the industry. A high COD removal was achieved by chemical oxidation with ozone and with ozone/UV; nevertheless, the oxidation does not reduce water conductivity. Thus, the reuse of the treated water is not possible. However, the advantage of this technique in comparison with NF is that there is no reject stream generation.

The use of a photocatalytic process in the presence of TiO_2 degrades many different types of dye chemicals, mainly nonbiodegradable organic substances in the effluent treated by the biological treatment process. It can also remove the color from the effluent completely. TiO_2 sensitized by photo-oxidation has been intensively studied and proved capable of oxidizing most organics, but the separation of TiO_2 after photoreaction is a major problem. TiO_2 can be immobilized on some carriers to enhance its separation from water after reaction; however, obviously, the productivity efficiency of the reaction depends on the surface revealed by catalysts being inversely proportional to the particle size. Therefore, the use of powder is more efficient. Suspended TiO_2, powder used as catalyst in photo-oxidation can be separated from slurry by a membrane cross-flow MF process and recycled to the photoreactor continuously. This photo-oxidation/MF integrated system can be very efficient.

4.05.2.2 Tannery Industry

Global usage of water in tanneries is 200–350 ml m^3 yr^{-1}. Moreover, the highly polluted effluents are derived in a quantity of the same order of magnitude. There are many references concerning the impact of the tanning industry on the environment, standards and regulatory limits, Intergovernmental Panel on Climate Change (IPPC) [79] with best practices [80], and available technologies [81]. However, tanneries are still one of the major sources of water pollution. During the tanning process, at least about 300 kg chemicals (lime, salt, etc.) are added per ton of hides. Tanning is the process of making leather from animal skins or hides (from bigger animals). The raw skins are taken directly from abattoirs to the tannery in their fresh condition, and immediately processed. The process of dressing up animal skin/hide into leather consists of three main stages: pre-tanning (beamhouse operations), tanning or tanyard operations, and wet finishing or post-tanning. The specific steps are listed in **Table 2**.

Table 2 Leather production stages

Operation	*Main wastes generated in textile manufacturing*
Preservation	Water, BOD, COD, salts, bactericides, insecticides
Soaking	Water, BOD, COD, alkali, enzymes, surfactants bactericides, insecticides
Unhairing, liming	hydrogen sulphide, gas, hair, sodium sulphide, lime hydrate sludge, BOD, COD, ammonia, organic N, alkali,
Lime fleshing, trimming, splitting	Lime fleshings, trimmings, BOD, COD, ammonia, organic N, alkali, sodium sulfide
Deliming, Bating	Ammonia, BOD, COD, sulfate acids, enzymes
Degreasing	Solvents or surfactants, greasy residues, BOD, COD
Pickling, tanning	BOD, COD, SS, acids, chromium, salts, fungicides, vegetable or other tanning agents, masking agents.
Retanning dyeing fat liquoring	BOD, COD, chromium, vegetable tanning agents, syntans, retanning neutralizing agents, dyes, fat liquor.
Finishing	Solvents, residues of dyes, pigments, and binder agents

The first stage, pre-tanning (beamhouse operations), involves the preparation for tanning where the skins or hides are washed, alkali-treated to remove hair and natural fat, and acidified to prepare for tanning. Beamhouse operations comprise several steps for conditioning and cleaning skins and produce the greatest part of the effluent load. Beamhouse operations include soaking, liming, unhairing, fleshing and trimming, deliming and bathing, and pickling and degreasing.

Soaking (at pH = 6–10, t = 10–30 °C) enables raw dry hides to regain their normal water content and to open the contract fibers of the dried skins and remove undesired substances such as dirt, manure, blood, the denatured proteins, and preservatives (sodium chloride and bactericides). The most important pollutants in the exhausted bath of the soaking effluents are salt, hide surface impurities, dirt, and protein substances. They are sent to a water treatment plant. The typical pollution load of soaking effluents in conventional processing includes the following: total suspended solids (TSS) = 11–17, COD = 22–33, BOD = 7–11, NH_3^-N = 0.1–0.2, total Kjeldahl nitrogen (TKN) = 1–2, Cl^- = 85–113, and SO_4^{-2} = 1–2. The average water consumption of soaking is 7– 9.2 $m^3\,t^{-1}$ rawhide.

Liming, unhairing, fleshing, and trimming (pH = 12.5–13, t = 10–25 °C) enable the tissue of epidermic matter including hair, proteins, degradation and elimination of mucoids, and swelling of the derma to be removed. After skinning at the slaughterhouse, the hide usually contains excessive meat and therefore fleshing is carried out before unhairing and liming. Lime, sodium sulfide, or sulfydrate is used to obtain unhairing, which is done by chemical dissolution of the hair and tissues in a bath. Sulfides, lime, decomposed hair keratin, globular protein, and other noncollagen protein, as well as saponified fractions of native fat, constitute the load of liming effluents making them the most polluted wastewater streams. Liming and unhairing produce a high COD effluent stream between 9 and 15 $m^3\,t^{-1}$ rawhide. A typical pollution load ($kg\,t^{-1}$ rawhide) in liming effluents, including washing waters in conventional process, is the following: TSS = 53–97, COD = 79–122, BOD = 28–45, S^{2-} = 3.9–8.7, NH_3^-N = 0.4–0.5, TKN = 6–8, Cl^- = 5–15, and SO_4^{2-} = 1–2.

Deliming and bathing (pH = 6–11, t = 20–35 °C) enable the removal of excess lime and hair residues together with the degradation of proteins. During this process, hair roots and pigments are removed. Skins are then neutralized in a bath containing salts derived from a strong acid and a weak alkali (mainly ammonium salts) together with proteolytic enzymes, to open the fibrous structure of derma and to increase the softness of the skins. This produces the major part of the ammonium load in the effluents. Calcium salts (mainly sulfates), sulfide residues, degraded proteins (collagen and hair), and residual proteolytic enzymatic agents constitute the main pollution load of deliming and bathing effluents. Typical pollution load ($kg\,t^{-1}$ rawhide) of deliming and bathing effluents includes the following: TSS = 8–12, COD = 13–20, BOD = 5–9, S^{2-} = 0.1–0.3, NH_3^-N = 2.6–3.9, TKN = 3–5, Cl^- = 2–4, and SO_4^{2-} = 10–26. Average water consumption of deliming with bathing is 7–11 $m^3\,t^{-1}$ rawhide.

Pickling (pH = 4, t = 20–35 °C) increases the acidity of the hide to a pH value of 3 by the addition of acid liquor (sulfuric, chloridic, formic, and lactic) and salts (sodium chloride, sodium sulfate, and salts of the acid used), enabling chromium salts to enter the hide. Salts are added to prevent the hide from swelling. Fungicides and bactericides are usually applied in a dose of 0.03–2% weight for preservation. Pickling effluents contain a very high concentration of chlorides (~10 $kg\,m^{-3}$), which causes a considerable problem for the biological plants.

Degreasing may be performed together with soaking, pickling, or after tanning to remove fats by leaching with organic solvents or surfactants. Organic solvents lead to a higher COD value in the effluent and they can cause problems in biological treatment plants of wastewaters [82–85].

The second stage, tanning or tanyard operations (pH = 3.2, t = 20–35 °C), involves the actual tanning, which is always accompanied by other chemical treatments. There are two possible tanning processes: chrome tanning and vegetable tanning. Chromium basic sulfate is the most widely used tanning substance. The process of chromium tanning is done after pickling; when the pH value is low. It is performed to protect leather against its decay, bacteria, and high temperature. It is based on the crosslinking of chromium ions with free carboxyl groups in the collagen. To fixate the chromium, the pH is slowly increased through the addition of a base. The chromium-tanned hide contains about 2–3 wt.% Cr(III). The exhausted bath from chromium tannage contains about 30% of the initial salt and it is sent to a cleaning-up plant where chromium salts create serious problems.

Chromium recovery from exhausted tanning baths is very important for the leather industry in

terms of its reuse and for the simplification of the polishing process of global wastewaters. The environmental impact of chrome (Cr) discharged from tanneries has been a subject of extensive scientific and technical dispute. Cr(VI) compounds are responsible for the majority of health problems associated with all chromium compounds. Normally, during the tanning process, only Cr(III) salts are used. Nevertheless, under certain conditions, Cr(III) can be transformed into Cr(VI), which is carcinogenic. Many studies report that effluents from the tanning industry often negatively affect human life, agriculture, and livestock. Residents, especially tannery workers, have been the victims of this pollution, which has led to severe eye diseases, skin irritations, kidney failure, and gastrointestinal problems. According to the World Health Organization (WHO) standard, the acceptable amount of chromium in drinking water is $0.05\,mg\,l^{-1}$. The groundwater around tanneries has been polluted with chromium up to 5 times the WHO standard, with a varying depth of up to 165 m. Limits on total chrome discharge in effluent vary widely between 0.05 and $10\,mg\,l^{-1}$ for direct discharges into water bodies and 1 and $50\,mg\,l^{-1}$ on indirect discharges into sewage systems. The traditional method for chromium recovery is based on the precipitation of chromium salt with NaOH followed by the dissolution of $Cr(OH)_3$ in sulfuric acid. However, the quality of the recovered solutions is not always optimal owing to the presence of metals, lipid substances, and other impurities. Chrome, chlorides, and sulfates are the main pollutants. A typical pollution load ($kg\,t^{-1}$ rawhide) of the chrome tanning effluents in a conventional process includes the following: TSS = 5–10, COD = 7–11, BOD = 2–4, $Cr^{2-} = 5$, NH_3^-, N = 0.6–0.9, TKN = 0.6–0.9, $Cl^- = 40$–60, and $SO_4^{2-} = 30$–55. The average water consumption of tanning is 3–$5\,m^3\,t^{-1}$ rawhide.

Vegetable tanning is usually accomplished in a series of vats with increasing concentrations of tanning liquor. Vegetable tannins are polyphenolic compounds of two types: hydrolyzable tannins (i.e., chestnut and myrobalan), which are derivatives of pyrogallols, and condensed tannins, which are derivatives of catechol. In some cases, as much as 50% by weight of tannin is incorporated into the hide.

The third stage, post-tanning, which finishes the surface, entails dyeing, fatliquoring, and filling up the fiber structure in wet conditions to obtain the proper filling, smoothness, and color. Before actually drying, the surplus water is removed to make the hides suitable for splitting and shaving. Splitting and shaving are done to obtain the desired thickness of the hide.

The composition of pollutants in the wet finishing effluent is complex due to the presence of dyes, fat liquors, and combined tanning agents, but the total amounts generated are smaller than in the previous steps. Chrome, salts, dyestuff residues, fatliquoring agents, syntans (to improve tearing resistance), vegetable tannins, and other organic matter, typically measured by COD, are the main pollutants. As for the chrome pollution generated in post-tanning operations, about 50% of the chromium emanates from retanning, while 20% is leached during dyeing and 30% during fatliquoring. Under normal conditions, a load of 0.03–0.05 kg Cr/t rawhide has been observed. A typical pollution load (in $kg\,t^{-1}$ raw hide) of effluents, including washing waters from post-tanning operations in conventional processing, is as follows: TSS = 6–11, COD = 24–40, BOD = 8–15, Cr = 1–2, $NH_3^-N = 0.3$–0.5, TKN = 1–2, $Cl^- = 5$–10, and $SO_4^{2-} = 1$. The average water consumption of post-tanning is 7–$13\,m^3\,t^{-1}$ rawhide.

Finishing (pH = 4–10, t = 20–60 °C) of the outer layer after retanning and drying is performed in a number of finishing operations. The purpose of these operations is to make the hide softer and to mask small mistakes. The hide is treated with an organic solvent or water-based dye and varnish. The finished end product has between 66% and 85% by weight of dry matter. Environmental aspects are mainly related to the finishing chemicals, which can also reach the effluent water. The finishing pollution load ($kg\,t^{-1}$ rawhide) discharged in effluents is not significant in terms of influence on the total pollution load from tannery effluents. The pollution load can be summarized as follows: TSS = 0–2, COD = 0–5, and BOD = 0–$2\,kg\,t^{-1}$. The average water consumption of finishing is 1–$3\,m^3\,t^{-1}$ rawhide.

The following treatment steps are typical and are frequently used in conventional tanneries which use three main treatment steps: mechanical treatment, effluent treatment, and post-purification, sedimentation, and sludge handling.

Mechanical treatment is usually the first treatment of the raw effluent, which includes screening to remove coarse material up to 30–40% of the gross SS in the raw waste stream. Mechanical treatment may also include the skimming of fats, grease, oils, and gravity settling. After mechanical treatment, physico-chemical treatment is carried out, with the chrome precipitation and sulfide treatment,

coagulation, and flocculation being also part of this treatment to remove a substantial percentage of the COD and SS. It is common practice to keep sulfide-containing effluent from the beamhouse separate and at a high pH until the sulfide is treated, because at a pH lower than 9 the formation of toxic hydrogen sulfide (H_2S) gas can occur. The sulfides in the deliming and pickle liquors can easily be oxidized in the drum by adding hydrogen peroxide, sodium metabisulfite, or sodium bisulfite. Where segregation of sulfide-bearing liquors is not possible, the sulfides are generally removed by means of precipitation with iron(II) salts and aeration. A disadvantage of this precipitation is the generation of high volumes of sludge. The levels that can be achieved in treating the mixed effluent are – depending on the mixing rate – 2 mg S^{2-}/l and 1 mg total Cr/l (e.g., if 50% of the mixed effluent consists of the sulfide-bearing effluent).

Post-purification, sedimentation, and sludge handling are the last steps in wastewater treatment. With sedimentation, the sludge in the wastewater treatment plant is separated from the water phase by gravity settlement. Up to 40% dry solids can be achieved after dewatering this sludge. The belt presses produce a sludge cake with up to 20–25% dry solids, centrifuges achieve up to 25–45% dry solids, and thermal treatment up to 90% dry solids. Energy is an important factor in these processes.

Reusing spent tanning floats in batch cycles is mostly required in tanning processes. According to the extent of their use, an increase in chrome utilization from 70% up to 95% and a decrease in chrome discharge from 2–5 kg t^{-1} to 0.1–0.25 kg t^{-1} rawhide should be considered. Reusing systems also decrease the sulfate load in effluents and according to the extent of their use, a decrease from 30–55 kg t^{-1} to 10–22 kg t^{-1} rawhide can be attained. Chrome recovery may be economical but the maximum payback period for installing a chrome recovery unit is 1.6 years [79].

Secondary treated tannery wastewater contains high concentrations of total dissolved solids (TDS) and other residual organic impurities, which cannot be removed by conventional treatment methods of filtration, stripping, or redox processes [86]. Some polluting components from tannery industry often do not fall within the regulatory limits. These solutions have a high salt concentration, exceeding the regulatory limits, for their discharge into a public sewerage; therefore, membrane processes may be the best solution.

Manufacturing of leather produces numerous by-products, solid wastes, and high amounts of wastewater containing different loads of pollutants and emissions into the environment. The uncontrolled release of tannery effluents to natural water multiplies the health risks for human beings and environmental pollution. Effluents from rawhide processing tanneries, which produce wetblue, crust leather, or finished leather, contain compounds of trivalent chromium (Cr) and sulfides in most cases. Almost all tanneries (80–90% of the tanneries worldwide) use Cr(III) salts in their tanning processes. In some parts of the world, the Cr(III) is obtained from Cr(VI) species, which are 100 times more toxic, but generally, tannery effluents are unlikely to contain this form. Organic and other ingredients are responsible for high BOD and COD values and represent an immense pollution load, causing technical problems, inducing sophisticated technologies and high costs regarding effluent treatment in leather production. The unutilized chemicals end up in the wastewater, contributing to a considerable amount of pollution. A typical list of chemicals used in tanning can be divided into three groups representing major, moderate, and minor potential hazards. The highest potential hazard group is comprised of:acetic acid, ammonia, calcium hydroxide, formaldehyde sulfuric acid, formic acid, glutaraldehyde, hydrogen peroxide, hydrochloric acid, muriatic acid, hydrosulfide (calcium hydrosulfide), sodium chlorite, sodium hydroxide (caustic soda), sodium sulfide, other sulfides and hydrosulfides, spirits, and oxalic acid. The moderate potential hazard group is comprised of: aluminum sulfate, amyl acetate (as lacquer constituents), amyl alcohol (as lacquer constituents), benzyl alcohol (lacquer solvent) carbon black, chromium salt (trivalent) enzymes, isopropyl alcohol perchloroethylene toluene, and white spirit. The lowest potential hazard group is made up of alums oils, acetone, albumen ammonium chloride, ammonium sulfate, borax, boric acid, casein, calcium chloride, castor oil china clay, ethanol (ethyl alcohol), fat liquors, fats, ferrous acetate, ferrous sulfate, gelatin, glues (for some glues may contribute to toxicity), lactic acid, lanoline, vegetable tanning extracts, lecithin waxes, paraffin, pigment dispersions, sequestering agents, silicones, sodium acetate, sodium citrate, sodium carbonate, sodium formate, sodium metabisulfite, sodium nitrite, sodium phthalate, sodium sulfite, sodium thiosufhate, solvent synthetic tannins, titanium salts, and wetting agents. Because of wide variations in potential toxic hazard, it is not

possible to categorize dyestuffs or fungicides into any single hazard group. Dyestuffs may vary widely in toxicity from potentially quite serious, if inhaled or ingested, to nontoxic. Biocides are used in tanneries to control the growth of various forms of life on the leather (e.g., TriNap 40).

The general advantages obtained from the introduction of membranes into operating steps of leather manufacture are the recovery and reuse of primary resources, which reduce the environmental impact, simplify the polishing processes of wastewater, and facilitate easy reuse of sludge, a decrease in disposal costs, a saving of chemicals and water, and a saving of direct and indirect energy. Membranes may be used for fractionation of these components, purification to the required level, and their concentration [87]. MF can perfectly reduce TSS, UF reduces all macromolecules and colloids, and NF reduces multivalent salts; RO is able to reclaim water to any required purity. PV can effectively remove and concentrate VOCs in pure form. The only problem is the economics of these operations. Membranes are still very expensive and replacement costs can be high. The integrated membrane processes permit the tanning cycle to be rationalized, realizing the recovery and the recycle of several chemicals utilized in the tanneries. A reduction of environmental impact, a simplification of cleaning-up processes of wastewaters, an easy reuse of sludge decrease of disposal costs, and saving of chemicals and water and of direct and indirect energy are some advantages from the above-described membrane operations. Possible membrane applications in specific tanning operations are presented in the following.

UF can be used to reuse the permeate in the pretanning steps or in the tannage, adjusting the tannin concentration to the desired value. Large quantities of insoluble substances in the retentate make this solution unsuitable for reuse. On polysulfone and ceramic membranes, more than 55% reduction of the COD and 75–80% reduction of color were obtained during the process. Four times higher concentration values were reached. In this case, a water washing, followed by an alkaline washing (pH 11), gave a good restoration of the initial flux [88]. Experimental tests on a pilot plant equipped with inorganic UF tubular membranes were carried out on the exhausted bath of tanning substances (chestnut, mimosa, and quebracho) according to a concentration operation mode.

UF can also be used in the soaking step to recover the water; however, preliminary treatments are necessary in order to remove the suspended materials. For instance, sedimentation permits the reduction of SS by 90%; then, steel spring filters (200–300 μm net size) could be employed to remove large particles avoiding clogging of the membranes. Subsequently, the organic components can be concentrated in the feed tank of the UF plant and discharged. Clear, salt-rich permeate could be reused in the pickling step after the adjustment of the salt concentration by NaCl. The recycling of freshwater and salt and the saving on wastewater cleaning-up cost should result in lower costs as compared to similar applications in other fields.

The application of UF to liming–unhairing effluents – which are highly polluting owing to the presence of sulfide, amines, by-products coming from degradation of hair and epidermis, and a high concentration of alkalis [89, 90] – enables water recovery in the permeate, sulfide, and solubilized lime containing low-molecular-weight proteic substances. This aqueous solution can be reused for the preparation of a new liming bath. The higher-molecular-weight components are concentrated in the UF retentate stream. UF membranes permit one to obtain a rejection to proteins of 60–85%, rejections to sulfides of 2%, and more than 85% to proteic and colloidal substances [90–92]. The classical unhairing–liming treatment, integrated in the membrane system, allows some benefits to be achieved related to a significant saving of chemicals (sulfides and auxiliary products) and water and to a reduction in wastewater treatment problems (COD reduction of about 30–35% in the global waste) by decreasing organic and inorganic substance concentration in the exhausted bath. UF can be used for sulfite recovery in the unhairing–liming step. MF as a pretreatment may be used in order to remove the coarse particles and colloidal lime present in the exhausted bath [84]; however, this stream must be previously screened on a coarse screen to remove and recover the hair detached from the skin and then forwarded to a UF module. Assuming for the UF step (characterized by a membrane rejection to sulfides of about 2%) a loss of 5–10% in the retentate stream, the amount of sulfide that is possible to recover with a UF system is about 55–60%. The possible recovery of water is about 70%. Application of enzymatic treatment combined with the UF plant instead to a classical unhairing–liming operation offers the economical and energetic benefit. This solution allows one to obtain both a significant reduction of sulfides (and auxiliary compounds) by substitution of a

relative small amount of enzyme (about 1% with respect to the weight of dry leather treated [85]), and a chemical recovery in the permeate stream (about 55–60%).

UF may be used in deliming operation to reduce the polluting load of the exhausted liquor, enabling a considerable reduction of fatty substances and COD in the permeate. Then, the permeate can be reused for the preparation of new bating baths or as washing water.

RO may be used for the treatment of exhausted liquor coming from the pickling, after an appropriate pretreatment, in order to recover the salt component in the retentate. The recovered solution could be reused in the pickling after adjustment of salt concentration to optimal level. The permeate solution could be employed for the preparation of soaking baths or as washing water. Some results on pressure-driven membrane operations, able to desalinate water discharged from filter press alter Cr^{3+} precipitation. Good rejection of RO membrane to chloride and sulfate ions suggested the use of this operation for obtaining water, to water reuse (including washings), or to send to biological treatment of final wastewater.

UF may be applied for the removal of fatty substances from degreasing bath, enabling reduction of washing cycles normally employed to remove the lipid substances from skins and, consequently, of water consumption. The rejection of membrane to COD and fatty substances with reference to initial feed is about 95%. Depending on hours of use per day of the UF plant, the payback period, as compared to other similar applications, should range between 1 and 4 years. A typical degreasing step requires a consumption of about 0.5 g of surfactants for each kilogram of treated leather. Using a UF plant to treat the exhausted bath from the degreasing operation, it is possible to obtain a good recovery of surfactants. These could be recycled to the degreasing step with a reduction in raw material cost. Furthermore, the reuse of fatty components from the retentate stream after some chemical and physical treatments, in the fat liquoring step, which can give a drastic reduction of the wastewater treatment costs, enables water to be recovered and reused in the another steps.

Membrane processes such as RO, NF, and UF could be employed to increase the tannin/nontannin ratio of the exhausted bath in order to promote their recycle. RO of chromium Cr^{3+} [83, 94] showed high salt concentrations in the final retentate, which suggested its possible reuse in the pickling step. The use of an NF membrane could be suitable for the separation of salt components from tannins. NF membranes retain tannins, whose molecular weight is 300–800 Da, or higher, as at higher tannin concentration they form molecular aggregates. By recycling the exhausted liquor in the feed tank (batch operation mode), it is possible to obtain a concentrated solution that could be reused in the tanning process and a permeate with a low organic content that could be sent to a treatment plant of final wastewaters. The removal of chromium may also be attained by using a combination of the UF and NF processes [95]. The UF membranes remove the SS components and fat substances giving rejections of 84% and 98%, respectively, with reference to initial feed. About 40% of organic nitrogen can be retained by the UF membrane, while the rejection for chromium approaches 28% [96]. In order to recover a tanning or retanning solutions the permeate coming from UF must be processed in a pilot plant equipped with an NF membrane where chromium rejection reaches 99.9%. The organic substances (as COD) are less retained with respect to chromium as shown by the increased concentration ratio of chromium/COD in retentate. Chromium concentration reached in the retentate (1.35% as Cr_2O_3) allows one to reuse the solution in the retanning step. A further concentration of the solution using a precipitation–dissolution method permitted one to obtain a solution (9.2% as Cr_2O_3) that can be reused as such in the chromium tanning. Another advantage of this process is the possibility to reuse the permeate in pickling step, considering the high chloride concentration of this solution. The recovered chromium solution can be used in tanning (after further concentration) and retanning processes.

The biological treatment of tanning wastewater can be coupled with a UF process in membrane bioreactor that permits biodegradation, cleaning-up, clarification, and disinfection. The bioreactor is constituted by an oxygenated feed tank in which the dissolved organic substances are decomposed by microorganisms in nitrogen, water, and carbon dioxide. The biomass is separated from the effluent by membrane and recycled in the feed tank. With this treatment, high-molecular-weight substances are rejected by the membrane and they can be further decomposed. The biomass concentration in the system can reach values 10 times higher than those obtained in conventional plants.

The membrane systems can be successfully applied for recovery of water from secondary treated tannery effluent, provided a suitable and effective pretreatment system prior to membrane is employed. In order to reuse water from tannery wastewater, the system comprising oxidation, NF, and RO membrane units, accompanied by several pretreatment operations, may be used [86]. Wastewater is prefiltered in sand filter and treated by photochemical oxidation (PCO). The next step is activated carbon filter (ACF), ion-exchange softener, and polypropylene cartridge filter 5 μm. Softener unit contains strong acids and cationic resins. Nanofilter with a pore size of 10 Å gives permeate which is sent to the RO unit. The maximum TDS removal efficiency of the polyamide membrane is more than 98% and the permeate recovery of about 78%. The water recovered from the membrane system, which had very low TDS concentration, is reused for wet finishing process in the tanneries. Combining nanomembranes and RO membranes improved the life of the membranes and high permeate recovery rate.

The application of RO for recovering hot water, colorants, and auxiliaries is an interesting approach already employed in the textile industry [97]. It could be successfully applied in the dyeing operation considering that the chemical characteristics of the feed solution are very similar to those measured on the dyeing solutions of the textile industry. In this sense, the RO could permit to recover dyeing substances in the retentate stream. The permeate solution could be reused as washing water or for the preparation of new dyeing baths.

4.05.2.3 Pulp and Paper Industry

Paper manufacturing sector comprises pulp mills, paper mills, and paperboard mills. Approximately 10–15 m^3 of effluents per ton of pulp [98] are produced and the presence of more than 250 different chemicals has been identified in these effluents [99] with 2500 $mg\,l^{-1}$ COD. Freshwater consumption is within the wide range 5–400 $m^3\,t^{-1}$, depending on technology. This must cover effluents the same order of magnitude and water in solid waste and evaporation ($\sim$1 $m^3\,t^{-1}$). The effluents contain biologically inactive substances that have major environmental impact, for example, toxicity and light-absorbing characteristics that influence the light-penetration properties of water, thereby inflicting death to most water-living organisms.

During treatment of paper mill effluent in mechanical pulping, process water is contaminated with dissolved and colloidal matter and also contains fiber fines and inorganic matter. In relation to the amount of pulp produced, effluent from production may cause a higher COD in the effluent than a kraft pulp mill. Mechanical pulping is often integrated with paper production. Therefore, the effluent to be purified and recirculated also has varying characteristics. The water reuse is carried out in many plants. Techniques that are conventionally used to treat wastewaters include aerobic and anaerobic treatments, lime and alum coagulation and precipitation, oxidation, and adsorption onto ion-exchange resins [100].

The IPPC directive gives a technical guidance for the pulp and paper sector [101] in general principles: "...waste reuse or recovery can prevent waste emissions" or "...recycling benefiting particularly from the integration of other activities with papermaking... "further motivation for recycling is to conserve process temperatures." This was putted also in detailed remarks concerning water reuse in pulp and paper sector, concerning for instance: water circuits for mechanical pulping, water circuits for chemical pulping and bleaching, water circuits for de-inking.

In bleaching plants, it is useful to recirculate the filtrates that use chlorine-containing chemicals back into the mill's process water system. The filtrate must then be treated in some auxiliary equipment, in which purified water is separated. However, recycling of bleaching effluents has the following main problems and also some risk from higher concentrations: accumulation of chlorides and nonprocess elements (NPEs) and the presence of strong chelating agents, such as citrate, tartarate, ethylenediamine-tetra acetic acid (EDTA), and diethyilenetriaminepenta acetic, which may also lead to lower quality of the product, for example, lower brightness and strength of the paper. Slime and deposit formations, scaling leading to blocking of pipes, shower nozzles, wires and felts; plugging, corrosion, problems, for example, buildup of chlorides, increased the consumption of process chemicals. Evaporation also has the problem of disposal of concentrates. The quality of the conventional biological treatment of wastewaters is not sufficient enough for reuse as process water.

Recovery of inorganic chemicals from kraft process-based black liquor (BL) is an integral part of pulp and paper industries. In the conventional process, BL from digester is concentrated in the multiple

effect evaporators and in direct contact evaporators from 100–150 kg m^{-3} to around 600 kg m^{-3} concentration. In many cases, the concentrated liquor is then incinerated in a furnace where organics (mostly lignin-based compounds) are burned and the smelt is then lixiviated and causticized to recover around 85% of inorganics [102]. The energy surplus of a modern pulp mill can amount to 7 GJ [103] per metric ton of pulp. In a mill that produces 2000 tons per day, this corresponds to 160 MW of heat. This energy surplus can be used to produce electricity or it can be exported from the mill as a solid or liquid biofuel. This fuel can replace fossil fuels in heat production, thus reducing the emission of greenhouse gases. The most promising fuel in this respect is lignin in BL.

The conventional recovery process involves the following major drawbacks [104]: substantial capital and energy investment in the evaporators and extensive loss of water. Taking these disadvantages into account, most of the small-scale paper industries, which have black liquor (BL) of concentration (in terms of TDS of the order of TDS 10–80 kg m^{-3}), discard the liquor as it is, or after some partial treatment, to river stream. This leads to severe water pollution, especially to those areas where pollution control rules are not strictly adhered. In order to overcome the disadvantages encountered in the conventional treatment processes for BL, constant research efforts are made to look for alternative treatment methods. When lignin is extracted from the BL, high-value cooking chemicals have to be recovered and returned to the process. This means that the economy of the separation process is highly dependent on the selectivity of the process.

Wastepaper processing is a very important part of paper manufacturing and more than 50% of the paper is produced from wastepaper. The main problem in wastewaters from this technology concerns the removal of the ink. The use of recycled wastepaper can have numerous environmental and operating benefits compared with the various virgin pulp production methods. It has been estimated that every ton of paper, if made from 100% recycled wastepaper, saves 24 trees. One ton of pulp made from deinked and bleached wastepaper requires 60% less energy to manufacture than does a ton of bleached virgin kraft pulp. Other benefits of wastepaper recycling are correlated with reduced capital and operating costs, reduced cost of purchase of raw material, reduced costs of energy and chemicals used, with the decrease in BOD5 load of the effluent, decrease of effluent volume, decrease of odor and carbon dioxide emissions, extension of municipal landfill life, reduction of landfill disposal fees, and the flexibility of the mills to sell to customers who prefer or need recycled paper. In the near future, it is expected that a significant amount of wastepaper recovered from municipal solid wastes will be used for this purpose, while printed wastepaper will increase in value as a raw material for better grades of paper, if the deinking technology is sufficiently developed.

The wastepaper recycling process includes the following four basic stages:

1. pulping of the wastepaper, which includes the defibering and dispersion of the inks and other contaminants,
2. deinking of the pulp by separation and removal of dispersed ink particles from the pulp,
3. bleaching of deinked pulp, and
4. treatment of the effluents and reuse.

Two principal deinking systems have been conventionally adopted by the paper industry, for example, flotation deinking and wash deinking.

Flotation deinking is extracting ink by foam generated in dispersed air flotation cells, mineral fillers and paper fines are not removed from the pulp; therefore, the yield is high but the physical strength of the deinked stock is poor. During the wash deinking, the ink, mineral fillers, and fiber fines are washed out at high dilution and papermaking fiber of good quality is obtained at the expense of a lower yield. In many cases, the deinking mills use various combinations of both systems [105]. Modern wash deinking technology consists of a careful matching of deinking equipment and chemistry. The performance of wash deinking systems greatly depends on the type and concentration of the deinking chemicals [106, 107]. Chemicals used are also important in the light of water management in this technology. The chemistry plays a great role in the following: swelling of the fibers, ink removal, wetting, dispersion, avoiding the redeposition of the inks upon the fibers, coagulation/sedimentation, and flocculation. The corresponding dosages of the chemicals usually used in wash deinking processes (added during pulping prior to washing as weight % on the oven dry fiber stock) and their function on the process include the following [108]: sodium hydroxide ($0 \pm 5\%$) for fiber swelling, ink breakup, saponification, and ink dispersion; hydrogen peroxide ($0 \pm 3\%$) for bleaching; sodium silicate (0–6%) for wetting, peptization, ink dispersion, buffering, and peroxide stabilization; sodium or

potassium phosphates (0–1%) for metal ion sequestration, ink dispersion, buffering, and peptization; sodium carbonate (0±5%) for buffering and water softening; chelating agents, such as diethylene triamine pentaacetic acid (DTPA) or EDTA, for metal ion sequestration; surfactants (0.2–1%) for ink removal, dispersion, wetting, emulsification, and solubilization; solvents (0–2%), such as C9–C14 aliphatic saturated hydrocarbons, for ink softening and solvation; and hydrophilic polymers (0–0.5%) or bentonite clays (0±3%) for ink dispersion and hindrance of ink redeposition. The wash-deinking effluent contains the chemicals used in washing, as well as the dispersed inks, the fillers, and the fiber fines. For each ton of deinked pulp produced, for example, from waste newspapers, the following quantities of wastes are approximately produced: 165 m^3 of wastewater, 20 kg of soluble BOD5, 54 kg of soluble COD, and 280 kg of sludge [109].

A high amount of water is needed in the deinking process with the great environmental impact of the effluent. Water recycling in a paper mill can have beneficial effects to the environment protection efforts; since the freshwater consumption minimizes, the chemical additives and energy cost decrease [110–112]. The wash-deinking effluent after its clarification is ready to be recycled back to the process. The clarified effluent may also be biologically treated prior to its recycle. Theoretically, the recycling ratio of sufficiently treated effluents can reach almost 100%; however, in fact, there is an upper limit because of the necessary bleed, the high moisture of the deinked stock, and the wastewater losses associated with the sludge removal [113]. The conventional methods of water recovery by deinking comprise chemical and biological steps.

Clarification of the chemically treated deinking effluent is assisted by coagulation and flocculation caused by the treatment of the effluent with polymers and sometimes with alum and lime. Bentonite clay used in conjunction with either polymers or alum has been suggested as an effective flocculent for such a treatment [114, 115]. There are two different processes that are conventionally used for the clarification of the chemically treated deinking effluent: dissolved air flotation (DAF) and sedimentation by gravity. The consistency of the sludge produced by the first process varies from 2% to 5%, while that produced by the latter varies from 0.4% to 3%, depending on the chemical additives used either in the deinking process or in the chemical treatment stage of the effluent [116].

The feasibility of the biological treatment of the clarified effluent is challenged by its high COD/BOD5 ratio, which diminishes its suitability for such a treatment. The carbon dioxide produced during the biological treatment neutralizes part of the sodium hydroxide needed in wash-deinking stage. In addition, the application of this treatment degrades most of the organic additives used in deinking and clarification. Compared to clarification, the biological treatment is much longer and the heat contained in the effluent is lost. For these reasons, the possibilities to save chemicals and energy by the recycling of the effluent are reduced. Finally, the clarified effluent contains some substances which act as biological inhibitors. Therefore, the rate of the biological treatment may be low and, consequently, the fixed and operational costs of this treatment are increased. Due to these reasons, the degree of BOD5 decrease during clarification is of great importance, while the application of a biological treatment may not be reasonable for water reuse, as the industrial practice has already shown [117]. In the case of the effluent recycling, the characteristics of the effluent depend mainly on its clarification process and on the recycling ratio of the clarified effluent [118]. It was found that the increase of the recycling ratio from 0% to 95% increased the BOD of the effluent from 17 to 206 mg l^{-1}, the COD from 41 to 670 mg l^{-1}, the TSS from 620 to 1294 mg l^{-1}, and the conductivity from 185 to 1315 mS cm^{-1}. This clearly shows the need for implementing advanced methods of separation for the deinking process.

Closing the water and chemical circuits may be beneficial for paper technology, resulting in economical and environmental benefits as well. Closing system enables the concentrations to be elevated in the circuit which benefits in the following: the higher concentrations improve retention of solutes into the paper web (at water closures below 15 m^3 t^{-1}); results in savings in raw material costs; less solid waste (sludge) generated as a by-product of wastewater treatment; the efficiency of the water treatment plant is increased at higher concentrations; and higher concentrations reduce energy requirements for heating, pumping, and drying (because higher water temperatures lead to faster dewatering). Reducing the freshwater input, in turn, reduces the water reaching the water treatment plant and, therefore, reduces the size of a new treatment plant, saves costs where water is purchased or disposed of to another party.

To overcome the problems with recycling in pulp and paper industries, the membrane purification technologies should be applied [119]. Membrane processes and membrane-based hybrid processes are very useful for the treatment of effluents from the pulp and paper industries both for internal recycling of water and for recycling all material streams, resulting in significant water saving with reduction of costs and release of toxic pollutants to environment simultaneously [120]. Prof M. Nystrom greatly contributed to the implementation of membrane processes in paper industry, focusing on the problem of circulation of the water, for example, application of UF and NF for paper machine circulation waters [121] and makeup waters [122–124], and for internal purification [125]. A systematic study on the application of pressure-driven membrane processes such as MF, UF, and NF for white water recovery was carried out by Nuortila-Jokinen *et al.* [126]; this research aimed to find conditions and membranes which ensure high flux and good separation effects. Permeate after UF was sufficient for reuse as wire part shower water. Permeate after NF could be used directly to reuse at all points of the process. In many cases, the water is produced by different techniques and mixed to achieve the required purity level.

RO system for recovery of water from acid bleaching effluents reuse for pulp and paper industry has been proposed by Hydrometrics Inc of Helena, Montana, USA – the system was referred to as HERO (high-efficiency reverse osmosis) [127]. Extensive laboratory and plant-scale studies [128, 129] were carried out to concentrate sulfite liquor and bleach plant effluent through RO. High-purity permeate stream and high rejection of organics were observed [130].

NF usually gives a very clean permeate and the permeate could be used as press section shower water and as a one-step operation for paper mill total effluent purification [98, 131]. The nanofiltered water can be used in paper machine circulation. The results showed that some commercially available membranes have both high permeability and good retention properties at the same time. OSMONICS, PTI Advanced Filtration, FilmTec (Dow Chemical Company), Nitto Denko, Hoechst (Celgard/Nadir), Koch Membranes, Hydranautics, Trisep and Fluid Systems. NF/ED hybrid process [132–135] was used for concentration of dilute pulping wastes [136] for treatment of bleaching effluents with process water recovery, for treating bleach plant filtrates from sulfite mills [137], and white water treatment [138]. NF membranes enable over 80% retentions for COD and total carbon (TC) to be achieved and multivalent ion retention exceeds 95%. The permeabilities of NF membranes when filtering paper mill waters have been from 3–16 $l/(m^2\ h\ bar)$. UF can be used as a pretreatment stage before the spiral-wound NF module to ensure that the NF modules are not plugged; however, NF without UF as a pretreatment method could be a more economical way to internally purify the paper mill process waters and effluents [125], and the other paper mill hot condensate water [139].

UF attracted the attention of many researchers as a suitable process for the treatment of pulp and paper effluent, where most of the polluting substances consist of high molecular mass compounds [100]. UF membranes can completely retain SS, colloidal material, anionic trash, and bacterial material. UF treatment of effluent can also result in 98% removal of color, 87% removal of COD, and 44% reduction in BOD [140], and the removal of salts lower than 10% depending on the source of the effluent and the type of membrane used. Permeabilities of UF membranes using paper mill waters have been from 50 to 375 $l/(m^2\ h\ bar)$, depending on the membrane, the module, and the source of the feed water. UF was directly used for paper mill water circulation including white water [141] and also for recycling of shower waters but only in less precise operations such as cleaning the paper machine, because it still contains low molar mass compounds and in many cases it does not qualify as press section shower water. The new efficient membrane modules were elaborated for mill-scale UF applications such as treatment of bleaching effluents and white water [142–144].

UF-based hybrid systems are still developed for further searching to reduce costs and to increase the capacity and separation effectiveness because of high demands on water quality and quantity in the pulp and paper industries. UF complexation for metal removal from pulp and paper industry wastewater has been intensively explored. Water-soluble polymeric ligands have shown to be powerful substances to remove trace metals from industrial wastewater through UF. The complexation–UF process was efficient for metal removal from wastewater, leading to a better effluent quality when compared to UF without any ligands addition [119]. The ozonation, adsorption, and a sequence of precipitation + UF + ion exchange for alkaline bleaching effluents resulted in removal of 16% COD, 33% absorbable organic halides (AOX), and 40–50% color. The evaporation

with UF is effectively used, especially when energy is easily available from combustion of liquor [145, 146]. An interesting technique for recycling the water in whole paper manufacturing system has been proposed by Conox Ltd [147], which is based on evaporation, UF, and oxidation of the concentrates. To avoid accumulation of inorganic ions and low molecular organic substances, fiber fines and nonsoluble wood extractives in the process water loop, the use DAF or UF was used as pretreatment before the main water purification step.

Membranes are used in treatment filtrates from kraft pulp mills using traditional chlorine bleaching [99, 148–150], and from chlorine-free kraft pulp mills [151] as well as for treatment of paper coating color effluents [152]. They have the ability to separate high-molecular-weight lignin from low-molecular-weight cooking chemicals. In the early applications, the aim of UF was to purify valuable lignosulfonate in spent sulfite liquor in order to use it as a chemical product [153, 154]. Fractionation of cooking liquor from kraft pulp mills by membrane processes has been studied since the 1970s. UF of kraft BL enables to separate lignin [155], which results in more product output and is less energy intensive compared to RO [156]. UF was generally employed mainly for the following purposes: separation of lignin compounds from low-molecular-weight inorganics [157, 158], fractionation of high-molecular-weight lignin compounds, purification of lignins by diafiltration [159, 160], and recovery of water [161]. To produce purified high-molecular-weight lignin, UF should be operated at low pressure and high alkalinity [157]. Purity of 80–90% of lignin was reported using a combination of UF and diafiltration [162]. UF was observed to reduce viscosity of kraft BL during removing high-molecular-weight lignin; BL was then concentrated further before putting into the furnace [163]. Thus, removal of high-molecular-weight lignin by UF was found to be feasible from the operational point of view [164] and economically attractive [165, 166]. The ceramic membranes [167] should be used because the temperature of BL is high, as is the pH. In the digester, the temperature is about 150 °C and the pH slightly below 14. UF of BL was studied by Bhattacharya and co-workers [104] and Walberg [168]with a tubular ceramic membrane, with a cutoff of 15 000 Da. The fluxes were 90, 110, and 130 l m^{-2} h^{-1} at 60, 75, and 90 °C and transmembrane pressure (TMP) was 100 kPa. The lignin retention was about 30%. The high flux was also observed during concentration of the BL. The average flux during concentration to a volume reduction of 0.9 was 66 and 90 l m^{-2} h^{-1} at 75 and 90 °C, respectively. The lignin purity was increased from 36% to 78% after concentration and diafiltration. ED [169, 170] has also been used for concentration and fractionation of BL, however. With time, interest has shifted toward UF of kraft BL [165, 171, 172, 173, 174].

4.05.2.4 Metal Finishing Industry

The metal finishing industry presents one of the most crucial industrial waste problems. A large volume of wastewater is generated by the metal plating industry. The electroplating industry is also a great water consumer and, as a consequence, one of the biggest producers of liquid effluent. In the metal plating industry, drinking water is generally used in the cleansing rinse of solvent, alkaline, and acid, while de-ionized water is employed in the plating rinse and final rinse. The water in the rinsing baths becomes contaminated during the cleaning or plating process due to the drag-out from previous process baths. Electroless metal plating is a chemical reduction process that provides a uniform plating thickness on the metal surface plating part, regardless of the configuration or geometry of the part, and has several unique advantages over conventional electroplating. The drawback of this operation is the demand of high purity rinse water (10–15 MΩ cm^{-1}) after solvent cleaning, alkaline cleaning, or acid cleaning to avoid spotting or deterioration of the plated part. Rinsing waters become contaminated during the plating process due to transport of contaminants from the previous plating baths. The contaminants may include solvents, oil and grease, organic compounds, heavy metals, such as chromium, copper, zinc, lead, nickel, and iron, as well as other cations and anions, depending on the cleaning or plating process. The spent final rinse water contains a much lower level of these heavy metals and monovalent ions (measured conductivity generally <30 μS cm^{-1}).

There are many technologies used that are directed at the recovery and reuse of water. Spent rinsing wastewaters are, generally, treated by conventional wastewater treatment techniques such as oxidation–reduction and/or precipitation to produce effluents that meet standards for discharge to the sewage system. There are cases where individual rinses after plating are treated to recover heavy metals. The conventional method for neutralization/precipitation is the most commonly used method for

treating wastewater generated from metal plating industries before being discharged into the public sewer. There is therefore growing interest in developing methods for reclaiming metals from plating waste stream and recovery of water using membrane technology [175].

RO, NF, and ED are commonly used membrane processes in the metal plating industry. RO process has become increasingly attractive for the treatment and recycling of wastewater in metal plating industries as it is highly efficient, easy to operate, and low on cost. In this technology, the simultaneous water recycling [176, 177] and recovery of valuable materials are of utmost importance because precious metals are used. There are many studies in the large [178] or pilot scale [179], as well as relevant patents. Sugita [180] and Spatz [181] patented methods for recovering gold and rinsing water in an electroplating process that utilized an RO membrane for water recycle treatment system for use in metal processing. Degenkolp and Scobey patented a method and apparatus for recovery of heavy metal ions from dilute aqueous solution [182]. Martyak *et al.* [183] developed apparatus and methods for treating electroless plating baths. Griffin obtained a US patent on plating rinse water treatment [184]. This process utilized an RO membrane to separate the metal salt from a wastewater stream. The metal salt was further concentrated employing cation-exchange (CX) and anion-exchange columns. In all these cases, the treated water was recycled. RO has been used for the treatment of electroplating waste water containing copper [185]. The results presented in literature [185] show that there is 75–95% recovery of water and nearly total removal of metals in the permeate. The treated water met requirements for discharge. Low-pressure RO membrane was used for Zn^{2+} and Cu^{2+} removal from wastewater [186]. A new, high-temperature-resistant, thin-film RO membrane from Osmonics-Desal was used in the high-temperature rinsing water from a degreasing during heat-exchanger manufacturing [187]. RO was also used for the treatment of contaminated water from rinsing baths for water recycling [176, 188, –189].

RO may also be used in combination with other processes. Wong *et al.* [190] used MF, NF, UV, and adsorption combined in a hybrid process that treated and recycled spent final rinse water from an electroless plating operation. After duly designed pretreatments, including wastewater stream segregation, removal particulates, microorganisms, and free chlorine are applied to reduce total organic carbon (TOC); heavy metal removal and concentrating was done on NF membranes and subsequent polishing step, in which the permeate was de-ionized using a mixed bed. The polished permeate stream was then recycled back to the plating operation rinsing system. The results showed high-quality product water without heavy metals, conductivity was $<5\,\mu S\,cm^{-1}$ and water recovery = 90%. The estimated payback period was between 13 and 18 months. The process is more applicable for reclaiming wastewater containing mainly heavy metals but low in monovalent ions. RO process, together with precipitation for [191] treatment of wastewaters containing copper, zinc, and chromium from metal finishing, was able to recover 95% of the water.

ED can be used for treatment of the rinsing effluent from stainless steel etching with a combined method including CX [192]. Etching bath used in this case contained nitric acid and hydrofluoric acid. The ED process enabled removal of residual acids and chromium salts. The effluent contained only small amounts of Cr^{3+} ions ($7–20\,g\,m^{-3}$), and its conductivity varied from 10 to $65\,\mu S\,cm^{-1}$. In this case, the ED supported CX effectively.

4.05.2.5 Electronic Industry

The semiconductor factory generally requires ultrapure de-ionized water to rinse their integrated circuit (IC) crystal chips, and requires large volumes of high-purity water. It was estimated that water consumption in electronics would increase rapidly from $4.088 \times 10^8\,m^3$ in 1999 and more than $5.223 \times 10^8\,m^3$ of water in 2000 and probably could increase steadily [193].

Chemical mechanical polishing (CMP) actually takes place in the semiconductor industry, the most important technique to provide planarization on interlevel dielectrics and metal layers of wafers. In general, the polishing slurry consists of 5–10% of very fine particles (in the range of nanometers to micrometers) and various chemicals including pH buffers such as KOH, NH_4OH, and organic acids; and oxidizers such as H_2O_2, $Fe(NO_3)_3$, or KIO_3. Surfactants are used to maintain a good stability of SS in the polishing slurry. Many dispersed powders, dissolved metal ions, or chemicals would remain on the surface of wafers during the chemical polishing process. Normally, electronic wastewater has high alkalinity, TSS content, and turbidity. Therefore, the qualities of electronic wastewater do not meet the effluent thresholds in any case if it is not treated.

Normally, treated wastewater is recycled to the UPW system before it is used for the rinsing of wafers. Potential treatment methods include coagulation/flocculation, flotation, electrodecantation, electrocoagulation, MF, UF, and cross-flow electro-MF. Among these techniques, cross-flow electrofiltration might be superior to the other ones in terms of the extent of pore clogging of membrane, formation of filtration cake, and the flux of permeate. More details of the performance of cross-flow electrofiltration of CMP wastewater can be found elsewhere [194, 195]. In some cases, reclaimed water quality can be used only for cooling purposes [196]. Due to the water supply shortage, the higher cost of wastewater treatment, and the upward trend of water price, there is a growing attention to water reduction, reclamation, and reuse [197].

The stringiest demands on water quality concern especially to wash semiconductor chips and wafers. It is particularly important to remove wafer surface particles from previous steps of wafer manufacturing and from polishing slurry. These undesirable particles must be cleaned before the wafer subsequent processes of chip fabrication [198]. Large quantities of such UPW are generally used as a cleansing rinse for wafer surfaces. The features on an IC are so small that trace amount of impurities in the water can render the IC inactive. Ion impurities can adsorb into layers of the circuit, altering the electrical characteristics and thus the properties of the product. Particles such as bacteria can disrupt additional layers or create electrical shorts between adjacent circuits. To eliminate bacterial contamination in the production of UPW, an advanced oxidation process (AOP) destroys bacteria via the use of H_2O_2, O_3, and/or UV light to remove the AOP by-products such as CO_2 and O_2 from the treated water [199, 200]. Oxygen concentration must be reduced to the ppb range to avoid uncontrolled native silica oxide growth in wafer-immersion systems. The production of UPW for semiconductor manufacturing employs degasification treatment near the point of use. Several methods are currently available for dissolved oxygen (DO) removal and the most conventional ones are the thermal and vacuum degassing systems. However, such physical systems are expensive and immense. Chemical methods provide an alternative to physical methods in the removal of DO from water: these include ion-exchange method using ion-exchange resins and the catalytic reduction of DO using catalyst resins and a reducing agent such as H_2 or HCOOH. These methods include the addition of sodium sulfite or hydrazine. The use of sodium sulfite undesirably increases the solid content of the water, while the use of hydrazine is undesirable because of its toxicity and problems of controlling the water chemistry affected by the by-product, ammonia. Therefore, addition of chemicals is of no interest in current UPW industries [201]. Therefore, UPW production for use in the semiconductor industry requires full elimination of organic and inorganic compounds, particles, and microorganisms from feedwater or reduction of their concentration to values below detection limit of the most advanced analytical methods.

UPW systems designed for the semiconductor manufacturing industry are very complex nowadays, especially involving UPW water with zero discharge, that is used in many hi-tech industries [202, 203]. The membrane processes are used in electronic industry for pure water production in various configurations. RO may be directly used for UPW production [204] processes. RO applies for removal of particles sizes of $5 \times 10^{-3} - 1 \times 10^{-4}$ μm. This range includes singly charged ions, including Na^+ and Cl^- [205]. Another major feature of the RO is the low specific power consumption, which amounts to 5 kW h m^{-3}. The production of the UPW with RO is usually carried out through the use of the two-pass system [206, 207], where high resistivity of product water is similar to the ion-exchange process (5–10 Ω cm^{-1}). RO may also be used in combination with the ion-exchange process post-treatment where main purpose of the RO is reduction of organic substances eluting from the ion-exchange process.

NF applies for removal of particle sizes of $5 \times 10^{-2} - 5 \times 10^{-3}$ μm. This range includes doubly charged ions, including Ca^{2+}, Mg^{2+}, and $(SO_4)^{2-}$. For some purposes, NF enables raw water to be treated in a single step to produce high-quality permeate without pretreatment (direct NF) [208] – the technique saves energy, there is a low use of chemicals, and the permeate is of a high quality with the favorable separation properties of NF membranes in terms of the removal of bacteria, viruses, color, hardness, and pesticides. RO, NF, and MD are widely used in technology that removes the bulk of the contaminants, including ions.

UF applies for removal of particle sizes of 0.15 – 5×10^{-2} μm. This range includes bacteria, SS, oil and grease, proteins, macromolecules, and colloids. MF applies for removal of particle sizes of 1.5–0.15 μm. This range includes coarse particles, microbial cells, and large colloids. UF and MF are used for

pretreatment and removal of microorganisms even after water purification.

Membrane contactors are commonly used in semiconductor manufacturing operations for the production of cleaning water. Membrane contactors and reactors are used for water degassing and also to add CO_2 to water to increase the aggressiveness of a rinse step [209] and for ozonation. Thus, removal or addition of dissolved gases from or to water or aqueous solutions can be accomplished very effectively using hollow-fiber membrane contactors [210–212]. Well-designed contactors, where water flow outside of the hollow fibers is directed transversely across banks of hollow fibers, exhibit significantly enhanced mass transfer coefficients and reduce the pressure drop. Membrane contactors used for water degasification [213] provide uniform water dispersion and they are insensitive to changes in flow rate. Removal of dissolved gases from UPW is currently one of the principal applications of these membrane contactors [214–218]. Nonporous membranes give higher selectivity of oxygen and other dissolved gases over water [219].

MD has been applied for desalination during the production of UPW [220, 221]. Dissolved gases can also be extracted from water by VMD and it can also be used for concentration of aqueous solutions containing nonvolatile components and for UPW production [197].

The electrically enhanced membrane processes are also used for ion removal. The pretreatment system combined RO and electrodeionization (EDI) technologies. The RO permeate water was then directed to an EDI module, which combines ion-exchange membranes, ion-exchange resins, and an electrical current [222–225]. The current also continuously regenerates the ion-exchange resins, avoiding the need for resin replacement. The RO/EDI unit used in these experiments delivered $10\,l\,h^{-1}$ of purified water to the storage reservoir.

Novel membrane reactors were developed for DO removal from water [201]. The reactors were fabricated from either a hollow-fiber membrane or a tubular membrane. A palladium catalyst was packed in the void space of the reactor made from the hollow-fiber membrane, while for the tubular-membrane reactor the catalyst was packed within the membrane tube. Hydrogen gas was employed as a reducing agent. Water-containing saturated DO was fed into the reaction compartment containing the catalyst particles, while the purified hydrogen was introduced countercurrently into the gas compartment of the reactors so that the normal physical and chemical processes for the DO removal take place simultaneously. Reaction with a reducing agent such as hydrogen in the presence of a catalyst [226] to form water is an attractive method as it produces no by-product to contaminate the product water.

Membrane reactors may also be used for photocatalytic reactions that allow in many cases a complete degradation of organic pollutants in very small and harmless species, without using chemicals, avoiding sludge production and its disposal. These processes are based on the electronic excitation of a molecule or solid caused by light absorption (usually UV light) that drastically alters its ability to lose or gain electrons and promote decomposition of pollutants to harmless by-products [58–60]. In high-purity water, the pH is close to 7 [227], and the main species present is hydrogen carbonate (HCO_3^-).

4.05.2.6 Pharmaceutical Industry

The pharmaceutical industry is facing new challenges in terms of novel biological products, for example, monoclonal antibody production, vaccines, proteins, cell harvest, virus, and sterile finishing. The specific challenges are imposed on product purity and safety of these biologic drugs, which must conform to the relevant regulatory codes (WHO, Food and Drug Administration (FDA), European Medicines Agency (EMEA), Medicines Control Agency (MCA), etc.). Therefore, appropriate separation processes for contaminant removal [228] such as microorganisms, viruses, and contaminating proteins, nucleic acids, toxins, and endocrine disruptors, and residual contaminants, such as DNA and host cell proteins, are of utmost importance for the pharmaceutical industry. This will place enormous stress on the separation processes from fermenter to final product.

Membrane processes with their outstanding selectivity of separation play a key role in the production of a wide range of medicines since pharmaceutical and biotechnology industry came of age [229]. Pharmaceutical industry applies a wide range of membranes from microporous through UF to NF/RO systems designed for sterile filtration, cell harvesting, protein fractionation, concentration and purification, small-molecule processing, endocrine disruptors, and toxin removal. Purification and selective recovery of specific diluted products from multicomponent mixtures need extremely selective

processes such as membrane affinity chromatography (MAC), liquid membranes, reactive extraction, and membrane reactors, where the physics of membrane processes are enhanced by means of chemical reactions. Even an extremely difficult separation of enantiomers from racemic mixtures is actually a well-established technology with important contribution of membrane processes coupled with chemical reactions.

The feasibility of various membrane processes, membrane reactors [230], and the newest achievements in their successful applications has introduced a new perspective for the pharmaceutical manufacturing, product recovery from fermentation broth [231, 232], the purification of water [233–235], and the treatment of industrial effluents contaminated with organics or heavy metals [73]. Membrane separation processes may have an improved efficiency and reduced operating cost in comparison with the traditional processes [236].

Large-scale membrane systems are already established for the removal of cells and viruses as well as to sterilize the final product (or media feeds, e.g., to fermenter vessels). Virus and DNA removal in biopharmaceuticals has received a great deal of attention in recent years [237]. The anxiety over DNA hazards was considered in the mid-1950s, because there was a concern that protein products might contain an oncogenic sequence in viral vaccines [238]. The FDA and the pharmaceutical industry have recently announced strict guidelines for impurities of virus and DNA contamination. The regulatory guidelines on residual amounts of DNA in mammalian cell culture products require DNA contamination less than 100 pg/dose [239]. Therefore, rejection of DNA in the protein solution has become important in the application of DNA removal in drug manufacturing using membrane technology [240].

Membranes could be used for fractionation of multicomponent mixtures such as fermentation broth, which is a very useful tool in pharmaceutical industry. In general, RO membranes reject organic matters, salts, and other low-molecular-weight micro-pollutants. Thus, RO process is employed to reduce the organic matter in the permeate and to concentrate TOC in the retentate. NF membranes retain bivalent ions but still are relatively permeable for monovalent ions. NF membranes, on the other hand, retain matters that can penetrate UF membranes. UF is used to remove large biopolymers and thus to improve TOC crystallization and recovery from the RO retentate. UF membranes freely pass all salts and most organic matters.

Membranes are also used for wastewater treatment in pharmaceutical industry. Traditional physicochemical and biochemical processes have been adopted in disposing antibiotic wastewater by some researchers [241, 242]. Nevertheless, in these processes, some useful antibiotics in wastewater could not be utilized, and these methods are not good enough because the antibiotics in wastewater restrain the growth of microbe, which lowers the effects of treatment. Most existing physical and chemical treatment methods are not effective in removing the high organic content from the waste liquor, while the toxic antibiotic residues in the wastewater seriously put biological treatment processes at risk. In the wastewater, COD ($10\,000$–$80\,000\,mg\,l^{-1}$), pH, and temperature fluctuate.

MF can be used for purification of vaccines and other medicines during manufacturing process. Vaccines are immunogens consisting of weakened or dead pathogens such as a bacterium or virus, or of a portion of the pathogen's structure that upon administration stimulates antibody production or cellular immunity against the pathogen but is incapable of causing severe infection. Cross-flow MF using hollow-fiber membranes can be used for purification of the protein polysaccharide conjugate vaccine since it is a scalable equipment that can be carried out under closed, sterile conditions. This was essential since dead-end sterile filtration of the large conjugate particle is not feasible [243]. MF with precipitation is used fractionation of the human plasma, which is the starting material for the manufacture of a number of important therapeutic proteins. The most abundant among these are human serum albumin (HSA) and human immunoglobulin, both of which are manufactured in bulk quantities. Human plasma has a total protein concentration of about $46\,kg\,m^{-3}$, out of which $32\,kg\,m^{-3}$ is HSA and $12.5\,kg\,m^{-3}$ is made up of immunoglobulin. Human immunoglobulin collectively refers to several classes of heterogeneous mixtures of proteins, members of each class being distinct from members of others. Individual proteins within each class have minor structural and molecular weight differences. Human immunoglobulin G (or HIgG) is the predominant immunoglobulin class and its concentration in plasma could be as high as $10\,kg\,m^{-3}$ [244]. HSA and HIgG are generally fractionated by precipitation-based techniques. The precipitating agent in such a technique could be a solvent such as ethanol and its derivatives

[245, 246], a chaotropic solvent [247], salting-out salt such as ammonium sulfate [248], a polymeric substance such as polyethylene glycol (PEG) [249], or a more specific substance such as an immunoprecipitant [250]. The precipitation step is usually carried out at a low temperature after which the precipitated protein is removed from the supernatant, generally by centrifugation [251]; however, the MF and/or UF could also be used to separate precipitated proteins [252, 253]. Integrated bioseparation technique for HIgG/HSA fractionation may be a combination of three separation processes, that is (1) *in situ* ammonium sulfate induced precipitation, (b) MF, and (c) membrane adsorption. The membranes for hydrophobic interaction based on membrane chromatographic separation of monoclonal IgG from bovine serum albumin (BSA) may be used for this purpose [254]. The membrane chromatographic process on its own is not particularly suitable for separation of HSA and HIgG, primarily due to the low solubility of the antibody (0.2 kg m^{-3}) in the high ammonium sulfate concentration-binding buffer (1.75–1.8 M). Using this integrated bioseparation technique, nearly complete separation of HSA and HIgG could be accomplished in just one step.

UF is used for recovery of antibiotics from fermentation broths. Antibiotics are very useful clinically, because some of them are highly effective against a microorganism but have minimal toxicity to people. They have made outstanding contributions to the health of the human beings in the last 70 years. An antibiotic is a bacteria-fighting medicine that is derived from a biological source (plant, mold, or other bacteria). Antibiotics are mainly produced by fermentation. They are harvested from the broths by solvent extraction and concentrated by vacuum distillation. Fermentation-based bioproduct manufacturing is typically capital intensive because large and usually complex fermenters and extensive equipment for multistep downstream processing are required to handle large-volume fermentation broths with a low product concentration. The cost of the low-yield high-volume downstream processes usually constitutes a large fraction of the cost of biochemicals [255, 256]. Improvement of the multistep downstream separation and purification could potentially make significant savings to these manufacturing processes. The production of antibiotics typically consists of fermentation, removal of biomass, solvent extraction, and crystallization [257]. Fermentation for the production of antibiotics is the first step in a long process sequence, which consists of product formation, recovery, and purification. UF has been increasingly used to separate cells from antibiotics, and substitutes using traditional processes such as drum filters and centrifuges. The main advantages of UF are related to reduction of environmental pollution, such as solid wastes and noise, and energy consumption. Recovery of antibiotics from the fermentation broth is a complex process, because fermentation broths are mixtures containing both dissolved and suspended matter and, for this reason, there are always membrane–solute interactions and, consequently, membrane fouling. The antibiotic is dissolved in the fermentation broth and must pass through the UF membrane, and therefore very low retention levels are desired (10%).

UF can be effectively used to remove emulsifiers from fermentation broths before solvent extraction. During solvent extraction, antibiotics are extracted into an immiscible organic phase, at certain pH values [258]. This extraction step is indeed well established; however, it does have a long-standing problem with emulsions. In fermentation broths, there exist some components in culture medium or metabolites, which are surface-active [259, 260] such as proteins and polysaccharides [261, 262], and may cause a stable emulsion during extraction. Thus, an expensive de-emulsifier is needed; consequently, high-speed and large-capacity centrifugal extractors are frequently used to accelerate the phase separation. The addition of de-emulsifier can also cause an environmental pollution problem, since chemical synthetic surfactant ending up in the waste stream is difficult to degrade. The practice showed that UF could significantly improve the extraction operation in terms of phase separation, elimination of the need for any de-emulsifier or wet agent, and increase extraction recovery and product quality. The experimental results show that UF is an alternative to the use of de-emulsifier or other wet agent to obtain good phase separation even by gravity without centrifugal extractor in solvent extractions and hence could improve the extraction operation [263].

Protein UF and MF have been studied under several different conditions by a number of researchers [264]. UF processes can be used for the fractionation of macromolecules and particularly of protein mixtures [265–268] and nucleic acids [269]. Protein fractionation is an important operation in the biotechnological industry [270]. Large-scale protein fractionation is both expensive and technically challenging. In recent years, membrane-based protein

fractionation techniques are being examined for their potential for combining high resolution and high productivity. Molecules that differ less than threefold in size can be separated by highly selective charged membranes with careful adjustment of buffer and fluid dynamics. When compared with the widely used electrophoresis and chromatographic separation, UF exhibits the advantage of a high throughput and easy scale-up. Fractionation of biological macromolecules such as proteins using UF is strongly influenced by operating and physicochemical parameters such as pH, salt concentration, permeate flux, and system hydrodynamics [271, 272]. The pH dependence of protein sieving coefficient can be explained in terms of the electrostatic layer effect and the electrostatic self-rejection effect [268]. The size of the aggregated proteins in solution is thought to significantly influence the flux and permeation of proteins through the virus removal membrane. The addition of NaCl to the γ-globulin feed solution was found to be effective in enhancing the flux and the transmission of proteins through virus removal membranes with nominal pore size of 15, 35, and 75 nm [273]. The enzymes may be purified in the same manner [228].

High-performance tangential flow filtration (HPTFF) is a new protein purification technology [274–276]. HPTFF can also be used to separate BSA from an antigen-binding fragment of a monoclonal antibody (FAB), achieving more than 900-fold purification, and 90% yield of the BSA. van Eindhoven *et al.* [277] developed a membrane system for the separation of BSA from hemoglobin, two proteins with essentially identical molecular weight, with more than 100-fold purification and nearly 70% yield. More recently, Cheang and Zydney [278] were able to obtain 100-fold purification and greater than 90% recovery of β-lactoglobulin (β-LG) from a binary mixture with β-lactalbumin (α-LA).

The separation of protein solutions through virus removal membranes was also reported in several publications [275]. UF may be successfully used for virus removal. Viruses are obligate intracellular parasites, designed through the course of evolution to infect cells, often with great specificity to a particular cell type. They tend to be very efficient at transecting their own DNA into the host cell, which is expressed to produce new viral particles. Virus infections have been reported many times to be caused by injection of plasma products and biological products containing trace impurity of virus into the human body [279]. Virus removal or inactivation methods [280] in the manufacturing processes of bio-products have been developed to avoid virus infection such as human immunodeficiency virus (HIV) infection from factor VIII. The regulation of virus-free biopharmaceutical products has been covered by governmental guidelines [281, 282]. Removing of a virus from the fluid using membrane has been tried by many researchers [283, 285]. The membrane removal method of viruses has already been introduced to the manufacturing process of several plasma products [286]. Compared to ultra-centrifugation, cross-flow filtration can process larger quantities of supernatant with a higher yield of active pseudotype vectors over the same period. Reports of tangential and dead-end UF using polysulfone or cellulose membranes have shown a recovery of up to 90% of the colony-forming vector particles in the retentate [287, 288]. The removal of Moloney murine leukemia virus (MoMuLV) uses 100-kDa molecular-weight cutoff UF modules [288]. Bacteriophage ΦX174, which has a mean diameter of 28 nm, was reduced to be less than 10−8 times (i.e., logarithmic rejection coefficient >8) after permeation through the membranes having a mean pore size between 35 and 50 nm.

UF can be used for gene diagnosis of poisoning which is often applied for the screening of bacterial toxins [289]. As compared with general examination, such as the bacterial culture method, gene diagnosis is a relatively fast and reliable method. In this method, identification of bacteria was carried out as follows: (1) isolation of bacterial gene from a specimen and (2) amplification. To isolate the gene from the bacterial body, which was chemically lysed, an electric field can be applied to the membrane. The required time for gene isolation was no more than 15 min. From these results, it was suggested that gene isolation using this membrane might be done automatically because it needed few apparatuses and processes.

NF can be used for purification of pharmaceuticals that are reaction products in the form of mixtures of organic/inorganic salts from organic components soluble in water. Organic synthesis results frequently in crude reaction mixtures containing both organic compounds and inorganic salts. These mixtures can be formed when mineral acids or bases are involved as catalysts or neutralization agents during the reaction. The subsequent purification is usually straightforward since mineral salts precipitate in organic solvents and organic molecules are extracted by solvents or/and salted out from water. The task is

more difficult with mixtures in water when the interesting organic molecule is hydrophilic, that is, completely (or at least very highly) soluble in aqueous media. In this case, the separation of organic/inorganic mixtures is long and tedious. During NF the higher the molecular weight, the higher is the retention factor. The flux and rejection show that it is not necessary to increase TMP to obtain the faster salt elimination. The best result is obtained with the highest velocity, which reduces membrane fouling. Under optimal experimental conditions, more than 99% of mineral salts can be eliminated [290, 291].

The molecular mass (MW) of antibiotics are in the range of 100–1200, coincident with the range of the NF membranes. Therefore, NF and RO are used for concentration of antibiotics. The experimental results show that NF is effective in concentrating antibiotics with proper molecular mass. Solutions of antibiotics with MW about 800–1000 Da are concentrated up to 10-fold. The rejection coefficient of antibiotics can be maintained at higher than 99%.

NF and RO are used for removal of estrogenic hormones as emerging wastewater pollutants. Pharmaceutically active compounds [292] and steroid hormones [293] have recently been studied in their environmental concentration range (in the order of $ng\,l^{-1}$). Natural estrogenic hormones, estradiol and estrone, are by far the most endocrine-disrupting chemicals. Their endocrine-disrupting potency can be several thousand times higher than that of other synthetic chemicals. Very low concentration (as low as $1\,ng\,l^{-1}$) of estradiol can result in a distinctive endocrine-disrupting effect in male trout. Estradiol controls the development of the female sex characteristics in humans and, together with the gestagens, control the reproductive process [294]. Estrogenic hormones are continuously discharged by humans and animals into the environment either directly or after undergoing wastewater treatment processes, which are often not designed or capable of removing such contaminants. Removal efficiency of conventional wastewater treatment plants greatly varies [295]. Consequently, these hormones are ever-present in most freshwater bodies receiving effluent. They are frequently detected in North America, Europe, Japan, Brazil, and China within the lower $ng\,l^{-1}$ range [296–298]. Estradiol concentrations ranging form 6 to $66\,ng\,l^{-1}$ have also been reported in groundwater in northwest Arkansas, USA [299]. Advanced technologies such as RO, advanced oxidation, and activated carbon adsorption can effectively remove estrogenic hormones [300]. Studies on the performance of such technologies concerning hormone removal are still very limited. The results indicate that estrone can adsorb onto the membranes to some extent, depending on membrane type and the solution chemistry [301]. Both sieving and adsorptive mechanisms are instrumental in maintaining high retention in NF membranes that otherwise exhibit relatively low ion retention [293].

Liquid membrane particularly can afford an attractive method for separation and purification of amino acids and antibiotics from dilute solution such as that obtained in fermentation broth. It is also possible to control enantioselectivity in liquid membrane process by proper choice of the carrier and appropriate pH condition of the aqueous amino acid solution [302].The commonly used carriers are the esters of phosphoric acids [303]. The bulk liquid membranes (BLMs) are the simplest laboratory tool for phase contacting, which is probably the first experimental rig [304]. There are some publications concerning purification of amino acids and antibiotics [305] by means of BLM; however, the practical significance of this solution is very limited. Emulsion liquid membranes (ELMs) [306] turned out to be an effective and inexpensive method with potential application for this goal. Various types of substances have successfully been recovered by means of this technique including organic acids, antibiotics [307], and amino acids [308]. SLM offers a potential attractive alternative to the conventional processes in that they combine the process of extraction and stripping in a single unit operation. Another advantage is the use of a low amount of organic extractant, resulting in lower chemical costs. Therefore, purification of amino acids [309], aromatic aminophosphonates, organic acids, and antibiotics [310] with SLM is the promising solution for pharmaceutical industry. The SLM technique is one of the novel approaches for efficient peptide purification and concentration [311]. The process may be enhanced by means of reactive extraction [312].

The MAC has become a well-established and distinctive method in separation technology [65]. Membrane chromatography has increasingly been reported as a potentially advantageous tool to purify proteins. Serum antibodies, enzymes, and monoclonal antibodies are the three largest application categories. Membrane chromatography is an ideal large-scale separation process for the purification and recovery of proteins [313] and enzymes [314], immunotoxins [315], immunoglobulins [316], lysozymes [317], supercoiled plasmid DNA [318],

protein receptors from streptococci-G [319], paraproteins from human plasma [320], antigen–antibody [321], clotting factor-VIII [322], oligopeptides [323], antithrobin III, and monoclonal antibodies [324]By this method, antibodies or other proteins, polynucleotides, and drugs for applications in life science can be isolated out of a complex biological mixture [325]. Receptors are often proteins, peptides, dyes, or special molecules, which are preferably covalently bound at the support. Numerous materials, such as nylon, polysulfone, chitosan, cellulose, and cellulose derivatives [326], were used to prepare matrices for MAC. In addition, the method for preparation of molecularly imprinted polymer (MIP) membranes as well as their separation mechanisms and transport properties have been reviewed by Piletsky *et al.* [327]. MAC solves the problem of separation of complex protein mixtures.

The immobilized metal affinity membrane chromatography (IMAC) was developed by combining immobilized affinity chromatography with membrane chromatography techniques, which may provide an alternative potential tool for separating the therapeutically relevant biospecies. IMAC is a chromatographic method applying the chelates (usually multidentates) coupled on the solid supports to immobilize metal ions (such as Cu, Ni, Co, Zn, Ca, Fe, or Al) [328], which could specifically interact though nonbonding single pair electron coordination with exposed electron-donating amino acid residues (such as histidine, cysteine, tryptophan, aspartic acid, glutamic acid tyrosine, aspartic acid, or glutamic acid) on biomolecule surface through nonbonding lone pair electron coordination [329]. Since there are many specific amino acid residues located on PGA, including 13 histidines, 28 tryptophans, 43 aspartic acids, and 36 glutamic acids [330], some of them are most probably exposed on the protein surface. The immobilized metal affinity membranes have been found to be applied in isolating or purifying enzymes, albumins, immunoglobulins, hemoglobin, ribonuclease, growth factors [331], etc. In addition, polyhistidine tags (such as His6) are usually used for those biospecies without directly accessible surface-exposed special residues and the resulting immobilized metal affinity isolation is very efficient [332, 333]. Affinity chromatography with the use of immobilized antibodies is a rapid and specific technique for isolating biologically active materials from a variety of different sources. This method has been used to remove antibodies and antigens [334, 335]. Immunoaffinity membranes are also used for direct medical applications such as amyloidosis which is a widespread complication in patients undergoing long-term hemodialysis (HD) [336].

Affinity membranes are used for the purification of human IgG from different sources, both in analytical HPLC systems [337] and on preparative scales [338]. Two types of applications could thus be envisaged for the functionalized hollow-fiber cartridge: biotechnological for the purification of IgG [339] and biomedical for the extracorporeal removal of pathological antibodies [340–342]. Antibodies were also purified with ion-exchange membrane chromatography [316]. Recombinant monoclonal antibodies have recently seen increasing importance as therapeutics in treating human disease such as cancer [343–347]. Hepatocyte growth factor (HGF) [348, 349] and HSA were also purified with immobilized metal affinity membranes [350]. Affinity membranes can be used for purification of enzymes such as peroxidase, which catalyze the oxidation of various electron-donor substrates, such as phenols and aromatic amines, and important [351] in organic synthesis for the biotransformation of various drugs and chemicals. [352–355]. Affinity membrane chromatography is used for separation of endotoxins [356] which are lipopolysaccharides present at the outer cell surface of Gram-negative bacteria and constitute one of the major problems in the formulation of pharmaceutical products [357]. Pyrogens are known to cause fever in humans and others mammals at very low concentrations and irreversible septic shock at higher doses [358].

Chiral specificity is fundamental in pharmacology and chemical biology [359] because stereochemistry plays a central role in controlling molecular recognition and interaction [360]. The chiral separation of one specific enantiomer from other is necessary for the production of pharmaceuticals and also food products. The word chiral derives from the Greek word *ceir* (*cheir*), meaning hand. Our hands are chiral – the right hand is a mirror image of the left – as are most of life's molecules such as (R)-alanine and (S)-alanine, which are mirror images of each other. In our cells, we find only one form of this amino acid, (S)-alanine. The same is true for enzymes, antibodies, hormones, and DNA. Enantiomers are two molecules that are mirror images of one another. They have the same chemical and physical properties but differ in their optical activity. Optical activity is defined by the degree and direction the molecule rotates plane-polarized light. If the molecule rotates the plane of

light clockwise it is called dextrorotary (d or +). If the molecule rotates the light counterclockwise it is called levorotary (l or –). A pair of enantiomers each rotates a plane of light to the same degree in opposite directions. A mixture containing equal amounts of each enantiomer is optically inactive as a whole. It is called a racemic mixture, or a racemate. A racemate can only be separated into its two constituent enantiomers by reacting it with another optically active compound. The products, called diastereomers, will not be enantiomers and can be separated on the basis of their different physical properties.

In 2000, the worldwide market for single-enantiomeric drugs was in excess of US$ 130 billion and 40% of all dosage-form drug sales were of single enantiomers. There is growing commercial interest in the production of single enantiomeric versions of many chiral pharmaceuticals, insecticides, pesticides, and nutraceuticals because of the large differences in biological activity and/or toxicity of the different enantiomers [361]. For example, the (S, S)-diastereomer of ethambutole is effective in the treatment of tuberculosis, but the (R, R)-diastereomer can cause blurred vision, eye pain, and, in some cases, complete blindness [362]. Many drugs that were originally sold as racemic mixtures have now been re-released as purified single enantiomers. Although many single enantiomer drugs are produced by stereoselective synthesis, there is also a growing need for separation techniques appropriate for the large-scale resolution (purification) of chiral molecules.

Separation of enantiomers is difficult because of their equal physical properties. The only way to tackle this problem is to apply the separation of enantiomers in a chiral environment. In the past decades, many research groups have focused their research on enantiomer separations. Most of this work has been performed for the separation of enantiomers on analytical scale. As a result, for almost every enantiomer pair an analytical method exists for the complete separation via, for example, gas chromatography, liquid chromatography, or capillary electrophoresis [363]. Chromatography is the most widely used method for the separation of racemic mixtures. Currently, separation of racemic mixtures is typically performed by column chromatography [364]. Some attempts were also done with molecularly imprinted materials [365], preferential crystallization [367], and solvent extraction [368].

In the production of enantiopure compounds, membrane technology is emerging as an alternative for the conventional resolution methods [369]. For the separation of enantiomers on a large scale [370] the membrane processes such as affinity UF, D, membrane extraction, liquid membranes, and membrane reactors are promising tools. Membrane-based enantiomeric separation has the advantage that it can be scaled up and that it saves energy, and should facilitate industrial-scale chiral separation [371].

Affinity UF uses a large stereospecific binding agent in free solution to selectively bind, and thus retain by a semi-permeable membrane, one of the stereoisomers [372, 373]. The performance of any affinity UF process [374] is strongly affected by the detailed binding interactions between the macroligands and the product/impurities [373]. Stereospecific binding requires multiple interactions between the macroligands and substrate in a very specific geometric orientation. The extent of binding is thus a strong function of solution pH and ionic strength, both of which can alter the magnitude of the underlying forces and change the geometric conformation of the macroligands and/or substrate. In several studies, UF experiments for the chiral separation were performed for mixed proteins [375] and amino acids [376].

UF also uses chiral porous membranes in channel-type permeation. The mechanism of the channel-type permeation is based on higher permeation of one specific enantiomer compared to opposite enantiomer through the membranes [377]. The mechanism of chiral separation in the affinity-based chiral UF is based on the adsorption of one specific enantiomer on the membranes that gives higher binding affinity than the opposite enantiomer [361,]. Dense membranes consist of a dense matrix of a chiral polymer that can invoke enantiospecific interactions during sorption and/or diffusion. This so-called solution/diffusion mechanism causes a selective permeation through the membrane. For the development of these membranes, several design criteria must be taken into account to arrive at membranes that show selective permeation [378]. Several recent studies [371, 379] demonstrated the feasibility of using affinity UF for the separation of D- and L-tryptophan based on the stereospecific binding of the L-stereoisomer by BSA. Data were only obtained at pH 7, which was well removed from the maximum binding conditions reported by McMenamy and Oncley [380]. Poncet *et al.* [381] and Gamier *et al.* [382] over a range of pH, with these binding curves, used to evaluate the purity and recovery for an affinity UF process. Additional

studies performed with tryptophan analogs showed a strong dependence on NaCl concentration, demonstrating the importance of electrostatic interactions on the binding [383]. One approach that can be used to enhance the performance of the affinity UF process is to use a multistage cascade. Dong *et al.* [384] have theoretically examined the behavior of multistage affinity UF processes for protein purification under conditions where the impurities had absolutely no binding interactions with the large affinity ligand.

There are several studies on the chiral separation of optical enantiomers using D membranes; however, the permeation of the enantiomers through the D membranes is extremely slow and the concentration of the permeate is quite dilute compared to the feed solution [385]. For large-scale enantiomer separation processes, the membrane extraction was reported by Carr and Cussler [386].

Considering liquid membranes, the best manner is to apply chiral carrier incorporated in the membrane phase. Such a molecule, by selective interactions with one of the enantiomers, causes its enrichment in receiving phase. Liquid membranes with an enantioselectivity carrier dissolved in a liquid transport the enantiomer via selective binding from the donating phase to the receptor phase. A large number of chiral selectors have been applied for this purpose, including crown ethers [387] or chiral complexes of transition metals [388]. Liquid membranes show that permeation of the enantiomers is driven by the concentration difference through the chiral membranes. Three classes of liquid membrane systems can be distinguished for the separation of enantiomers. One system makes use of emulsion liquid membranes [389], supported liquid chiral membranes [390], and bulk [391]. However, the general problem of liquid membranes is their lack of long-term stability [392].

Liquid membranes may also be used as an environment of chemical reactions. The examples of liquid membrane reactors for enzymatic bioconversion [393] or hydrolysis [394] have been described in literature [395]. Dispersion-free reactive extraction utilizing microporous hollow fiber (HF) membrane has been demonstrated to eliminate several practical shortcomings of the liquid membrane technique for biomolecules [396]. A biphasic enzyme membrane reactor shows remarkable advantages in the hydrolysis of water-insoluble substances. The membrane provides reaction sites and fixes the aqueous/organic interface, thus promising stable operation. When reaction products are soluble in water, one isomer is removed into an aqueous phase as product and the other isomer remains in an organic phase, which implies the simultaneous recovery of both isomers with much simple downstream processing. Recently, multiphase membrane reactors have received much resolution of racemic 2-hydroxy acids through lipase-catalyzed reaction [397, 398] and in enzymatic preparation of optically active compounds [399–401]. Another routine is chemical synthesis of a racemate in combination with a resolution step [402] or stereoselective transformation [403]. Optically active 2-hydroxy acids are important chiral building blocks in organic synthesis [404], and some researchers have demonstrated the optical resolution of racemic 2-hydroxy acids through lipase-catalyzed reaction [397].

4.05.2.7 Beverage Production

The primary steps in processing beverages are raw material handling and processing, mixing, fermentation, and/or cooking, cooling, bottling and packaging, and cleanup. Wastewater and solid waste are the primary waste streams for the beverage and fermentation sector. Solid wastes result from spent grains and materials used in the fermentation process. Wastewater volume of soft-drink processes is lower than in other food-processing sectors, but fermentation processes are higher in BOD and overall wastewater volume compared to other food-processing sectors. CF-MF is attracting increasing technical and commercial interest as an alternative method for fluid clarification/pasteurization/sterilization in the brewing [405, 406]. The cider and fruit juice industry use MF for microbiological stability, clarification and spent fluid recovery with improved product quality [407–410]. The fouling of the MF membranes is the main reason that hinders the membrane application in the beverage industry [411]. During the filtration of feeds of biological origin, membrane fouling can be caused by pore-size constriction, pore blocking or the deposition of cells, cell debris, and/or other particles, such as macromolecules or macromolecular aggregates, on the top surface of the membrane, resulting in a decrease in the permeate flux. According to Belfort *et al.* [412], colloidal fouling occurs in two stages: internal and external. Internal fouling is caused by the deposition or adsorption of small particles and macromolecules within the internal structure of the pores. Membrane fouling during the processing of complex fluids, such as fermentation broths, results from adsorption pore

blocking and from cake formed by the retained species [412, 413, 414]. The respective impact of these different fouling mechanisms strongly depends on the composition of the fluid to be filtered, of the hydrodynamic conditions, and on the membrane characteristics [415, 416]. It is also strongly influenced by physico-chemical interactions that occur between the fluid constituents and the membrane surface and pore walls, as well as by physico-chemical interactions between these constituents [414–418]. Even though macromolecules present in beverages (proteins, polyphenols, polysaccharides, etc.) are much smaller than the pore size of typical MF membranes, they cause significant fouling. Membrane fouling causes inconsistent beverage quality, uncertainty over productivity, and large flux/quality variations among different brands filtered on one membrane system [419]. The economical flux rates are reported to range between 10 and 100 $kg\,h^{-1}\,m^{-2}$ [420]. The mechanisms of fouling and flux decline in beer MF are now better understood and documented [421, 422] and also the relationship between membrane fouling and the permeate quality variations under different system configurations and operating regimes, as well as flux enhancement techniques especially with high-frequency backflushing and membrane cleaning [423].

Membrane systems for recovery of chemicals offer a useful tool to increase both the environmental and economical effectiveness of any cleaning-in-place (CIP) system. In food and beverage industry, a large quantity of drinking water is used in the cleaning of plants or packing containers and become wastewaters. Most of this water is consumed by the bottle cleaning machines. A bottle cleaning machine requires 150–200 ml water per bottle; an older one up to 600 ml. This corresponds to a consumption of 20 000 $m^3\,yr^{-1}$ for a medium-sized company and 250 000 $m^3\,yr^{-1}$ for bigger ones. The costs of fresh- and wastewater are about 3–4 Euro m^{-3} and are a significant part of the process costs. In addition, purchase of cleaning chemicals and water represents a significant cost, which is desirable to be minimized without compromising on cleaning effectiveness. Therefore, the best solution is to recycle the water and cleaning solutions agents [424].

Pressure-driven membrane separation processes such as MF, UF, and nanofiltration NF are suitable for treating spent alkaline cleaning solutions [425]. Although RO has greater separation efficiency for impurities, it has to be ruled out, due to the significant pH changes that are possible by RO (rejection of hydroxide ions). However, the efficiency of membrane processes can be considerably affected by surface-active substances from cleaning additives, which may cause a flux decline [426, 427]. Application of NF membrane was possible. RO in combination with NF should meet the requirements. Calculations have shown the payback period of 3.3–4.6 years for 50% and 90% water recovery, respectively, by assuming membrane price at 90 Euro m^{-2} [428].

4.05.2.8 Fruit Juices and Pulps Production

The world market for fruit juices is about US$ 5.0 billion yr^{-1} [429]. There is a key demand for fruit juices with the original characteristics of the fresh fruits and free from chemical additives. This results in the search for new technologies that are able to improve the sensorial, nutritional, and microbiological quality of the fruit juices since thermal processes largely affect the characteristics of fruit juices.

Clarification is an essential step taken before other specific treatments such as removing polyphenolic compounds, bitterness, tartness, and acids with adsorbent resins [430], deacidification by ED [431], and recovery of natural color substances [432]. Recently, large varieties of new products, based on clarified fruit juice, are available. For these products, transparency and homogeneity are two essential characteristics, which can be achieved only by completely removing all SS [433]. Traditional clarification applied to the raw fruit juice includes application of pectin-hydrolyzing enzyme, centrifugation, or diatomaceous earth filtration after agglomeration [434]. For the beverage stabilization, treatment of gelatin, bentonite, and silica gel is widely used [435]. Conventional methods of juice clarifying and stabilizing process are not only complicated but also labor intensive, time consuming, and therefore expensive.

Membrane processes can be alternative to fruit juice preservation and conservation, because they does not involve the use of heat treatment [436]. The advantages of membrane processes in relation to the thermal processes are the use of mild temperature and pressure conditions, which maintain the nutritional quality [437] and the sensorial attributes of the juice's freshness and aroma. Compared to the conventional methods, the membrane filtration, by contrast, offers the following benefits: high

productivity and cost reduction through yield improvement, high quality of product, eliminates the use of diatomaceous earth, lower labor, material, and energy operating costs, less time and waste disposal, and allows enzyme recovery reuse, thereby reducing total enzyme consumption to about one-third [438]. Membrane processes such as MF and UF [439] are widely applied in many fields: clarification, concentration, and fractionation in juice processing, recovery of useful components from wastewater, and enzyme purification. RO is a membrane process that can used to preconcentrate fruit juices, avoiding high temperatures. Thus, minimum thermal damage is caused and lower capital and operating costs are required. Several research works using RO for juice concentration have been published over the last few years [440].

Application of membrane filtration to the clarification of fruit and vegetable juices has been extensively studied during the past 25 years [441–443]. UF was introduced to clarify apple juice and to obtain a stable clear product. The advantages of UF for clarification of apple juice are based on the avoidance of filtering aids, which is the most important one in terms of cost effectiveness [444], and present disposal problems [445]. Successful development of membranes with increased service life, separation capacity, and chemical resistance has been a driving force for increasing use of membrane separation processes [444]. Several studies have been published concerning the quality of ultra-filtered apple juice in comparison with conventional clarification techniques. UF has been investigated for the clarification of pear [446], grape, orange, lemon [447], apricot, peach and pear pulps [448], star fruit [449], kiwifruit [450], guava [451], pineapple [452], and passion [453] juice. Besides, UF has been used in conjunction with ion-exchange resins to deicide passion juice [454] and to debitter grapefruit juice and grapefruit pulp [455]. Application of MF for clarification of fruit juices is also presented in literature [456].

One of the basic unit operations of fruit juice technology is the concentration process where the solid content of the juice is increased from 10% up to 65–75% by weight [457]. The fruit juices are concentrated to reduce liquid volume, which in turn lowers storage, packaging, and transport costs. An increased concentration of solids also assists in preventing microbial spoilage of the juice concentrate [458]. In industrial juice processing plants, the juice concentration step is usually coupled with aroma-stripping and the stripped aroma concentrate is later added back to the concentrated juice [459]. Conventionally, fruit juices are concentrated under vacuum in multiple-effect evaporators [407]. In this step, most of the aroma compounds are lost to the vapor phase on account of their high volatility in aqueous solutions. In order to avoid the resulting impairment of the flavor quality of the final product, these aroma compounds must be recovered and then added back to the concentrated juice before packing. Membranes are used especially for reducing the astringency and for clarifying and concentrating the juice of exotic tropical fruits such as pineapple [460], cashew [461], acerola [462], and passion fruit that are marketed worldwide, principally because of their pleasant unique aroma and flavor which is extremely sensitive to change because of heat processing [463]. The juice concentration can be performed by means of MF [464], UF [465], osmotic distillation [466], and MD [467] to separate juices into a fibrous concentrated pulp, and a clarified fraction free of spoilage microorganisms. This can be applied for fruit and vegetable juices and some pharmaceutical products [456, 468]. Fruit juice processing needs separation of some undesired substances such a polyphenols and pectins that spoil juice quality. Unfavorable changes, for instance, haze formation and coloration, may occur during storage, causing loss of product quality [469]. Polyphenolic compounds with relatively low molecular weights have been found to be responsible for physico-chemical deterioration of apple juices and concentrates during storage [445]. A number of agents, including, gelatin, bentonite, activated carbon, casein, ion-exchange waxes, and polyvinylpolypyrrolidone (PVPP), have been studied for the removal of polyphenols from fruit juices [470]. Membranes are used for the removal of polyphenols in the apple juice production in two possible process routes: (1) fining with gelatin, bentonite, and silica gel followed by an MF step, or (2) UF followed by a post-stabilization step, which can be either a batch PVPP process or an in-line filtration with adsorption waxes. The amount of naringin and other bitter compounds in orange juice must be carefully controlled in orange juice production; otherwise, juices, which have low commercial value, are obtained. Molecular recognition is a new method of selective separation or identification of various components in multicomponent mixtures, which recently attracted attention of many researchers who dealt with manufacturing [471], analytical chemistry [472], and separation [473, 474]. This method may be applied

for selective removal of various undesired components from fruit juices, such as acids and bitterness, to improve taste and flavors of the natural juices. Trotta *et al.* [475] applied the imprinting technique for removal of flavonoid naringin (4,5,7-trihydroxyflavanone-7-rhamnoglucoside), a component present in the rind of the oranges and other citrus fruits that contribute to the bitter taste of the orange juice such as limonin, hesperidin, and other molecules.

Pectins are polysaccharides which have an average molecular weight of 70 000 Da, and are normally obtained from natural plants and fruits such as citrus and apple pomace. They are widely used as gelling agents for the production of jams, jellies, and other foods [476]. Fructo-oligosaccharides (FOSs) are considered to be a promising functional food or food ingredient [477–480] and enzymatic technology. UF [481, 482] and NF appear to be a potential industrial-scale method for purification and concentration of oligosaccharide mixtures [478]. Suitable NF membranes have to be found for FOS purification, which not only have high rejection for FOS but also have low rejection for low-molecular-weight sugars [480, 483].

4.05.2.9 Wine Production

Wine making differs from other beverage production technologies in that the quality properties of the final product are not exactly predictable [484]. Crude wine following the alcoholic and malolactic fermentations is a multicomponent system, including numerous solutes (organic acids, salts, and polyphenols), macromolecules and colloidal size-range aggregates and particles, microorganisms, yeast, lactic bacteria, and various large particles such as cell debris and potassium hydrogen tartrate (KHT) crystals. Colloids in wines are formed by pectins and yeast providing polysaccharides and molecular aggregates resulting from the association of small solutes during wine aging and/or as a result of physico-chemical changes (temperature, redox potential, etc.). This colloidal state in wines is not accurately defined at this time [485].

When the musts have not sufficient potential alcohol content, it is necessary to increase their sugar concentration [486]. This happens in two cases: the grapes are not sufficiently mature or the rain, just before the vintage, blows up the mature grapes with water. The chaptalization (adding sugar into must) is used for long time as palliative method. With this technique, the whole of other components remains nearly identical.

After fermentation, wine presents a turbidity problem that is not well accepted by the final consumer. The wine turbidity is caused by suspended material such as yeast residues and macromolecular compounds with colloidal behavior [487]. One of the most common operations includes a filtration stage normally achieved by diatomaceous earth filters. However, the already-exhausted substrate will soon be considered a hazardous waste, involving disposal costs. Alcoholic fermentation during winemaking leads to a decrease in the KHT salt solubility [488] due to the presence of ethanol. As a consequence, at normal storage temperatures, an untreated wine is supersaturated in KHT and undesirable precipitation can occur in the bottles. KHT is a natural constituent of grapes [489]. The formation of crystalline salts of potassium bitartrate (KHT) leads to loss of stability of a wine. For the stabilization of wines, the several methods used include the addition of metatartaric acid [490] and proton exchange, which is sometimes used [491]. Cold treatment can be applied in different ways [492], but the most widespread is holding for 1 week at a temperature near to the freezing point of the wine. The excess of this salt is also traditionally removed by cooling the wine to 4 °C over several days to induce KHT precipitation prior to bottling [493]. To accelerate this treatment, KHT crystal seeds are normally added. The crystallization kinetics of KHT depends on many factors such as temperature [494], KHT initial supersaturation [495], crystal seed granulometry [496, 497], wine composition, [498], and colloidal mater [499]. There are different disadvantages of these methods. The complexity of the cold stabilization process does not allow a precise control of the final KHT concentration achieved by this technique. Besides, this operation can affect wine quality due to the simultaneous precipitation of polysaccharides and polyphenols together with the KHT crystals [500]. This treatment produces a stabilizing effect in dry white wines, while this is not so clear in red and natural sweet wines [501] and sherry. Sherry wines are liquor wines elaborated in the south of Spain, whose manufacture has been broadly described by Perez Rodrýguez [502]. One of the main problems arises from the use of natural sweet wines, because their high colloid content inhibits KHT crystallization during their later tartrate stabilization. Moreover, such cold treatment has high costs and it is time consuming.

Although membranes and many different technologies have been implemented in wine manufacturing, it is still a very traditional process [503]. Membranes are used in wine making technology mainly for three purposes: in wine chaptalization, clarification, and stabilization.

Two membrane methods of wine chaptalization were recently authorized: vacuum evaporation (VE) and RO. These techniques enable to increase the sugar concentration in must by water content reduction. Therefore, all components favorable or not for wine quality are concentrated, which is very interesting for correction of a must elaborated with the mature water-inflated grapes. Contrary to the VE, in RO the separation occurs without phase exchange. The first tests of must concentration by using RO in red wine elaboration have been done in the 1970s [504] and were carried out with cellulose acetate membranes. Since RO becomes increasingly attractive in spite of restrictions imposed by legislation that delay its development [505]. The new membranes appear more adapted to the must concentration and the installations as well. The retention rates are higher than 99.5% and the extracted water contains very few organic components and minerals [506].

Membrane filtration for wine clarification is emerging as a very promising technology for this purpose because of its ability to perform wine clarification/filtration/sterilization in a single step in continuous operation with CIP strategies. [507]. The use of CF-MF for clarification and microbiological stabilization of wine experiences a continual progression [508]. The most frequently used membrane pore sizes in wine MF are 0.1 and 0.22 μm for white wines and 0.2 μm for red wines [509]. When a CF-MF mode is involved, some commercial companies recommend the utilization of the smallest pore-size MF membranes. Pall highly recommends their 0.1-μm and 0.22-μm polysulfone membranes; Sartorius the 0.1 μm PES and 0.2 μm PP; Microdyn and Vaslin Bucher the 0.2 μm polypropylene membranes; and Koch its 500 kDa UF PES membranes even in red wine filtration. Many authors warn that if very small pore-size membranes are used, some unwanted flavor and color changes in the treated wine can be introduced [510].

The limitations of the cold tartaric stabilization method led to the development of other KHT removal techniques such as ion-exchange resins [511] and ED [512]. The treatment by ion-exchange resins consists of equilibrating the wine with a cation-exchange resin that replaces the wine potassium ions by hydrogen or sodium ions [513]. The first application of ED to the tartrate stabilization of wines was carried out by Wucherpfennig [514] and subsequently by many authors [515]. ED is based on the separation of differently charged ions, by the use of selective permeable membranes, under the action of an electric field. Contrary to the cold precipitation, where the KHT removal is fixed, ED offers the possibility of reaching any degree of KHT removal through the variation of the ED operating time. One should emphasize that this is assessed through the wine saturation temperature (T_{sat}) [516]. Since then, different studies have demonstrated that ED treatment stabilizes appropriately white, rose, and red wines [517, 518].

Wine is a very complex medium including dissolved constituents, colloids, and large particles, which may all be implied in membrane fouling. As with other complex media, the process performances are still limited in terms of permeate flux due to severe membrane fouling [519] that results in a reduction in permeation rates, affecting the economic viability of the process, and a risk of excessive polysaccharide and polyphenol retention, which affect product organoleptic quality [520]. Considering this complexity, different fouling mechanisms may be associated with the building of deposits during wine processing [521], such as solute and colloid adsorption on the membrane surface or in its pores, pore blocking, and formation of a surface deposit. Several studies [522] performed on organic and inorganic materials have pointed out that polysaccharides [522] and polyphenols are responsible for membrane fouling on inorganic [523] and polymeric membranes [524].

4.05.2.10 Beer Production

The brewing sector holds a strategic economic position with world beer production exceeding 1.35 billion hectoliters per year in 1999 [525]. Beer is the second most consumed beverage in the world after tea, and it continues to be a popular drink. The brewing industry has an ancient tradition and is still a dynamic sector open to modern technology and scientific progress. Brewing has always been a water-intensive industry, generating significant volumes of wastewater. A large brewery might generate more than 60 000 m^3 of wastewater from keg washing, cask washing, filter backwashing, CIP rinsing, tunnel pasteurizer overflow, and bottle rinse lines.

Brewers are very concerned that the finishing techniques they use are the best in terms of product quality and cost effectiveness. A great deal of work is being done to maintain or increase brightness and clarity, which are important quality factors [526]. During production, beer alternately goes through three chemical and biochemical reactions: mashing, boiling, and fermentation and maturation; and three solid–liquid separations: wort separation, wort clarification, and rough beer clarification [527]. Conventional beer clarification process employs filter press or pressure vessel filters which are commonly precoated with porous particles of diatomaceous earth (DE) as the filter aids, which play an important role not only in acting as a second filtration barrier, but also in absorbing the chill haze components.

MF in the beer industry is a promising alternative to traditional clarification processes such as DE filtration, because it eliminates the residues generated by this kind of treatment and the need for filter aids and associated handling and disposal problems [528, 529], reduced beer losses, high solids handling capacity, and the substitution of heat pasteurization and, therefore, a better product quality and cost saving [530, 531]. MF can also combine clarification, stabilization, and sterile filtration in one single continuous operation [532, 533].

UF and RO are used extensively in the brewing industry on feedwater, and so the technology should be easily transferable to the wastewater treatment side of the business. Reuse of recovered water could provide a raw supply for boiler feed, washdown water, vehicle washers, cask/keg wash, or pasteurizer wash.

4.05.2.11 Aroma Processing

The aroma is one of the most important attributes of food, and is directly linked to the quality of the product and the consumer's acceptance [534]. Aroma compounds have small molecules with a molecular weight generally lower than $400\,g\,mol^{-1}$. When working with aroma compounds it is important to distinguish between natural, nature-identical, and artificial aromas. Natural aromas are isolated directly from the natural source, plant, or animal. Natural-identical aromas are produced synthetically, but they are chemically identical to their natural counterparts. Finally, artificial aromas are also produced synthetically. Although they have the same sensory profile and other features as natural aromas, their chemical structure is different. The prices of naturally, biologically, and synthetically produced aromas vary significantly, for example, c-decalactone (peach aroma) costs 1400 $\$\,kg^{-1}$ as natural extract but only 75 $\$\,kg^{-1}$ as a synthetic product, and raspberry ketone (raspberry aroma) costs 3000 $\$\,kg^{-1}$ as natural extract, and 58 $\$\,kg^{-1}$ when synthetically produced (Aldrich, 2000). The prices of biologically produced aromas, if available, range between these two prices, but are generally one order of magnitude lower than those of natural aromas [535].

Aroma can be classified [536] into three categories: low-boiler behavior, moderate high-boiler behavior, and very high-boiler behavior. Aroma profiles of fruit juices usually comprise a mixture of a large number of VOCs. The individual aroma components differ according to their molecular structure, which in turn defines the solubility, the boiling point, and the volatility of each type of compound [537]. Aroma, in particular, is formed by a mixture of hundreds of different organic compounds, which are present at very low concentrations, typically at $mg\,l^{-1}$ or $\mu g\,l^{-1}$ levels.

The efficient and economical recovery of aroma compounds is a challenge for the food and cosmetics industries. To recover aromas from natural sources, conventional separation processes, such as adsorption, steam distillation, solvent extraction or air stripping, are often applied. However, these processes have disadvantages, which might affect the quality of the product, such as the requirement of a solvent or adsorbent, which must be separated from the aroma compounds in a purification/desorption step to avoid contamination of the product, deterioration of the aroma due to high temperatures and oxidation, high energy consumption, and limited range of applicability. After evaporation, the volatile aroma compounds are subsequently trapped by condensation in an aroma recovery unit, where the efficiency of the trapping varies depending on the particular conditions and on the aroma compounds in question [538]. During high-temperature distillation, the aroma profile of juices undergoes irreversible changes. As was noted for black currant juice, the changes included formation of furan derivatives and sulfides, an increase in the concentration of aldehydes, and a general decrease in the concentration of terpenoids [539, 540]. Thus, in addition to a significant consumption of energy, the conventional aroma stripping process coupled to the juice concentration has serious drawbacks, including heat-induced transformations of sensory attributes (color, taste, and

aroma) and loss of nutrients (vitamin C) [541] and thus lower their market values. Besides these major chemical and organoleptic changes, the overall aroma transfer with the conventional aroma recovery unit is imperfect, transferring only 40–65% of the total volatiles into the aroma concentrate [542].

In order to overcome the limitations of these conventional processes, the membrane process has been widely considered as an alternative process for aroma recovery. The key advantages of membrane processes over conventional processes in aroma recovery include high selectivity, low energy consumption, physical separation mechanism, moderate operating temperature, and no additives are required. Among the various membrane processes, PV [543] is considered one of the most promising for the recovery, concentration, or removal of natural aromas in the food industry, taking technical aspects and cost into account [535]. PV may offer an effective way for a selective recovery with reduced loss of aroma since it can operate at mild temperatures. The general applicability of PV is using hydrophobic membranes to recover aroma compounds from aqueous model solutions such as alcohols, lactones, esters, aldehydes, ketones, sulfuric compounds, pyrazines, and hydrocarbons. PV is capable to concentrate very dilute flavor compounds from flavor distillates and extracts. Usually, these flavor distillates and extracts originate as dilute solutions with the concentration of flavor compounds less than 300 ppm [544]. Compared to traditional concentration processes, such as adsorption, steam distillation, vacuum distillation, solvent extraction, and air stripping, PV has the following advantages: no heat damage to heat-sensitive flavor compounds; low energy consumption; no additional separation treatment for added solvents or adsorbents; and minimum loss of flavor compounds [545–547].

PV has been used for recovery of the apple juice aroma, which is highly volatile consisting of over 300 different compounds, including three main groups of compounds: esters, aldehydes, and alcohols, as well as ethers, fatty acids, lactones, terpenes, and ketones. The major compounds thought to be responsible for apple flavor are ethyl butanoate, ethyl-2-methyl butanoate, and hexanal. The total aroma concentration in apple juice is about 200 ppm, but can vary significantly depending on the variety and origin of the apples, as well as factors such as storage and ripening conditions [12]. The unique aroma profile of black currant (*Ribes nigrum* L.) juice comprises more than 60 constituents with a certain profile of terpenoids, aliphatic esters, carbonyl compounds, and alcohols that make up the characteristic black currant aroma of the juice [548] and may be achieved by application of PV. PV of methylantranilate, a model flavor compound of grape juice aroma, through several membranes, including polydimethyl siloxane/polycarbonate (PDMS/PC) blends and poly (ether-block amide) (PEBA), has been investigated [549, 550]. Most published research in orange aroma concentration was carried out using commercial composite PDMS; PDMS membranes in the plate and frame geometry, namely Pervap B 1060 or Pervap 1070, which contains incorporated silicates [551]. Ethyl butanoate (ETB) and ethyl hexanoate (ETH) are important aroma components found in pineapple and banana juices that can be separated by PV, on PDMS membranes membrane developed by GFT, and homogeneous membrane manufactured by Dow Corning [552].

Bioreactor producing aroma compounds can be easily coupled with PV because the low feed temperature during the PV allows the preservation of temperature-sensitive compounds and this technique is well fitted [553]. The feed operating conditions are generally compatible with cell life (low temperature and low pressure in the feed). Finally, the continuous removal of the VOCs produced in the culture media, which are often strong inhibitors or metabolisms intermediates, can lead to an increase of the reactor yield.

There are two possible approaches for employing vapor permeation in aroma recovery. In the first one, the membrane module is fed with the exiting gaseous stream from the evaporators. However, since juice concentration takes place at low pressures, the driving force for mass transfer across the membrane would be low and, consequently, a large membrane area would be required. Alternatively, an aroma-rich gaseous stream at atmospheric pressure can be produced by the injection of an inert gas into the juice before its concentration, that is, by gas stripping. Such an approach not only increases the driving force for mass transfer but also precludes any thermal degradation of aroma components from occurring in the evaporators, being, therefore, regarded as more suitable. Owing to the high dilution of the target components in the feed stream, commercial aroma recovery plants are somewhat complex [554]. Operation usually takes place under vacuum so as to minimize thermal degradation of aroma compounds. However, the losses of valuable volatile constituents with the vent gases, already observed in systems

operating at atmospheric pressure, considerably increases at low pressures, which would result in aroma concentrates unable to closely resemble the flavor of the original juice. In order to overcome this problem, expensive gas washing and condensation systems have to be included in the plant [555].

The other membrane processes that are used for flavor processing are vapor permeation, vacuum MD, RO, NF, liquid membranes, membrane extraction contactors, and hybrid processes such as membrane reactors.

RO can be used for concentrating the aroma of fruit juices [556] such as apple juice [12], lemon juice [557], and even tomato [558] and mushroom [559] flavor. The advantage of the RO seems to be the conservation of the full composition of aroma constituents, which concern volatile and less volatile components [560]. RO can also be used for recovery of valuable components from processing waters with cooking juices of sea products containing two kinds of flavoring compounds. The first one consists in low-MW compounds ($\sim$400 g mol^{-1}), very volatile and belonging to various chemical classes (aldehydes, ketones, alcohols, esters, N- and S-containing compounds, etc). These compounds provide the pleasant cucumber/green, almond/nutty, potato, etc. aromas, which characterize seafood products such as components of roasted shrimps [561] or salted shrimps [562], squid [563], brew of cooked clam (*Meretrix lusoria*) [564], odorant compounds of mussels (*Mytilus edulis*) [565, 566], and aroma components of cooked tail meat of lobster [567, 568]. The second kind of compounds consists of water-soluble flavor compounds including low-MW free amino acids (taurine, glutamic acid, glycine, etc.), peptides, nucleotides (purine derivatives), quaternary ammonium bases, organic acids (lactic acid), sugar (glucose and ribose), and inorganic salts (Na′, K^+, and Cl^-).

Membrane contactor, in liquid–gas configuration, could also be a promising process for aroma compound separation [569, 570], including tomato industry effluent [571]. Liquid–liquid extraction of aroma compounds with hollow-fiber contactors has been recently examined in few studies [572], such as recovery of 2-phenylethylalcohol (rose-like aroma) or recovery of gamma-decalactone (peach-like aroma), produced by fermentation. These studies revealed that membrane extraction was a very promising method with respect to other techniques such as adsorption, PV, or simple liquid–liquid extraction [573]. The application of vapor MD for aroma recovery is described in literature for fruit juices and beverages [574], orange juice [405], and black currant juice [575]. Direct MD has been investigated by Drioli and co-workers [576] for concentration of aroma compounds.

4.05.2.12 Sugar Processing

The raw juice contains sucrose and various impurities. Raw cane sugar (or brown sugar) normally contains 94–98.5% sucrose and 1.5–6% non-sucrose components, such as reducing sugars, organic acids, amino acids, proteins, starch, gums, coloring matter, and other suspended matters. Polysaccharides and different colorants are mainly responsible for the quality of refined sugar after crystallization [577, 578].

Purification of the syrup, an intermediate product in sugar beet processing, is an important operation, which precedes sucrose crystallization [579]. For many years, this problem was solved by chemically induced precipitation of undesired non-sucrose compounds, after adding calcium oxide and carbon dioxide to the syrup solution or the addition of lime and sulfur dioxide, followed by boiling the treated juice (liming-sulfitation process) at 98–105 °C and then adjusted to a pH value of about 7. The clarification is also done by phosphatation/carbonation treatment and the decolorization is achieved by use of bone char, ion exchange, or their combination [580, 581]. The manufacture of plantation white sugar by the double sulfitation process broadly involves the syrup sulfitation. To this end, after sedimentation, the clear juice is pumped to evaporators to increase the Brix up to 60-/65, followed by treating the syrup with sulfur dioxide. The clarified juice is dark yellowish brown in color and somewhat hazy due to the presence of nonsugar impurities such as dextrans and waxes in the colloidal form. It is then sent to vacuum pans for crystallization (pan boiling), usually in batch-type vacuum pans, and then centrifuged. Next, sugar is dried and crystals are packaged [582].

Membranes in sugar industry are used for both the cane and beet sugar industries. It was found that the permeate obtained by membrane filtration possesses better quality, for example, higher clarity, lower viscosity, reduced color, and reduced calcium oxide content than the clarified juice produced by the conventional double sulfitation process. Consequent benefits include sugar quality [583, 584], higher crystal yield [585, 586], energy savings due to reduced evaporator steam consumption [587], and increased

capacity of evaporators, vacuum pans, crystallizers, and centrifuges [588]. Application of membrane processes can avoid the use of very large quantities of chemicals, and so will also produce a much smaller quantity of pollutants.

Membrane processes such as MF/UF/NF , ion exchange, or ED can be used for decolorization and removal of other impurities [577]. This has been explored extensively both in laboratory [589, 590] and factory trials [591, 592]. The purified juice is processed by MF, then by UF. UF process [593] is applied for a reduction of non-sucrose compounds [594] in sugar beet syrup, for example, impurities such as waxes, dextrans, and gums. Some experiences acquired from sugar cane juice UF [577, 581] can be applied to the purification of syrup in sugar beet processing. It was found that UF yields a juice of great purity and better quality.

UF is used for sugar solution clarification [584, 595]. It was proven to be technically superior to lime treatment because it yields a juice of higher purity and better color quality and is free from starch and acidified substances [586, 596]. The permeate can be evaporated and crystallized by conventional means to produce white sugar. Most of the studies on clarification and decolorization of brown sugar solutions were made using organic membranes of different configurations and molecular weight cutoff (MWCO) [597]. In order to obtain reliable decolorization, a membrane of 15 kDa MWCO can be used [577]. For instance, the PES membranes (5–100 kDa MWCO) and mineral CARBOSEP membranes (15–50 kDa MWCO) were used for decolorization. With membranes of MWCO between 30 and 50 kDa, approximately 50% reduction in color was obtained. [583].

NF is used for the color removal when UF level is unacceptable. NF uses of negatively charged membranes. The more negatively charged multivalent anions and higher-molecular-weight organics are retained while monovalent salts pass through the membrane. NF was found suitable for recovering up to 99% and sodium chloride in the permeate [598, 599] and removing organic matter from the regeneration effluent.

ED can be used for the removal of inorganic matter from clarified sugarcane juice [597, 600] where 50–70% of salts can be removed and the purity of sugar crystals obtained can be up to 99%. Although some minerals such as phosphates, silica, and magnesia are partially removed by clarification, potassium, sodium, and low concentrations of sulfates are not completely removable with the ED process.

Some papers involved problems of sugar purification such as analysis of retention and flux decline during UF of limed sugarcane (clarified) juice [601], influence of start-up procedure on CF-MF of raw cane sugar [602], separation of fructose from a mixture of sugars using UF of raw cane sugar remelt [603], the effects of operating parameters, membrane, and module properties during white sugar manufacture [581, 584, 604].

4.05.2.13 Honey Processing

Honey is a complex mixture of sugars, enzymes, wax, and lipid along with insignificant quantities of minerals, amino acids, organic acids, vitamins, ash, pollen, and propolis [605]. Sugars present in honey are laevulose and dextrose besides sucrose and maltose in minor quantities. The major enzymes present in honey are invertase, amylase (diastase), and glucose oxidase, along with small quantities of catalase and acid phosphatase. Diastase and invertase are nutritionally important enzymes present in honey. Diastase hydrolyzes carbohydrates for easy digestibility, while invertase hydrolyzes sucrose and maltose. Glucose oxidase is another important enzyme in honey which catalyzes glucose to form gluconic acid and hydrogen peroxide. Honey also contains a wide range of vitamins such as A, B, C, D, E, and K.

To process such a complex mixture for consistent product quality, retaining most of the nutritional value and imparting a better product appeal, is a real challenge for the processing industries. Studies on honey proved its widespread usage other than its nutritional value. The increasing usage of honey demands better processing methods on a large scale. It is difficult to completely destroy the microorganisms present in honey by traditional thermal processing methods practiced by the industries. Besides, thermal processing results in reduction in enzymatic activity.

Anticipated benefits of membrane processing of honey include no cloudiness or sedimentation/granulation in the product, reduced viscosity, commercially sterile product, and consistent quality characteristics. Itoh *et al.* [606] used different membranes with 7000, 30 000, and 80 000 MWCO in honey processing and reported that bacteria and protein could be eliminated from honey by using UF membranes. The applications of ultrafiltered honey

in gel formulations, cosmetics, and pharmaceutical preparations besides its use as sweetener in tea/coffee and fruit beverages have been reviewed by the National Honey Board (NHB), USA [607]. Ultrafiltered honey is devoid of desirable enzymes and proteins, and hence cannot be regarded for applications related to health foods. Attempts were also made using membrane technology to produce a honey that is free of microorganisms and suspended matter, but containing a significant concentration of enzymes. The UF studies revealed that UF membranes completely rejected enzymes and totally eliminated yeast cells in honey. The complete rejection of amylases by 100 000 MWCO UF membrane could be due to the formation of dynamic active layer on the membrane surface. The average permeate flux obtained was rather small – 1.15 $kg\,m^{-2}1\,h^{-1}$. It is possible to produce clarified honey and enzyme-enriched honey using a combination of MF and UF membranes in the process.

4.05.2.14 Vegetable Industry

Vegetable washing generates waters with high loads of particulate matter and some dissolved organics. It may also contain surfactants. Annually, within the European Union, over 2 million tons of juice from the potato starch production is generated. This stream consists mainly of water with a high concentration of potassium and has a high COD (minimally 20 000 mg O/l) due to the presence of, among others, proteins, amino acids, and sugars. Within the grain and vegetable food-processing industry, wastewater is high in SS, and organic sugars and starches and may contain residual pesticides. Solid wastes include organic materials from mechanical preparation processes, that is, rinds, seeds, and skins from raw materials. For the most part, solid waste that is not resold as animal feed is handled by conventional biological treatment or composting.

Membranes in vegetable and grain production are used for filtration, concentration of vegetable and plant proteins such as soy, canola and oat, soy milk whey and soy protein isolate, starch, gluten and potato starch recovery, corn syrup and maltodextrin clarification, removal of soy sauce crystalline deposits, xanthan gum concentration prior to extraction, corn mud removal, and removal of catalyst from hydrogenated oil. Starch and sweetener industry uses membrane filtration to replace traditional separation methods such as filter presses and rotary vacuum filters in a number of process steps. The primary benefits are elimination of handling/disposal of DE (kieselguhr) and increase in product yields. These include clarification of corn syrups such as dextrose and fructose concentration of starch wash water, dextrose enrichment, depyrogenation of dextrose syrup, and fractionation/concentration of steep water.

RO is used for recovery of process water in potato-starch factory. RO systems provide a low cost of 99.9% bacteria-free water. Besides, the permeate has extremely low contamination with color, taste, and odor. Over 99% of the organic pollution and solids can be removed during RO treatment and enables 80% of the water demand for the factory to be supplied by recirculation.

A great deal of efforts has been focused on the recovery of protein [608–611] by UF and RO membranes. Pretreated potato fruit juice [612] comprises: water 75–80, starch 15–20, fibers 1.5, proteins 1.5–1.8, amino acids 1.5–1.8, sugars + salts + acids 2–2.5. The proteins in this stream, with an average molecular weight of about 50 kDa, are in their native form. Pea protein concentrates and isolates are commercially available and are valuable functional ingredients widely used in food formulations [613, 614]. They may be produced by alkaline extraction [615–617]. These processes generate a large amount of effluent. Besides the large portion (20–30 g/100 g) of pea, protein remains in the pea whey and cannot be recovered by the current processing methods. Consequently, the pea whey discharge not only results in protein loss, but also poses a major environmental liability [614, 616, 618]. The loss of protein in the discharge causes a major economic loss for the commercial operation. UF membranes were tested for preparation of protein isolates directly from protein slurries [619] of chickpea [620] and yellow pea [614].

MF membranes may contribute in recovery of energy from wastewaters. Water and energy consumption in starch sector is very high. In wheat starch production only during deglutination the water consumption is 11–15 $m^3\,t^{-1}$ wheat flour and then discharged as a wastewater. Simultaneously, food industry sector seeks the cheap energy to treat huge amount of wastewaters, which may contain high-strength dissolved and suspended organic matter. Anaerobic wastewater treatment systems in such cases had advantages over aerobic ones in not only energy efficiency but also less sludge yield and production of gas useful for fuel. Wastewater from wheat starch production can also be converted into methane

in membrane-based two-phase methane fermentation system with 20 kg m^3 d^{-1} of COD loading [621].

4.05.2.15 Edible Oil Industry

According to International Olive Oil Council statistic the annual total production of edible oils was 26 528 million tons, including palm oil (11.420), rapeseed (0.473), soybean (95.95), and sunflower (0.775). The production of olive oil was a 2.719 worldwide whereas 80% in Europe, e.g. 2.148. There are approximately 10 800 mills over the world which use about 260–640 millions m^3 of the water during oil manufacturing.

Pressing followed by solvent extraction is the most widely followed method to handle a variety of oilseeds, namely groundnut, coconut, palm kernel, sunflower, cotton seed, and rapeseed [622], which contributes to nearly 50% of the total vegetable oil produced in the world. The extraction processes are generally mechanical (boiling for fruits and pressing for seeds and nuts) or involve the use of solvent such as hexane. After boiling, the liquid oil is skimmed; and after pressing, the oil is filtered; whereas after solvent extraction, the crude oil is separated and the solvent is evaporated and recovered. The major vegetable oil producers in the world mix the expeller oil and solvent extracted oil before refining. The conventional refining has many drawbacks such as high energy consumption, loss of neutral oil, use of chemicals and water in various steps, and loss of nutrients and natural antioxidants during the high-temperature and long-duration processing steps. Particularly, a bleaching operation using activated clay is very harmful considering the loss of biological value of the oil.

The oil refining technology comprises the following sequence of steps. Degumming is used for removal of phospholipids, suspended matters, sugars, and metals by dehydration followed by separation through gravity settling or centrifugation. Water degumming process removes hydrated phospholipids and recovers gum as lecithin. Gum conditioning removes both hydrated and nonhydrated phospholipids using phosphoric and citric acid. Acid degumming removes anhydrous phospholipids. Pre-neutralization involves the removal of free fatty acids (FFAs) from the oil. During bleaching, neutralized oil is bleached with bleaching earth and carbon to remove color and residual matter. The soap splitting is a process in which soap solution/water waste oil from pre-neutralization unit is drawn and split up to get free oil using sulfuric acid. This helps in recovery for trapped oil. Pre-deodorization is used only for mustard and rapeseed oil, where neutralized mustard/rape seed oil is stripped with 4 m^3 steam kg^{-1} oil at 160 °C. This removes the sulfuric compounds causing odor from the oil. During hydrogenation, neutralized oil after deodorization is treated with hydrogen under controlled conditions, which result in physical and chemical changes of oil from liquid to solid by conversion of unsaturated fatty acids of oil into saturated acids. During blending and post-neutralization, the hydrogenated (hardened oils) oils are blended together and the final blend is neutralized to free the hardened oils from FFAs and catalyst. During post-bleaching and post-deodorization the hardened oils after FFA removal, oil is bleached and deodorized using suitable agents for removal of odiferous and other volatile compounds to below the taste threshold. During vitaminization, pre-chilling and packing blended oil after post-neutralization, post-bleaching, and post deodorization is supplemented with vitamin A (25 IU mg^{-1}) and vitamin B (21 IU mg^{-1}) Pre-chilling is a process for cooling the refined oil before filling into the pouches or containers

Olive oil production is specific because it is based on long tradition, and also because olive oil is one of the oldest agricultural industries in the Mediterranean region, and is still of primary importance for the economy of most of the Mediterranean countries [623, 624]. Pressing is the oldest and most common method of oil extraction and virgin olive oil are consumed without any further treatment. The quality of the virgin or pressed oil is good because the natural antioxidants are retained without loss of nutrients. However, its quality cannot be compared with the refined oil on certain aspects as some of the contaminants and impurities, mainly phospholipids, color pigments, FFAs, and oxidation products, are not removed.

Oil processing generates approximately 10–25 m^3 of wastewater per ton (t) of product. The wastewater is high in organic compounds, such as organic acids, sugars, tannins, pectins, and polyphenolic substances, resulting in a BOD of 20–35 kg t^{-1} and a COD of 30–60 kg t^{-1} that make them difficult to treat [625]. In addition, the wastewaters are high in dissolved solids (10 kg t^{-1}), oil and fat residues (5–10 kg t^{-1}), organic nitrogen (0.5–0.8 kg t^{-1}), and ash residues (4–to 5 kg t^{-1}). Most of the solid wastes (0.7–0.8 kg t^{-1} of raw material), which are mainly of vegetable origin, can be processed into by-products

or used as fuel. The treatment of the olive mill wastewaters is very expensive. The costs (fixed and operational), with the implementation of conventional treatment technologies (such us aerobic or anaerobic digestion), have been estimated to be the 50% of oil production total expenses [626]. The presence of phytotoxic compounds inhibits bacterial activity [627]. Besides, oil wastewaters also contain inorganic compounds such as chloride, sulfate, and phosphoric salts of potassium as well as calcium, iron, magnesium, sodium, copper, and traces of other elements [628].

Good pollution prevention best practices [629, 630] in the oil industry focus on the preventing, handling (e.g., collect waste product for use in by-products such as animal feed), substitution of materials (i.e., use citric acid instead of phosphoric acid in degumming operations), and also on changes in the process itself such as "...Where appropriate, give preference to physical refining rather than chemical refining of crude oil" or "Reduce product losses through better production control" or "Recover solvent vapors to minimize losses" or "Optimize the use of water and cleaning chemicals", or "Recirculated cooling waters". Particular IPPC recommendations claim that: "... operators should aim to achieve lower rates at the intake of the effluent treatment system. Hexane, if used, should be below 50 mg/l in wastewater. The BOD level should be less than 2.5 kg/t of product, with a target of 1–1.5 kg/t. Effluents from Vegetable Oil Processing (milligrams per liter) should meet the following parameters: value pH 6–9, BOD<50, COD< 250, TSS<50, Oil and grease<10, Total nitrogen<10. One of the key Issues is "Design and operate the production system to achieve recommended wastewater loads and recirculate cooling waters."

All of these recommendations may be fulfilled by applications of membrane processes that assure not only a significant reduction of BOD and COD values, but also the possibility of selectively recovering some valuable compounds that could be used in the same production cycle or as raw material for other processes [631–633].

The removal and recovery of phospholipids from vegetable oil using membrane techniques is the operation that has received most attention because phospholipids can be a valuable by-product [634]. The removal of phospholipids (degumming) is the first step of the crude vegetable oil refining process [635]. Many phospholipids and triglyceride oils are lost by destructive treatment with the alkaline agents [636]. Due to the similarity in molecular weight (MW) between triglycerides (900 MW) and phospholipids (700 MW), it would be difficult to separate them by a membrane. However, phospholipids have some characteristics, such as to be surfactants in nature, to have both hydrophobic and hydrophilic groups, and to form reverse micelles in nonaqueous environment. Such micelles have an MW of 20 000 Da, so phospholipids can be separated from triglycerides using appropriate membranes [637].

Membrane (UF, RO, and NF) processes have been introduced in order to overcome severe oil losses and wastewater contamination in the area of the oils and fats industry for degumming of micelle [638]. Micelle-enhanced UF for the degumming of hexane-oil micelles was reported by many authors [637, 639, 640] concluding that suitable hexane-resistant membranes are necessary for the subsequent steps of the proposed membrane purification process. There are reports on removal of FFA from model vegetable oils by alcohol extraction of FFA followed by membrane separation [641] Several research groups have actively investigated solvent-resistant membranes [642–645].

UF membranes for refining of vegetable oils without added solvent achieved 93% retention of phospholipids in the pilot scale [646, 647]. Polymeric composite membranes (nonporous) can be used for various steps of the vegetable oil processing without addition of solvents by using the polyamide (PA), polysulfone (PSf), polyvinylidenfluoride (PVDF), polyimide (PI) [638], and polyacrylonitrile (PAN). Polyimides have been known for their excellent solvent and high temperature resistance in spite of their low processability.

The conventional methods that are used for the treatment of an effluent, which comes from the degumming, deacidification, and deodorization steps [648, 649], are aerobic or anaerobic digestion where the ratio of BOD to COD should be >0.6 [650]. However, an effluent from the vegetable oil industry usually has its BOD/COD ratio around 0.2, which could cause destruction of microorganisms useful for the biodegradation. Other methods such as multiple effect evaporation or incineration is highly energy intensive and, hence, very expensive.

Membrane separation techniques such as O yield excellent results when applied judiciously in such cases [651, 652]. The effect of process variables such as feed pressure and feed concentration on membrane performance with respect to percent

rejection of TDS, COD, BOD, and color was extensively studied [653]. UF of oil emulsions may be easily adapted to olive mill wastewaters. The olive mill wastewaters contain various compounds potentially useful for diverse applications, as a raw material in various biotechnological processes or as animal food [654]; however, this could have limitations due to some toxic characteristics of the waste. Generally, the microbial pretreatment of olive mill wastewaters positively affects its composition, often solving toxicity problems. Oil in effluents is often emulsified in the form of stabilized emulsions. In that case, the destabilization by addition of chemical reagents (acids, salts, or polyelectrolytes) was conventionally used before separation of the oil from the water phase by decantation, centrifugation, flotation, etc.

Cross-flow filtration [655–658] has the advantage of reducing or avoiding the use of chemical reagents. Sridhar *et al.* attained high rejection of TDS (99.4%) and COD (98.2%) with complete rejection of color and BOD on TFC polyamide RO membrane with a reasonably high flux of $52.5\,l\,m^{-2}\,h^{-1}$ [648]. The zero-discharge treatment system has been designed for Tri Valley Growers [659], an olive processing facility with a production capacity of 128 t of olives per day in Madera. This system comprises UF and RO for final polishing with 80% recovery of the wastewater. Permeate is reclaimed for reuse in the plant and the remaining 20% retentates from the UF and RO systems are sent to an evaporator, which concentrates it to $19\,m^3$ per day of concentrate (60% solids), which is then manufactured into animal feed. Ahmad *et al.* [660] described a treatment system based on membrane technology (RO and UF) with pretreatment comprising chemical pretreatment and adsorption on activated carbon. Results from the total treatment system show a reduction in turbidity NTU = 0%, COD = 98.8%, and BOD = 99.4% and reclaimed water can be recycled back to the plant as a boiler water. Another successful membrane installation [661] was in the treatment of a flow of $150\,m^3\,d^{-1}$ of alkali/chlorine and acid washdown from a mayonnaise/salad dressing production facility. In this case, a concentration factor of 120 was achieved coupled with a monthly saving of $1600 in sewer discharge costs. In both these cases, there was a saving in operating costs, leading to an overall payback time of less than 1.5 years.

4.05.2.16 Dairy Industry

Total cow milk production was 512.7 million tons in 2003. The leading producers of cow milk continue to be in the European Union followed by North America and Asia. International trade estimates suggest that whole milk powder was the most important product in international dairy trade in 2003 with 1.7 million tons. Skim milk powder, cheese, and butter had total trade volumes estimated at 1.3 million tons, 1.37 million tons, and 0.9 million tons, respectively, and 5.27 million tons of milk products became traded and consumed. Milk is approximately 87% water and 13% solids, which means that more than 40 million tons of milk has been processed and at the same time more than 35 million tons diary wastewaters have been emitted to environment by diary industry. All processed milk products, which include cheese, butter, ice cream, and yogurt, originate from fluid milk. The primary steps in processing are clarification or filtration, blending and mixing, pasteurization and homogenization, process manufacturing, packaging, and cleanup.

One of the most successful applications of membrane technology in dairy industry is the processing of whey [662]. The whey, mainly resulting from bovine cheese production, is normally transformed into whey protein concentrates (WPCs) and whey protein isolates (WPIs) of high economical value due to the high nutritional [663] and functional properties of its proteins. Whey is a raw material in production of protein concentrates (WPCs) and individual whey protein concentrates (IWPCs), which can be used as food additives or may be fractionated into individual whey proteins [636, 664]. WPCs are ingredients widely used in the food industry in a variety of formulated products, such as dairy, bakery, meat, beverage, and infant formula products [665] due to the excellent functional properties of their proteins [666]. Most researchers focused mainly on the fractionation processes as well as on the enhanced processing and functional properties of delipidized whey powders [667, 668]. For about 20 years, the dairy industry has been preparing a wide range of whey protein concentrates with a relative purity of 35–85% protein in total solids by cross-flow UF accompanied with diafiltration [669].

The whey treatment is a serious environmental problem caused by diary industry because in many cases the whey, resulting from cheese production, is disposed of into public sewage, since the majority of the existing plants do not possess the technology for the recuperation of its components. In small-scale plants, the utilization of whey does not seem to be a problem since it may be used as complementary feedstock for animal feed. However, larger-scale

production makes the use of complex and expensive treatment.

Membrane processes were successfully introduced to the dairy industry in the late 1960s. Membrane applications in diary industry concerns removal of bacteria, casein, and off-flavor from milk or whey; removal of fat from milk and skimmilk; reduction of carbohydrates in fluid milk and ice cream; concentration of whole milk enrichment and fluid milk protein; concentration and de-mineralization of whey to reduce energy costs; fractionation of milk proteins [670, 671]; purification of bovine whey protein (e.g., b-lactoglobulin, a-lactalbumin); concentration of 35–95% sweet whey and acid whey; standardization of cheese vat protein of milk prior to cheese production; production of high-value WPC up to 82–85% and WPI 90%; and clarification of brine and recovery alkaline from wastewaters. A number of recent studies have demonstrated the feasibility of using membrane systems for the separation of proteins with very similar molecular size [213, 672] to separate albumin [278] from whey.

Membrane processing of fluid milk components can be carried out without imparting a phase change by the addition of heat, or an enzyme, as done in most cheese-making techniques. The milk is modified by separating, clarifying, or fractionating selected components from the others using differences in their relative molecular weights and pore sizes of the membranes.

CF-MF has became increasingly important in the dairy industry, both for the removal of bacteria and for fat, caseins and whey proteins separation [673] MF of milk and milk products can reduce the microbial loading of bacteria and viruses, thereby prolonging life and reducing the severity of pasteurization [674]. MF has been introduced for the removal of spores [675] and several types of microorganisms [676] from milk to enhance the suitability of membrane-treated milk for cheese production. MF process provides a means to isolate healthful components in milk and incorporate them into the new products that consumers are beginning to demand. MF can yield a casein-enriched cheese milk that would be ideal for semihard cheeses such as cheddar. MF can separate the large components that are in milk such as fat to concentrate the cream from milk. The smaller pore-size membranes allow a separation of the casein from the milk serum or whey proteins. In addition, MF can be used to produce WPCs [677], to clarify cheese brine [678], in the separation of casein from whey proteins [679], and to improve product quality [680].

The use of UF in the dairy industry has increased considerably during the last 20 years, especially in the area of cheese manufacture [681, 682]. UF technology has been successfully used for the manufacture of cheeses such as feta, camembert, quarg, cream, and cottage cheese [683] and for standardization of milk for the manufacture of a range of cheese varieties. Using concentrated milk in cheese production could reduce rennet and starter culture requirements, depending on the application. In addition, it could reduce a cheese plant's wastewater processing costs. UF permeate contains solids (primarily lactose), an RO unit should be installed to concentrate the permeate solids. UF is used for fractionating of whey proteins from the lactose and from the milk proteins and can reject proteins and fat. UF has proved to be the system of choice for preparing WPCs with good functional properties; however, membrane fouling, caused by several whey components, is a drawback in UF [684].

NF rejects the lactose, which may also be purified and washed out from the minerals. RO enables to pass water only, thus may be used as a unique process to concentrate the whole milk. The concentration by means of RO is used in whey processing, being an alternative to expensive evaporation techniques used in milk processing. NF and RO are used in dairy industry to concentrate and to give value to the milk constituents in nonfood applications and to simultaneously produce treated water that can be reused in the dairy factory. The target quality of the treated water depends on the requirements for the type of reuse (CIP, cooling, boiler feed, etc.); it must be similar to the characteristics of drinking water ($KMnO_4$ oxidizability <5 mg O_2/l, TOC <2 mg l^{-1}) but for some reuses the requirements are more drastic (requirements for boiler feed water: conductivity $<40\,\mu S\,cm^{-1}$, Ca^{2+} <0.4 mg l^{-1}). Examples of water reuse as boiler feed water are given in literature with COD values between 10 and 52 mg O_2/l.

NF and RO are convenient operations for treating effluents at source and achieving quality for water and lost components for reuse. RO of skim milk was presented by Cheryan *et al.* [685] for the purpose of concentrating dry matter as a substitute to evaporation which avoids thermal damage to food components. Desalination is also necessary for further use of whey as a raw material for other valuable products such as baby food or for the recovery of

proteins. Processes which can be used for the desalination of whey are ion exchange (IE), ED, NF, and RO are reported in literature [686, 687]. These processes have been investigated for more than 25 years [688]. In The ED industrial plants, demineralization achieves a level of 50%.

Food poisoning caused by consuming dairy products contaminated with *S. aureus* enterotoxin has been frequently reported. Even low concentrations of enterotoxin (0.5–0.75 ng ml^{-1}) in milk and dairy products caused food poisoning [689]. Membrane filtration is widely used for microbiological analysis of water, drinks, and solid products [690]. Several attempts to enumerate *L. monocytogenes* with the most probable number technique have been reported [691, 692]. However, these methods are extremely labor-intensive and do not provide accurate results. Recently, membrane filtration was applied to the detection and enumeration of *L. monocytogenes* [693, 694]. The microbiological analysis techniques, such as hydrophobic grid membrane filtration (HGMF), including a filtration stage, have been already agreed by the Association of Official Analytical Chemists (AOAC) for several bacterial species in food.

Dairy effluents essentially made of diluted milk are responsible for a 1–3% loss in milk components [695, 696]. The white water is generated during starting, equilibrating, stopping, or rinsing operations. Besides, these process waters, which contain diluted fractions of the dairy products, significantly contribute to the total wastewater production. Since process water recycling requires a significant reduction in lactose and ionic content in the permeate, the treatment must include a final step of NF or RO [696–698] to concentrate and to give value to the milk constituents in nonfood applications; to simultaneously produce treated water that can be reused in the dairy factory. Another waste stream of the dairy sector is from equipment and tank-cleaning wastewaters. These waste streams contain waste milk and sanitary cleaners and are one of the principal waste constituents of dairy wastewater. Water recovery in dairy industry is carried out also from cleaning solutions and the so-called white water. Desalination of recycling water in dairy industry is very important [699].

NF is reported to be an efficient membrane separation for the recovery of cleaning solutions [700, 701]. The major limiting factor in membrane processes applied in dairy industry is the fall in flux with time due to fouling [702] and concentration polarization (CP) [703, 704]. During the first 2 min of filtration, a salt and lactose layer form on the membrane, which results in a rapid flux decay due to buildup of osmotic pressure. In the second stage, which lasts about 8 min, the permeate flux rises as a protein layer forms, which prevents further transport of salts and lactose to the membrane, resulting in a decrease in osmotic pressure. [705]. Phospholipids cause rapid decrease in UF membrane performance [706]. MF fouling is caused by pore blocking, cake buildup, or a combination of both effects [423, 707], which necessitates frequent chemical cleaning to maintain the permeability and selectivity of the membrane process, while maintaining hygienic operation conditions [708]. Membrane cleaning is considered an essential step in restoring membrane performance and maintaining hygienic operation [423, 709]. In order to maximize the efficiency of the cleaning process in terms of time, water and cleaning agent's consumption, the entire cleaning of the membrane is usually divided into two main steps: rinsing [710, 711] and cleaning [712]. Enzymatic agents can improve cleaning efficiency, as well as reduce the amount of chemicals needed and energy costs by working at a lower temperature. Moreover, they are biodegradable and the preparation of tailor-made cleaners is possible [713]. The possibility of reusing the cleaning solutions is very important from the economic point of view.

4.05.2.17 Meat Industry

Animal slaughter and processing produces very strong organic waste from body fluids, such as blood, and gut contents. The primary steps in processing livestock include rendering and bleeding, scalding and/or skin removal, internal organ evisceration, washing, chilling, and cooling, packaging, and cleanup. Animal blood is a by-product of slaughterhouses, and contains proteins of a high biological value as well as being a possible source for biotechnology products. Blood contains about 18% proteins, almost as much as lean meat, and is sometimes referred to as liquid protein. Because of its high nutritional value, blood as food additive is cost-competitive in comparison with other proteins, such as soy and milk proteins, used in sausage formulations. The dry proteins have excellent gelling properties and emulsifying capacity and can be used for the production of yoghurt, cheese, and cakes [714]. Protein concentrates prepared from whole blood are excellent emulsifiers [715]. Whole blood proteins exhibit emulsification capacities and

emulsion stabilities equal to or greater than that of proteins of other organ and tissue concentrates including muscle proteins [716]. Plasma and globe protein isolates prepared from slaughter blood are ideal emulsifiers under optimum conditions of pH and protein concentration [717]. Vacuum evaporation, freeze drying, and gel filtration are the processes that can be used for concentrating blood proteins without degrading their delicate and revenue-producing properties; however, UF of plasma proteins is more efficient than plasma freezing [718] or chemical coagulation. Bioreactors with aerobic [719] and anaerobic digestion [720] are used for wastewater treatment. In the latter case, the biogas is produced as the source of energy recovery.

Wastewater from slaughterhouses contains a large variety and quantity of contaminants, characterized mainly by a complex mixture of protein substances, lipids, and fibers. Wastewater is also frequently contaminated by significant levels of antibiotics and growth hormones from the animals and by a variety of pesticides used to control external parasites. Insecticide residues in fleeces are a particular problem in treating waters generated in wool processing. In meat, poultry, and seafood-processing facilities, the main problem is pathogenic organisms. Wastewaters with high pathogenic levels must be disinfected prior to discharge. Typically, chlorine (free or combined) is used to disinfect these wastewaters. Ozone, ultraviolet radiation, and other disinfection processes are gaining acceptance due to stricter regulations on the amount of residual chlorine levels in discharged wastewaters. Various techniques, which include anaerobic digestion, precipitation with ammonium sulfate, and MF, are used in the treatment of abattoir effluent. Wastewater treatment of slaughterhouse effluents can also be the source of valuable proteins for sale. Much work was also conducted on protein recovery from wastewater by UF [716].

In meat production, membranes are used for filtration, concentration, and deashing of pork, bone, or beef gelatin beef tallow clarification, gelatin primary clarification, meat brine clarification for bacteria removal and brine reuse, beef wash water porcine bovine blood plasma, and chicken blood, gelatin production. Application of membranes in meat technologies enable to avoid the extremely heavy loaded (BOD) wastewaters from abattoirs by recovery of proteins from animal blood.

The plasma is concentrated in membrane processes such as UF, RO, or cryo-concentration before atomization or cooling. UF concentration of blood proteins is faster, very simple, and the energy requirements are very low; are not thermal and do not alter the solute; and, finally, concentration, fractionation, and purification can be carried out simultaneously. UF is also 50% less expensive than vacuum evaporation for animal blood concentration [721] Optimum parameters of concentrating blood plasma by UF have been presented in many papers [722], including influence of feed flow rate, membrane pore size, and pressure on protein concentration [661, 723].

Animal blood is the principal organic pollutant discharged in wastewaters. Some reports concerning blood separation [722] and fractionation in industrial scale [724] encourage using membrane processes for simultaneous recovery of water from waste effluents – NF [725], NF/UV integrated system [726]. The UF PES membranes with a 40 000 MWCO and the RO membranes made of cellulose acetate were used to treat effluent from red meat abattoirs [727]. A cost for treating the effluent was $\$0.62\,m^{-3}$ versus $\$1.16\,m^{-3}$ for anaerobic digestion.

4.05.2.18 Sea-Products Industry

Sea-products processing industry is characterized by high-level water consumption and by the production of various aqueous effluents more or less salted [728–730]. During fish and sea-products processing, the water consumption is about 0.2–0.4 m^3 per ton of fish having very high organic load. The term process wastewaters comprises all liquid effluents from the processing of fish, shellfish, and crustaceans, usually washing, cooking, or pressing waters. This concerns especially three groups of effluents: the seawater pumped together with the fish during its unloading from the ships to the factories, the wastewaters generated during the fishmeal production, and the specific wastewaters that are produced during the surimi processing. In order to avoid peak discharges, this effluent is diluted with the cooling waters from the overall process, prior to its disposal, the total flow rate, and COD becoming $1000–1200\,m^3\,h^{-1}$ and $3–9\,g\,O_2\,l^{-1}$, respectively.

Cooking or brining operations use lower amounts of water but produce more charged effluents, in particular, in canning industries. For instance, water consumption ranges from 0.4 to 1 dm^3 per kg of food product for trade activity. It may reach $200\,m^3\,d^{-1}$ for fillet washing or fish conveying but shrimp cooking requires only about 10. If the capacity of the

cooking line is large enough, the recovery of material may appear economically feasible. For instance, a shrimp cooking line with a 2000 ton yr^{-1} capacity will be able to produce about 15 ton y^{-1} of organic material.

Bail water is used for pumping the fish as a carrier medium and its consumption during fish transportation reaches 1–10 m^3 per ton of unloaded fish, with high organic load (COD = 7000–49 000 mg O_2 l^{-1}). These wastewaters are usually drained into the sea without any treatment, having a negative impact on the environment caused by the direct discharge of these waters into the sea.

Membrane technology has a great potential for the concentration, fractionation, and purification of soluble and insoluble materials of sea products. Membrane processes are used in fish processing for recovery of fish meat and soluble proteins, oils, and greases. [729].

The outstanding advantages of membrane processes over the coagulation/flocculation and DAF processes are the good quality of the permeate, which can be disposed directly into the sea or preferably recycled into the plant, and the possibility of simultaneously recovering and concentrating the proteins that reduces the total costs. Another important advantage of pressure- driven membrane processes is that they are particularly suitable for the concentration and purification under mild conditions of sensitive biological substances of high added value (e.g., proteins, enzymes, and hormones) without using heat or chemicals.

RO and UF [731, 732] may be feasible at the beginning of fish meal processing, for example, for in the clarification of bail water. RO is a suitable technique for the preconcentration of the solids from 5–6% up to approximately 20% [733] from stickwater and for the separation of proteins and salts from fish-press waste, which contains high levels of organic matter (BOD = 75 g l^{-1}, COD = 130 g l^{-1}). Anaerobic treatment was inefficient in this case due to the high salt contents (50–130 g l^{-1}), whereas UF (10 kDa) proved to be efficient. RO, UF, and MF are used in fish processing for treatment of effluents with simultaneous recovery of water [734, 735]. NF is also an efficient and ecologically suited environmental technology for decontamination and recycling of the wastewaters generated during the fish meal production, as it allows both the recycle of water (permeate stream) and proteins (concentrate stream) into the fish meal process. The effluent generated in a fish meal plant can be pretreated by MF membranes [736].

UF was also used in processing of clams and oysters [737], lobster and shrimps [738]. Fish gelatins produced from fishery by-products are potential alternatives to mammalian gelatins [739, 740], especially since the bovine spongiform encephalopathy – mad cow desease (BSF) crisis caused by prions. UF may be an effective means to produce fish gelatins of upper quality and particularly may be successful to concentrate fish gelatin solutions [741–743]. In addition, UF can provide a further product improvement through the removal of salts from the gelatin liquors by operating in the diafiltration mode [744].

Several studies overviewed the various applications of membrane technology in the fishing industry such as the wastewater treatment and protein recovery [745], the production from fish protein concentrates and hydrolysates, the processing of biochemicals from marine raw materials [746], and the recovery and concentration of proteins from the stickwater [747] of a fish plant by using UF. During fish fillet processing with membranes, UF and RO are used for the treatment of fish processing wastewaters, and purification of proteins [748–750]. Approximately 90% of enzymes can be recovered by tubular UF membranes of 25 kDa [751]. Crab processing is another example where UF membranes of 50 kDa are suitable for the treatment of the effluent discharged from the cooker [752–754] The effluents from minced fish, crab claw, fish scaling, and washing steps were processed at lower MWCO membranes (0.5, 10, and 30 kDa) [755, 756]. Recovering solids from surimi wash water by membrane filtration has been reported by several authors [757]. Systematic investigations on commercial membranes proved that MF and UF could be technically feasible as a preconcentration step, for example, before spray-drum- or freeze-drying in order to stabilize proteins before adding value [758]. The application of membrane distillation has been recently patented [759, 760] for the recovery of proteins from boiled and compressed fish waters [761].

MF enables the solids recovered from the surimi wastewater to be directly added to surimi to increase yield without affecting its quality [757]. In this case, solids recovered by UF (30 kDa MWCO) had a dark color and an unpleasant odor. The wastewaters from surimi processing contains approximately 2–5 g l^{-1} of water-soluble proteins [731], being the total protein loss during the washing and dewatering about 30% of the deboned meat mass and, therefore, is suitable for

the recovery and reuse of proteins and the water as well, either by direct recirculation to the process or by subsequent use in animal feed or human consumption [762, 763]. However, the protein concentrations are usually too low to be economically recovered by means of conventional separation processes.

Reviews on the application of membrane filtration to seafood wastewaters [764, 765] pointed out that a fish processing used UF to fractionate the proteins and oils from the brine. During the salting of herring, approximately 200 l of brine is formed per ton of fish, containing proteins and low molecular aroma components. Recovered brine could be reused at least 5 times to store fish [733, 766]. UF was used for the treatment of the defrosting waters by UF [767] with a cellulose acetate membrane where the permeation flux ranged from 101 to 48 $l\,m^{-2}\,h^{-1}$.

In some cases, the application of membranes opened a new unexpected technology and product. For instance, oil and grease (520–13 700 $mg\,l^{-1}$ oils [768]) that were recovered from the fish processing effluents by means of UF were subsequently used as resources in plastic production on the condition that it can be effectively recovered in pure form. The commercial Norway fish oil used fatty acid ethyl esters [769] for cationic polymerization [770]. Polymers derived from renewable natural resources are inexpensive, environmentally friendly, and can be made biodegradable after use [771].

References

[1] Koltuniewicz, A. B., Drioli, E. *Membranes in Clean Technologies, Theory and Practice*; Wiley-VCH: Weinheim, 2008(ISBN-10: 3-527-32007-5; ISBN-13: 978-3-527-32007-3).
[2] Grove, P. B., Ed. *Webster's Third New International Dictionary of the English Language*; Merriam-Webster: Springfield, MA, 1993.
[3] Dickey, N. H., , *et al.*, Ed. *New Encyclopedia*; Funk and Wagnalls: New York, 1995.
[4] Lipnitzki, F., Field, R. W. Ten, P.-K. *J. Membr. Sci.* **1999**, *153*, 183–210.
[5] Gienger, J. K., Ray, R. J. *AIChE Symp. Ser.* **1988**, *84* (261), 168–175.
[6] Binning, R. C., James, F. E. *Pet. Refiner.* **1958**, *37*, 214–215.
[7] Stephan, W., *et al. J. Membr. Sci.* **1995**, *99*, 259–272.
[8] Pettersen, T., Lien K. M. *J. Membr. Sci.* **1995**, *99*, 21–32.
[9] Eliceche, A. M., *et al. Comput. Chem. Eng.* **2002**, *26*, 563–573.
[10] Bausa, J., Marquardt, W. Using Shortcuts for the Design of Hybrid Membrane/Distillation Processes. In *AIChE Annual Meeting 1998*, Miami, FL, 16–21 November 1998.
[11] Lu, Y., *et al. Desalination* **2002**, *149*, 1–87.
[12] Alvarez, S., *et al. J. Food Eng.* **2000**, *46*, 109–125.
[13] Sommer, S., *et al. Desalination* **2002**, *149*, 15–21.
[14] Marx, S., *et al. J. Membr. Sci.* **2002**, *209*, 353–362.
[15] Wu, Y., *et al. J. Membr. Sci.* **2002**, *196*, 179–183.
[16] Essam El-Sayed, *et al. Desalination* **2000**, *128*, 231–245.
[17] Helal, A. M., *et al. Desalination* **2003**, *154*, 43–66.
[18] Poddar, T. K., Sirkar, K. K. *J. Membr. Sci.* **1997**, *132*, 229–233.
[19] Roizard, D., *et al. Desalination* **2004**, *162*, 41–46.
[20] Mark, E., *et al. Sep. Purif. Technol.* **2001**, *22*, 377–382.
[21] Shah, M. R., *et al. J. Membr. Sci.* **2004**, *241*, 257–263.
[22] Bhide, B. D., *et al. J. Membr. Sci.* **19981**, *40*, 27–49.
[23] Kentish, S. E., Stevens, G. W. *Chem. Eng. J.* **2001**, 149–159.
[24] Castilho, L. R., *et al. J. Membr. Sci.* **2002**, *207*, 253–264.
[25] Drioli, E., Circuscoli, A., Curcio E. *Membrane Contactors: Fundamentals, Applications and Potentialities*; Membrane Science and Technology Series 11; Elsevier: 2005.
[26] Lawson, K. W., Lloyd, D. R., *J. Membr. Sci.* **1996**, *120* (1), 111–121.
[27] Mulder, M. *Basic Principles of Membrane Technology*; Kluwer, 1996. pp 224–232, 418–424.
[28] Baticle, P. C., *et al. Sep. Purif. Technol.* **2000**, *18*, 195–210.
[29] Kryvoruchko, A., *et al. Desalination* **2002**, *144*, 243–248.
[30] Blocher, C., *et al. Water Res.* **2003**, *37*, 4018–4020.
[31] Mavrov, V., *et al. Desalination* **2003**, *157*, 97–104.
[32] Lazaridis, N. K., *et al. J. Membr. Sci.* **2004**, *228*, 83–88.
[33] Turano, E. *J. Membr. Sci.* **2002**, *209*, 519–531.
[34] Liu, Q. L., Chen, H. F. *J. Membr. Sci.* **2002**, *196*, 171–178.
[35] Daub, K., Dittmeyer, R. In *Proceedings of the 15th International Symposium on Chemical Reaction Engineering* (ISCRE 15), Newport Beach, CA, USA, September 1998; pp 13–16.
[36] Daub, K., *et al. Chem. Eng. Sci.* **1999**, *54*, 1577–1589.
[37] Mohan, K., Govind, R. *AIChE J.* **1988**, *34*, 1493–1503.
[38] Mohan, K., Govind, R. *AIChE J.* **1986**, *32*, 2083–2086.
[39] Mohan, K., Govind, R. *Ind. Eng. Chem. Res.* **1988**, *27*, 2064–2070.
[40] Itoh, N. *AIChE J.* **1987**, *33*, 1576–1578.
[41] Sun, Y. M., Khang, S. J. *Ind. Eng. Chem. Res.* **1990**, *29*, 232–238.
[42] Vemiya, S., *et al. Ind. Eng. Chem. Res.* **1991**, *30*, 585–589.
[43] Song, I. K., Lee, W. Y. *Appl. Catal. A: Gen.* **1993**, *96*, 53–63.
[44] Kita, H., *et al. Chem. Lett.* **1987**, 2053–2056.
[45] David, M. O., *et al. J. Membr. Sci.* **1992**, *73*, 129–141.
[46] Okamoto, K., *et al. J. Chem. Eng. Jpn.* **1993**, *26* (5), 475–481.
[47] Kita, H., *et al. Chem. Lett.* **1988**, 2025–2028.
[48] Keurentjes, J. F. F., *et al. Chem. Eng. Sci.* **1994**, *49*, 4681–4689.
[49] Feng, X., Huang, R. Y. M. *Chem. Eng. Sci.* **1996**, *51*, 4673–4679.
[50] Bagnell, L., *et al. J. Membr. Sci.* **1993**, *85*, 291–300.
[51] Liu, Q., *et al. J. Membr. Sci.* **1999**, *159*, 233–241.
[52] David, M. O., *et al. Trans. Inst. Chem. Eng.* **1991**, *69*, 335–340.
[53] David, M. O., *et al. Trans. Inst. Chem. Eng.* **1991**, *69*, 341–346.
[54] Liu, Q., *et al. J. Chem. Eng. Chin. Univ.* **1997**, *11* (2), 172–176.
[55] Calabrò, V., *et al. J. Membr. Sci.* **2002**, *206*, 217–241.
[56] Molinari, R., *et al. J. Membr. Sci.* **2002**, *206*, 399–415.
[57] Hyung, H., *et al. Ozone Sci. Eng.* **2000**, *22*, 637–652.
[58] Rajeshwar, K. *Chem. Ind.* **1996**, *2*, 135.
[59] Schiavello, M. *Photoelectrochemistry, Photocatalysis and Photoreactors, Fundamentals and Developments*; Reidel: Dordrecht, 1985.

[60] Pelizzetti, E., Serpone N., Eds. *Photocatalysis: Fundamentals and Applications*; Wiley: New York, 1989.
[61] Regnault, C., *et al. J. Chromatog. A* **2004**, *1030*, 289–295.
[62] Pitiot, O., *et al. J. Membr. Sci.* **2000**, *166*, 221–227.
[63] Brandt, S. *Biotechnology* **1988**, *6*, 779–789.
[64] Krause, S., *et al. Biotechnol. Technol.* **1991**, *5*, 199–204.
[65] Zou, H., *et al. J. Biochem. Biophys. Methods* **2001**, *49*, 199–240.
[66] Orhon, D., *et al. Water Sci. Technol.* **2001**, *43*, 223–230.
[68] Balcioglu, A., Arslan, I. *Water Sci. Technol.* **2001**, *43*, 221–228.
[69] Ciardelli, G., *et al. Water Res.* **2001**, *35*, 567–572.
[70] Voigt, I., *et al. Sep. Purif. Technol.* **2001**, *25*, 509–512.
[71] Drioli, E. *Water Sci. Technol.* **1992**, *25*, 107–25.
[72] Joshi, M., *et al. J. Membr. Sci.* **2001**, *189*, 23–40.
[73] Marcucci, M., *et al. Desalination* **2001**, *138*, 75–82.
[74] Van der Bruggen, B. M., *et al. Sep. Purif. Technol.* **2001**, *22*, 519–528.
[75] Tang, C., Chen, V. *Desalination* **2002**, *143*, 1–20.
[76] Ciardelli, G., *et al. Conservat. Recycl.* **2000**, *31*, 189–197.
[77] Bes, A., *et al. Desalination* **2003**, *157*, 73–80.
[78] Marcucci, M., *et al. Desalination* **2002**, *149*, 137–143.
[79] Bes, A., *et al. Desalination* **2003**, *157*, 81–86.
[80] European Commission, Directorate-General Joint Research Centre, Institute for Prospective Technological Studies (Seville) Technologies for Sustainable Development European Integrated Pollution Prevention and Control (IPPC) Bureau: ''Reference Document on Best Available Techniques for the Tanning of Hides and Skins'', 2001.
[81] Ludvík, J. *Unido Regional Programme for Pollution Control in the Tanning Industry in South-East Asia*, Us/Ras/92/120/11-51.
[82] Protrade/GTZ ''*Ecology and Environment in the Leather Industry – Technical Handbook''*, Eschborn, 1995.
[83] Cortese, B., *et al. Mat. Concianti* **1978**, *5*, 167–178.
[84] Cassano, A., *et al. Desalination* **1997**, *113*, 251–268.
[85] Cassano, A., *et al. J. Soc. Leather Technol. Chem.* **1998**, *82*, 130–143.
[86] Cassano, A., *et al. Clean Prod. Process.* **1999**, *1*, 257–263.
[88] Suthanthararajan, R., *et al. Desalination* **2004**, *164*, 151–156.
[89] Cassano, A., *et al. J. Membr. Sci.* **2001**, *181*, 111–126.
[90] Aloy, M., Vulliermet, B. *Industrie du Cuir* **1998**, *2*, 43–54.
[91] Drioli, E., Molinari, R. *Acqua Aria* **1984**, *3*, 231–243.
[92] Cortese, B., Drioli, E. *Inquinamento* **1978**, *20*, 51–63.
[93] Drioli, E., *et al. Acqua Aria* **1982**, *4*, 391–402.
[94] Cortese, B., *et al. Mat. Concianti* **1976**, *52*, 511–520.
[98] Cassano, A., *et al. Wat. Sci. Technol.* **1999**, *40*, 443–450.
[100] Molinari, R., *et al. Desalination* **1995**, *100*, 125–132.
[101] Cassano, A., *et al. Desalination* **1996**, *108*, 193–199.
[102] Fabiani, C., *et al. Desalination* **1996**, *108*, 183–193.
[104] Drioli, E., *1st Symposium Internationale sobre l'Ambiente y los Residuas Industriales*, Venezuela, Caracas, November 1976.
[105] Manttari, M., *et al. J. Membr. Sci.* **1997**, *137*, 187–199.
[106] Zaidi, A., *et al. Water Sci. Technol.* **1992**, *25* (10), 263–276.
[107] Jönsson, A. *Nordic Pulp Pap. Res.* **1987**, *1*, 23–29.
[108] Technical Guidance Note IPPC S6.01 Integrated Pollution Prevention and Control (IPPC) Technical Guidance for the Pulp and Paper Sector IPPC Version 2, November 2000.
[109] McDonald, R. G. *Pulping of Wood*; McGraw-Hill: New York, 1969.
[110] Final Report from the MISTRA Program the Ecocyclic Pulp Mill (KAM), *Program Period 1, 1996–1999*, *KAM Report A32*, STFI, Stockholm, Sweden, 2000.
[111] Satyanarayana, S. V., *et al. Sep. Purif. Technol.* **2000**, *20*, 155–167.
[112] Horacek, R. G., Forester, W. Tappi Press: Atlanta, GA, 1993; pp 179–180.
[113] Woodward, T. W. Tappi Press: Atlanta, GA, 1990; Vol. 1, pp 281–288.
[114] Renders, A. *Tappi J.* **1993**, *76*, 155–161.
[115] Woodward ,T. W. *A Practical Guide*; Tappi Press: Atlanta, GA, 1992; pp 179–206.
[116] Vlyssides, G. A., *et al. Commun. Soil Sci. Plant Anal.* **1996**, *28*, 509–520.
[117] Crow, D. R., Secor, R. F. Tappi Press: Atlanta, GA, 1990; Vol. 1, pp 273–280.
[118] Horacek, R. G. In *Deinking Seminar*, Notes, Session Number 5-1, Atlanta, GA, 22–24 June 1992.
[119] Kuhn, D., Tappi Press: Atlanta, GA, 1996; pp 333–337.
[120] Krofta, M., Wang, K. L. In *Proceedings of the 43rd Purdue Industrial Waste Conference*; Lewis Publishers: Chelsea, MI, 1989; pp 673–687.
[121] Mahony, H. Tappi Press: Atlanta, GA, 1993; pp 239–247.
[122] Vlyssides, G. A., Economides, G. D. *Fresenius Environ. Bull.* **1997**, *6*, 734–739.
[123] McBride, D. Tappi Press: Atlanta, GA, 1993; pp 249–259.
[124] Evans, J. C. W. In *Paper Recycling*; Miller Freeman: San Francisco, CA, 1993; pp 47–183.
[125] Woodward, T. W. *Pulp Paper* **1986**, *November*, 59–63.
[126] Vieira, M., *et al. J. Membr. Sci.* **2001**, *194*, 273–276.
[127] Platt, S., Nystrom, M. *Desalination* **2004**, *161*, 123–136.
[128] Nuortila-Jokinen, J., In *Proceedings of the 4th IAWQ Symposium on Forest Industry Wastewaters*, Tampere, Finland, 8–11 June 1993; p 11.
[129] Nuortila-Jokinen, J. In *International Environmental Conference*; Tappi Press: Atlanta, GA, 1995; Book 2, pp 847–859.
[130] Nuortila-Jokinen, J., *et al. Pap. Puu.* **1994**, *76*, 256–261.
[131] Nuortila-Jokinen, J., *et al.* 'Proceedings of the Euromembrane'95', Anthony Rowe: Chippenham, UK, **1995**; Vol. I, pp 521–524.
[132] Nuortila-Jokinen, J., *et al. J. Membr. Sci.* **1996**, *119*, 99–115.
[133] Nuortila-Jokinen, J. *et al. Desalination* **1998**, *119*, 11–19.
[134] Atkinson, S. *Membr. Technol.* 136.
[135] Ammerlaan, A. C. E. Wiley, A. J. *Tappi J.* **1969**, *52*, 1703–1715.
[136] Wiley, A. J., *et al. Tappi J.* **1972**, *55*, 1671–1679.
[137] Wiley, A. J., *et al. Tappi J.* **1967**, *50*, 455–467.
[138] Manttari, M., *et al.* In *2nd Nordic Filtration Symposium*, Lappeenranta: Finland, 11–13 August 1996; pp. 17–101.
[140] Geraldes, V., de Pinho, M. N. *J. Mem. Sci.* **1995**, *102*, 209–221.
[141] Beaudoin, L., *et al. Sci. Technol. Eau* **1992**, *25*, 486–497.
[142] Luque, S., In *3rd European Workshop on Lignocellulosics and Pulp*, Stockholm, Sweden, 28–31, August 1994.
[143] Jonsson, A. S. *Nordic Pulp Paper Res. J.* **1987**, *2*, 23–29.
[144] Wiley, A. J., *et al. J. Water Pollut. Control Fed.* **1970**, *42*, 279–283.
[145] Wickstroem, P. In *Proceedings of the Minimum Efluent Mills Symposium*; 1997; San Francisco, CA, pp 79–83.
[146] Teppler, M., In *Third Nordic Filtration Symposium*, Copenhagen, 25–27 May 1997.
[148] Lien, L., Simonis, D. In Proceedings of the TAPPI International Environmental Conference, 1995.
[150] Dorica, J. *J. Pulp Pap. Sci.* **1986**, *53*, 172–177.
[151] Teppler, M., et al. In *PTS Symposium*, Miinchen, Germany, 28 November 1996; pp 28–41.

[152] Dahlquist, E. et al. In *Proceedings of the Vth World Filtration Congress*, Nice, France, 6–8 June 1989; Vol. I, pp 484–487.
[143] Jonsson A. S. In *Membranteknik – tillampningar inom skogsindustrin.* Svensk Papperstidn, 93, 1990; pp 35–38.
[144] Paatero, J., et al. In *Proceedings of the 2nd EcoPaperTech Conference, Economy and Ecology in Papermaking Technolgy*, Helsinki, Finland, 1–5 June 1998.
[145] Gerbasi, B., et al. In *79th Annual Meeting, Technical Section, CPPA*, Montreal, QC, Canada, 26–27 January 1993; pp A197–A205.
[146] Salovius, L., et al. In *18th International Mechanical Pulping Conference*, Oslo, Norway, 15–17 June 1993; Book 3, pp 433–448.
[147] Bertel Myréen, Finland Conox Ltd., Commercial Brochure 1993.
[148] Dorica, J. *J. Pulp Paper Sci.* **1986**, *12*, 51–72.
[149] Jansson, A., Wirnrnerstedt, R. *Desalination* **1985**, *53*, 181–189.
[150] Rosa, M. J., de Pinho, M. N. *J. Membr. Sci.* **1995**, *102*, 1–20.
[151] Filth, F., *et al. Desalination* **2001**, *133*, 155–165
[152] Jonsson, A. S., *et al. Desalination* **1996**, *105*, 263–276.
[153] Bansal, I. K., Wiley, A. J. *Environ. Sci. Technol.* **1974**, *8*, 1085–1090.
[154] Forss, T., *et al. Pulp Paper Can.* **1979**, *80*, 411–415.
[155] Wallberg, O., *et al. Desalination* **2003**, *154*, 187–199.
[156] Kovasin, K., Norden, H. V. *Svensk Papperstidn.* **1984**, *87*, 44–47.
[157] Drouin, M. P., Desroches, M. J. *AIChE Forest Prod. Div.* **1988**, *2*, 58–65.
[158] Wilde, F. G. *Desalination* **1988**, *67*, 495–512.
[159] Olsen, O. *Desalination* **1980**, *35*, 291–302.
[160] Tanistra, I., Bodzek, M. *Desalination* **1998**, *115*, 111–120.
[161] De, S., Bhattacharya, P. K. *Tappi J.* **1996**, *79*, 103–120.
[162] Claussen, P. H. *Pulp Paper Can.* **1978**, *79*, 81–89.
[163] Hill, M. K., *et al. Sep. Sci. Technol.* **1988**, *23*, 1789–1798.
[164] Lin, S. U. 'Wood Chemistry Symposium', Stockholm, **1981**; Vol. 4, pp 44–54. Stockholm.
[165] Kirkman, A. G., *et al. Tappi J.* **1986**, *69*, 110–114
[166] Li, J., *et al. Can. J. Chem. Eng.* **1996**, *74*, 110–117.
[167] Bamier, H., *et al. Pap. Puu* **1987**, *69*, 581–583.
[168] Wallberg, O. *Desalination* **2003**, *156*, 145–153.
[169] Misra, A. K., Bhattacharya, P. K. *J. Mem. Sci.* **1987**, *33*, 83–92.
[170] Misra, A. K., Bhattacharya, P. K. *Can. J. Chem. Eng.* **1984**, *62*, 723–734.
[171] Woerner, D. L., McCarthy, J. L. *AIChE Symp. Ser.* **1984**, *80* (232), 25–33.
[172] Hill, M., Fricke, A. L. *Tappi J.* **1984**, *67*, 100–103.
[173] Woemer, D. L., McCarthy, J. L. *AIChE Symp. Ser.* **1986**, *82*, 77–86.
[174] Woemer, D. L., McCarthy, J. L. *Tappi J.* **1987**, *70*, 126–129.
[175] Benito, Y., Ruiz, M. L. *Desalination* **2002**, *142*, 229–234.
[176] Hewitt, D. E., Dando, T. J. Water Recycle Treatment System for Use in Metal Processing. US Pat. 39,73,987, 1975.
[177] Sato, T., *et al. Desalination* **1977**, *23*, 65–78.
[178] Kremen, S. S., *et al. Desalination* **1977**, *20*, 71–86.
[179] Cai, X., *et al. J. Membr. Sci.* **1997**, *123*, 235–246.
[180] Sugita, N. Process and Apparatus for Recovery of Precious Metal Compound. US Pat. 4880511, 1989.
[181] Spatz, D. D. Metal Reclamation Process and Apparatus. US Pat. 3637467, 1972.
[182] Degenkol, D. J., Scobey, F. J. Method and Apparatus for Recovery of Heavy Metal Ions From Dilute Aqueous Solution. US Pat. 4137290, 1979.
[183] Martyak, N. M., et al. Apparatus and Methods for Treating Electroless Plating Baths. US Pat. 5277817, 1994.
[184] Griffin, G. Plating Rinse Water Treatment. US Pat. 5932109, 1999.
[185] Chai, X., *et al. J. Membr. Sci.* **1997**, *123*, 235–242.
[186] Ujang, Z., Anderson, G. K. *Water Sci. Technol.* **1996**, *34*, 247–253.
[187] Jonsson, A. S., Wennerbeck, J. *Desalination* **1997**, *114*, 175–181.
[188] Kamizawa, C., *et al. Desalination* **1978**, *27*, 261–279.
[189] Qin, J.-J., *et al. J. Membr. Sci.* **2002**, *208*, 213–221.
[190] Wong, F. S., *et al. Sep. Purif. Technol.* **2002**, *29*, 41–51.
[191] Kremen, S. S., *et al. Desalination* **1977**, *20*, 71–84.
[192] Wisniewski, J., Suder, S., *Desalination* **1995**, *101*, 245–253.
[193] Corlett, G. *Solid State Technol.* **2000**, *43*, 201–206.
[194] Yang, G. C. C., *et al. Water Res.* **2003**, *37*, 785–792.
[195] Yang, G. C. C., *et al. Water Sci. Technol.* **2002**, *46*, 171–176.
[196] You, S.-H., *et al. Conserv. Recycl.* **2001**, *32*, 73–81.
[197] Michael, C. L. *Solid State Technol.* **1996**, *27*, 70–75.
[198] David, G. G., Raymond, C. L. *ASCE J. Environ. Eng.* **1994**, *120*, 72–86.
[199] Bhaumik, D., *et al. J. Membr. Sci.* **2004**, *235*, 31–41.
[200] Sengupta, A., *et al. Sep. Purif. Technol.* **1998**, *14*, 189–200.
[201] Tan, X., Li, K. *Chem. Eng. Sci.* **2000**, *55*, 1213–1224.
[202] Dey, G., *et al. Ultrapure Water* **2001**, *September*, 43–56.
[203] Hellera, M. *Expert Syst. Appl.* **1998**, *14*, 341–353.
[204] Ikeda, T., *et al. Desalination* **1994**, *98*, 391–400.
[205] Wu, M., *et al. Desalination* **2004**, *161*, 223–233.
[206] Al-Enezi, G., Fawzi, N. *Desalination* **2002**, *153*, 281–286.
[207] Ho, S., *et al. J. Membr. Sci.* **2003**, *211*, 157–165.
[208] Futselaar, H., Schonewille, H. *Desalination* **2002**, *145*, 75–80.
[209] Dax, M. *Semicond. Int.* **December 1996**.
[210] Gabelman, A., Hwang, S.-T. *J. Membr. Sci.* **1999**, *159*, 61–106.
[211] Cornelissen, I., et al. In *Proceedings of the Fourth International Symposium on Ultraclean Proceedings of Silicon Surfaces*, Ostend, Belgium, 21–23 September 1998.
[212] Wikol, M. J., et al. *14th Internatonal Symposium on Contamination Control*, *44th Annual Technical Meeting*, Phoeniz, AZ, May 1998.
[213] Huang, X., Cho, K. *Ultrapure Water Europe '96*, Amsterdam, The Netherlands, 25 September 1996.
[214] Yagi, Y., *et al. IEEE Trans. Semicond. Manufact.* **1992**, *5*, 121.
[215] Tai, M. S. L., *et al. J. Membr. Sci.* **1994**, *87*, 99–105.
[216] Macklin, S. H., Haas, W. E., Miller, W. S. *At the International Water Conference*, Pittsburgh, PA, 30 October 1995.
[217] Wiesler, F., Sodaro, R. *Ultrapure Water* **1996**, *13* (6), 53–56.
[218] Costello, M. J., *et al. J. Membr. Sci.* **1993**, *80*, 1–11.
[219] Krygier, V. Pall Corporation, Personal Communication, 25 November 1998.
[220] Lawson, K. W., Lloyd, D. R. *J. Membr. Sci.* **1997**, *124*, 1–15.
[221] Banat, F. A., Simandl, J. *Sep. Sci. Technol.* **1998**, *33*, 201–216.
[222] Darbouret, D., Stewart, B. M. *Am. Lab. News* **1998**, *30*, 36–43.

[223] Wang, J., *et al. Desalination* **2000**, *132*, 349–356.
[224] Denoncourt, J. P., Moulin, J. Electrodeionization Process for Purifying a Liquid. US Pat. 5,593,563, 1997.
[225] Hegde, R. S., Lexington, C. G. US Pat. 4,430,226, 1984.
[226] Bayer, A. G. *At Ionenaustauscher/Katalysatoren*, *Geb.* 1990, *B106*, 1–6.
[227] Nora, C., *et al. Ultrapure Water* **2002**, *19*, 56–65.
[228] Higuchi, A., *et al. J. Membr. Sci.* **2002**, *210*, 369–378.
[229] Christy, C., Vermant, S. *Desalination* **2002**, *147*, 1–4.
[230] Hellenbrand, R., *et al. Ind. Eng. Chem. Res.* **1997**, *536*, 5054–5062.
[231] Guu, Y. K., *et al. J. Agric. Food Chem.* **1997**, *45*, 4096–4100.
[232] Nguyen, M. H., *et al. Austr. J. Dairy Technol.* **1997**, *52*, 75–78.
[233] Ericsson, B., Hallberg, M., Wachenfeldt, J. *Desalination* **1997**, *108*, 129–141.
[234] Dewitte, J. P. *Desalination* **1997**, *108*, 153–157.
[235] Kharaka, Y. K., *et al. Appl. Geochem.* **1996**, *11*, 797–802.
[236] Rautenbach, R., VoBenkaul, K. *Sep. Purif. Technol.* **2001**, *22*, 193–208.
[237] Higuchi, A., *et al. J. Membr. Sci.* **2004**, *236*, 137–144.
[238] Bolger, R., *et al. Biotechniques* **1997**, *23*, 532–545.
[239] Hirasaki, T., *et al. J. Membr. Sci.* **1995**, *106*, 123–132.
[240] Higuchi, A., *et al. J. Membr. Sci.* **1996**, *116*, 191–199.
[241] Yang, J., *et al. Environ. Sci.* **1997**, *18*, 83–95.
[242] Balcioqlu, I. A., Otker, M. *Chemosphere* **2003**, *50*, 85–95.
[243] Meacle, F., *et al. J. Membr. Sci.* **1999**, *161*, 171–184.
[244] Foster, P. R. In *Kirk Othmer Encyclopedia of Chemical Technology*; Howe-Grant, M., Ed.; Wiley: New York, 1994; pp 977–1021.
[245] Cohn, E. J., *et al. J. Am. Chem. Soc.* **1946**, *68*, 459–475.
[246] Stryker, M. H., *et al.* In *Advances in Biotechnological Processes*; Alan, R. Ed. Liss: New York, 1985; Vol. 11, pp 275–336.
[247] Narhi, L. O., *et al.*, *Anal. Biochem.* **1997**, *253*, 246–252.
[248] England, S., Seifer, S., *Meth. Enzymol.* **1990**, *182*, 285–306.
[249] Polson, A., *et al. Biochem. Biophys. Acta* **1964**, *82*, 463–473.
[250] Salabe, G., *et al. Clin. Chem. Lab. Med.* **2000**, *38*, 597–602.
[251] Neal, G., *et al. Biotechnol. Bioeng.* **2003**, *81*, 149–157.
[252] Levesley, J. A., *et al. Sep. Sci. Technol.* **2000**, *35*, 633–649.
[253] Taylor, G., *et al. Chem. Eng. Commun.* **1994**, *129*, 227–250.
[254] Ghosh, R. *J. Chromatogr.* **2001**, *923*, 59–64.
[255] Asenjio, J. A., Leser, E. W. In *Downstream Processing of Natural Products*; Verrall, M., Ed., Wiley: New York, 1996; pp 23–137.
[256] Krijgsman, J. In *Product Recovery in Bioprocess Technology*; Jenkins, R. O., Ed. Buterworth-Heinemann: London, 1992; pp 1–13.
[257] Li, S. Z., *et al. Sep. Purif. Technol.* **2004**, *34*, 115–123.
[258] Hatton, T. A. In *Comprehensive Biotechnology*; Moo-Young, M., Ed., Pergamon: Oxford, 1985; Vol. 2, p 439.
[259] Schroen, C. G. P. H., Woodley, J. M. *Biotechnol. Prog.* **1997**, *13*, 276.
[260] Li, S. Z. *Surfactant Ind.* **1993**, *2*, 11–15.
[261] Nabais, A. M. A., Cardoso, J. P. *Bioprocess Eng.* **1999**, *21*, 157–163.
[262] Liu, H., *et al. Biochem. Eng. J.* **1998**, *2*, 187–196.
[263] Brites Alves, A. M. A. M., *et al. Desalination* **2002**, *148*, 181–186.
[264] Oussedik, S., *et al. Desalination* **2000**, *127*, 59–65.
[265] Ghosh, R., Cui, Z. F. *J. Membr. Sci. 167,* **2000**, 47–53.
[266] Ghosh, R. *Biotechnol. Bioeng.* **2001**, *74*, 1–11.
[267] Shukla, R., *et al. Bioseparation* **2000**, *9*, 7–19.
[268] Ehsani, N., *et al. J. Membr. Sci.* **1997**, *123*, 105–119.
[269] Kahn, D. W., *et al. Biotechnol. Bioeng.* **2000**, *69*, 101–106.
[270] Ghosh, R. *J. Membr. Sci.* **2004**, *237*, 109–117.
[271] Wan, Y., *et al. Desalination* **2002**, *144*, 301–306.
[272] Ghosh, R. Cui, Z. F. *J. Membr. Sci.* **2000**, *175*, 75–84.
[273] Higuchi, A., *et al. J. Membr. Sci.* **2001**, *186*, 1–9.
[274] Christy, C., *et al. Desalination* **2002**, *144*, 133–136.
[275] Cheang, B., *et al. J. Membr. Sci.* **2004**, *231*, 159–167.
[276] Zydney, A. L., van Reis, R. In *Membrane Separations in Biotechnology*; Wang, W. K., Ed., Marcel Dekker: New York, 2001; pp 277–298.
[277] van Eijndhoven, H. C. M., *et al. Biotechnol. Bioeng.* **1995**, *48*, 406–417.
[278] Cheang, B. L., Zydney, A. L. *Biotechnol. Bioeng.* **2003**, *83*, 201–210.
[279] Hirasaki, T., *et al. J. Membr. Sci.* **2002**, *201*, 95–102.
[280] Horowitz, B., *et al. Transfusion* **1985**, *25*, 516–523.
[281] Committee for Proprietary Medical Products *Biologicals* **1991**, *19*, 247.
[282] CPMP Guidelines Validation of Virus Removal and Inactivation Procedure, 1991.
[283] Madaeni, S. S., *et al. J. Membr. Sci.* **1995**, *102*, 65–73.
[284] Urase, T., *et al. J. Membr. Sci.* **1996**, *115*, 21–34.
[285] Jacangelo, J. G., *et al. Am. Water Works Assn. J.* **1991**, *83*, 97–111.
[286] Tomokiyo, K., *et al. Clin. Rep.* **1991**, *25*, 271–282.
[287] Cruz, P. E., *et al. J. Biotechnol. Prog.* **2000**, *16*, 350–357.
[288] Kuiper, M., *et al. J. Biotechnol. Bioeng.* **2002**, *80*, 445–453.
[289] Sugawara, T., *et al. Desalination* **2002**, *148*, 165–169.
[290] Capelle, N., *et al. J. Membr. Sci.* **2002**, *196*, 125–141.
[291] Zhang, W., *et al. Sep. Purif. Technol.* **2003**, *30*, 27–35
[292] Heberer, T., *et al. Acta Hydrochim. Hydrobiol.* **2002**, *30*, 24–33.
[293] Schäfer, A. I., *et al. Environ. Sci. Technol.* **2003**, *37*, 182–188.
[294] Turan, A. *Excretion of Natural and Synthetic Estrogens and Their Metabolites: German Environmental Agency*; Berlin, 1995.
[295] Johnson, A. C., Sumpter J. P. *Environ. Sci. Technol.* **2001**, *35*, 4697–4703.
[296] Shen, J. H., *et al. Toxicology* **2001**, *166*, 71–78.
[297] Kolpin, D. W., *et al. Environ. Sci. Technol.* **2002**, *36*, 1202–1221.
[298] Tabata, A., *et al. J. Water Sci. Technol.* **2001**, *43*, 109–116.
[299] Peterson, E. W., *et al.*, *J. Environ. Qual.* **2001**, *29*, 826–834.
[300] Ternes, T. A., *et al. Environ. Sci. Technol.* **2002**, *36*, 3855–3863.
[301] Nghiem, D. L., Schäfer, A. I. *Environ. Eng. Sci.* **2002**, *19*, 441–451.
[302] Haensel, R., *et al. Chem. Eng. Sci.* **1986**, *44*, 1811–1815.
[303] Yagodin, G., *et al. Proc. ISEC* **1986**, *86*, 677–681.
[304] Bloch, R., *et al. Ind. Eng. Chem. Process Des. Dev.* **1967**, *6*, 231–244.
[305] Sahoo, G. C., *et al. J. Membr. Sci.* **1996**, *112*, 147–154.
[306] Ho, W. S. W., Li, N. N. In *ACS Symposium Series 642*; American Chemical Society: Washington, DC, 1996; pp 208–221.
[307] Sahoo, G. C., *et al. Chem. Eng. Commun.* **2000**, *179*, 89–99.
[308] Eyal, A. M., Bressler, E. *Biotechnol. Bioeng.* **1993**, *41*, 287–295.
[309] Saikia, B., Dutta, N. N. *J. Membr. Sci.* **2003**, *225*, 1–13.
[310] Ghosh, A. C., *et al. Sep. Technol.* **1995**, *5*, 121–132.
[311] Drapala, A., Wieczorek, P. *Desalination* **2002**, *148*, 235–239.
[312] Sahoo, G. C., *et al. Bioproc. Eng.* **1999**, *20*, 117–125.

[313] Zeng, X. F., Ruckenstein, E. *Biotechnol. Prog.* **1999**, *15*, 1003–1019.
[314] Svec, F., Frechet, J. J. M. *Ind. Eng. Chem. Res.* **1999**, *38*, 34–48.
[315] Dosio, F., *et al. J. Chromatogr. A.* **1999**, *830*, 29–35.
[316] Dancette, O. P., *et al. J. Chromatogr. B.* **1999**, *723*, 61–69.
[317] Sasagawa, N., *et al. J. Chromatogr. A.* **1999**, *848*, 161–168.
[318] Giovannini, R., *et al. Anal. Chem.* **1998**, *70*, 3348–3354.
[319] Kasper, C., *et al. J. Chromatogr. A.* **1998**, *798*, 65–72.
[320] Birkenmeier, G., Dietze, H. *J. Chromatogr. B* **1997**, *704*, 63–68.
[321] Charcosset, C. J. *Colloid Interface Sci.* **1998**, *203*, 485–487.
[322] Strancar, A., *et al. J. Chromatogr. A* **1997**, *760*, 117–123.
[323] Alifrangis, L. H., *et al. J. Med. Chem.* **2000**, *43*, 103–13.
[324] Lutkemeyer, D., *et al. J. Chromatogr.* **1993**, *639*, 57–66.
[325] Klein, E. *J. Membr. Sci.* **2000**, *179*, 1–27.
[326] Gerstner, J. A., *et al. J. Chromatogr. A* **1992**, *596*, 43–47.
[327] Piletsky, S. A., *et al. J. Membr. Sci.* **1999**, *157*, 263–278.
[328] Gaberc-Porekar, V., Menart, V. *J. Biochem. Biophys. Methods* **2001**, *49*, 335–343.
[329] Tsai, Y.-H., *et al. J. Chromatogr. B* **2002**, *766*, 133–143.
[330] Schumacher, G., *et al. Nucleic Acids Res.* **1986**, *14*, 5713–5725.
[331] Hari, P. R., *et al. J. Biomed. Mater. Res.* **2000**, *50*, 110–115.
[332] Mateo, C., *J. Chromatogr. A* **2001**, *915*, 97–109.
[333] Wu, C. Y., *et al. J. Chromatogr. A* **2003**, *996*, 53–65.
[334] Kojim, K. *J. Biochem. Biophys. Methods* **2001**, *49*, 241–251.
[335] Korolkov, V. I., *et al. Lett. Pept. Sci.* **2000**, *17*, 53–61.
[336] Munoz-Gomez, J., *et al. Ann. Rheum. Dis.* **1985**, *44*, 729–733.
[337] Wu, X., *et al. J. Chromatogr. B* **1992**, *584*, 35–43.
[338] Vijayalakshmi, M. A. In *Molecular Interactions in Bioseparation*; Ngo, T., Ed., Plenum: New York, 1993, p 257.
[339] Bueno, S. M. A., *et al. J. Chromatogr. B* **1995**, *667*, 57–65.
[340] Denizli, F., *et al. React. Funct. Polym.* **2000**, *44*, 207–217.
[341] Castilho, L. R. *Series Fortschritt-Berichte-Reihe 17*; VDI-Verlag: Düsseldorf, 2001.
[342] Castilho, L. R., *et al.* In *Animal Cell Technology: From Target to Market*; Kluwer: Dordrecht, 2001; p 379.
[343] Carter, P., *et al. Proc. Natl. Acad. Sci. U.S.A.* **1992**, *89*, 42–85.
[344] Bodey, B., *et al. Anticancer Res.* **1996**, *16*, 517–525.
[345] Anderson, D. R., *et al. Biochem. Soc. Trans.* **1997**, *25*, 705–718.
[346] Longo, D. L. *Curr. Opin. Oncol.* **1996**, *8*, 353–359.
[347] Baselga, J., *et al. J. Clin. Oncol.* **1996**, *14*, 737–742.
[348] Wang, M. Y., *et al. Biotechnol. Prog.* **2000**, *16*, 146–154.
[349] Tsai, Y. H., *et al. J. Chromatogr. B* **2002**, *766*, 133–145.
[350] Yang, L., *et al. Sci. China Ser. B: Chem.* **1998**, *41*, 596–601.
[351] Sakharov, I. Y., *et al. Plant Sci.* **2001**, *161*, 853–860.
[352] Santarelli, X., *et al. J. Chromatogr. B* **2002**, *739*, 63–76.
[353] Fitton, V., *et al. J. Biochem. Biophys. Methods* **2001**, *49*, 553–564.
[354] Fitton, V., *et al. J. Chromatogr. B* **2001**, *754*, 135–143.
[355] Sanchez, J., *et al. J. Chromatogr. B* **2001**, *753*, 45–63.
[356] Kassab, A., *et al. J. Chromatogr. B* **2000**, *746*, 123–130.
[357] Freitas, S. *J. Membr. Sci.* **2004**, *234*, 67–73.
[358] Sharma, S. K. *Biotechnol. Appl. Biochem.* **1986**, *8*, 5–12.
[359] Rikken, G. L. A., Raupach, E. *Nature* **2000**, *405*, 932–934.
[360] Kuhnle, A., *et al. Nature* **2002**, *415*, 891–893.
[361] Romero, J., Zydney, A. L. *J. Membr. Sci.* **2002**, *209*, 107–119.
[362] Stinson, S. *Chem. Eng. News* **2001**, *79*, 79–97.
[363] Fanali, S. *J. Chromatogr. A* **1996**, *735*, 77–80.
[364] Li, S., Purdy, W. C. *Chem. Rev.* **1992**, *92*, 1457–1464.
[365] Ramstrom, O., Ansell, R. J. *Chirality* **1998**, *10*, 195–204.
[366] Gupta, M., Mattiason, B. In *Highly Selective Separations in Biotechnology*;, Blackie Academic and Professional: London, 1994; pp 7–33.
[367] Walters, H., *et al. Anal. Biochem.* **1991**, *197*, 1–18.
[368] Giorno, L., Drioli, E. *Membr. Technol.* **1999**, *106*, 6–11.
[369] Hutt, J. *Chirality* **1991**, *3*, 161–164.
[370] Thoelen, C., *et al. J. Membr. Sci.* **2001**, *186*, 153–160.
[371] Romero, J., Zydney, A. *Sep. Sci. Technol.* **2001**, *36*, 1571–1590.
[372] Romero, J., Zydney, A. *Biotechnol. Bioeng.* **2002**, *77*, 256–265.
[373] Higuchi, A., *et al. J. Membr. Sci.* **2003**, *221*, 207–218.
[374] Higuchi, A., *et al. Desalination* **1993**, *90*, 127–136.
[375] Higuchi, A., *et al. J. Membr. Sci.* **1994**, *93*, 157–164.
[376] Kim, J. H., *et al. J. Membr. Sci.* **2003**, *213*, 273–283.
[377] Higuchi, A., *et al. J. Membr. Sci.* **2002**, *205*, 203–212.
[378] Aoki, T., *et al. Macromolecules* **1999**, *32*, 79–85.
[379] Randon, J., *et al. J. Membr. Sci.* **2000**, *175*, 111–120.
[380] McMenamy, R., Oncley, J. *J. Biol. Chem.* **1958**, *233*, 1436–1440.
[381] Poncet, S., *et al. Sep. Sci. Technol.* **1997**, *32*, 2029–2038.
[382] Gamier, F., *et al. Sep. Purif. Technol.* **1999**, *16*, 243–254.
[383] McMenamy, R. *J. Biol. Chem.* **1964**, *239*, 2835–2845.
[384] Dong, X., *et al. Bioprocess Eng.* **1997**, *16*, 229–235.
[385] Thoelen, C., *et al. J. Membr. Sci.* **2001**, *186*, 153–163.
[386] Ding, H. B., *et al. AIChE J.* **1992**, *38*, 1493–1499.
[387] Shinbo, T., et al. *Sen-I Gakkaishi 52*, 105–110.
[388] Tsukube, H., *et al.*, *Chem. Commun.* **1996**, 477–487.
[389] Pickering, P. J., Chaudhuri, J. B. *J. Membr. Sci.* **1997**, *127*, 115–130.
[390] Bryjak, M., *et al. J. Membr. Sci.* **1993**, *85*, 221–228.
[391] Newcomb, M., *et al.*, *J. Am. Chem. Soc.* **1979**, *101*, 4941–4947.
[392] Keurentjes, J. T. F., *et al. J. Membr. Sci.* **1996**, *113*, 351–359.
[393] Scheper, T., *et al. Enzyme Microbiol. Technol.* **1987**, *9*, 625–631.
[394] Scheper, T., *et al. Chem. Eng. J.* **1984**, *29*, 1331–1342.
[395] Behr, J. P., Lehn, J. M. *J. Chem. Soc.* **1973**, *95*, 6108–6110.
[396] Chan, C. C., Wang, S. S. *J. Membr. Sci.* **1993**, *76*, 219–232.
[397] Adam, W., *et al. Eur. J. Org. Chem.* **1998**, *54*, 2013–2018.
[398] Kanerva, L. T., Sundholm, O. *Acta Chemica Scandinavica* **1993**, *47*, 823–825.
[399] Giorno, L., *et al. J. Chem. Technol. Biotechnol.* **1995**, *64*, 345–352.
[400] Sakaki, K., *et al. J. Membr. Sci.* **2001**, *184*, 27–38.
[401] Ceynowa, J., Koter, I. *Acta Biotechnol.* **1997**, *17*, 253–263.
[402] Sheldon, R. A. *Chirotechnology: Industrial Synthesis of Optically Active Compounds*; Marcel Dekker: New York, 1993.
[403] Jacques, J., *et al. Enantiomers, Racemates, and Resolutions*; Wiley/Interscience: New York, 1981.
[404] Collins, A. N., Sheldrake, G. N., Crosby, J., Eds. *Chirality in Industry*; Wiley: Chichester, 1992.
[405] Gana, Q., *et al. J. Membr. Sci.* **2001**, *194*, 185–196.
[406] Van Den Horst, H. C., Hanemaaijer, J. H. *Desalination* **1990**, *77*, 235–258.

[407] Ramteke, R. S., *et al. J. Food Sci. Technol.* **1993**, *30*, 391–402.
[408] Short, J. L. *Desalination* **1988**, *70*, 341–352.
[409] Freemanet, G. J., *et al.* In *Eds.* Fermented Beverage Production Lea, A. G. A., Ed. Blackie Academic and Professional: London, 1995; pp 334–359.
[410] Moller, H., In *Proceedings of the EuroMembrane'97*, University Twente, 1997; pp 122–124.
[411] Trägårdh, G. In *Food Processing: Recent Developments*; Gaonkar, A. D., Ed. Elsevier: 1995.
[412] Belfort, G., *et al. J. Membr. Sci.* **1994**, *96*, 1–58.
[413] Gan, Q., *et al. Trans. I. Chem. E.* **1997**, *75*, 3–12.
[414] Liew, M. K. H., *et al. Biotechnol. Bioeng.* **1995**, *8*, 108–120.
[415] Li, H., *et al. J. Membr. Sci.* **2000**, *172*, 135–143.
[416] Ma, H., *et al. J. Membr. Sci.* **2000**, *173*, 191–213.
[417] Bacchin, P., *et al.* In *AICHE J*. 1995, 368–382.
[418] Vernhet, A., Moutounet, M. *J. Membr. Sci.* **2002**, *201*, 103–112.
[419] Fillaudeau, L., Carrère, H. *J. Membr. Sci.* **2002**, *196*, 39–57.
[420] Burrell, K. J., Reed, R. J. R. *Filt. Sep.* **1994**, *31*, 399–405.
[421] Pazourek, J., *et al. J. Chromatogr. A* **2000**, *874*, 111–119.
[422] Kelly, S. T., Zydney, A. L. *Biotechnol. Bioeng.* **1997**, *55*, 91–100.
[423] Gan, Q., *et al. J. Membr. Sci.* **1999**, *155*, 277–289.
[424] Stacne, H. *Tensidhandbuch*; Hanser Verlag: Munchen, 1981.
[425] Traghardh, G., Johansson, D. *Desalination* **1998**, *119*, 21–29.
[426] Schildbach, S., Kahm, V. *Brauwelt* **2000**, *33/43*, 1333–1336.
[427] Rogener, F., *et al. Sep. Purif. Technol.* **2002**, *28*, 207–217.
[428] Commercial brochure N. E. M Business Solutions Recovery of spent CIP Solutions.
[429] Matta, V. M., *et al. Alimentaria* **2000**, *309*, 127–130.
[430] Carabasa, M., *et al. J. Food Eng.* **1998**, *37*, 25–41.
[431] Goloubev, V. N., Salem, B. *Industries Agricoles et Alimentaires* **1989**, *106*, 175–177.
[432] Vaillant, F., *et al. J. Food Eng.* **2000**, *47*, 195–202.
[433] Vaillant, F., *et al. J. Food Eng.* **2001**, *48*, 83–90.
[434] Valentas, K. J., Rotstein, E., Singh, R. P. *Handbook of Food Engineering Practice*,; CRC Press: Boca Raton, FL, 1997.
[435] Vural, G., *et al. J. Food Sci.* **1998**, *63*, 504–516.
[436] Gao, L., Beveridge, T., Reid, C. A. *Lebensm.-Wiss. U.-Technol.* **1997**, *30*, 23–29.
[437] Vaillant, F., *et al. J. Food Eng.* **2000**, *47*, 195–202.
[438] Rosch, E. *Confructa* **1985**, *30*, 27–30.
[439] de Bruijna, J. P. F., *et al. Lebensm.-Wiss. U.-Technol.* **2003**, *36*, 397–406.
[440] Alvarez, V., *et al. J. Membr. Sci.* **1997**, *127*, 25–34.
[441] Borneman, Z., *et al. Sep. Purif. Technol.* **2001**, *22*, 53–61.
[442] Vladisavljevic, G. T., *et al. J. Food Eng.* **2003**, *60*, 241–247.
[443] Rao, M. A., *et al. J. Food Sci.* **1987**, *52*, 375–382.
[444] Tzeng, W. C., Zall, R. R. *J. Food Sci.* **1990**, *55*, 873–888.
[445] Schneider, T., Czech, B. *Fruit Process.* **1994**, *10*, 302–312.
[446] Kirk, D. E., *et al. J. Food Sci.* **1983**, *48*, 1663–1666.
[447] Kijseoglu, S. S., *et al. Food Technol.* **1990**, *44*, 90–97.
[448] Chiampo, F., et al. In *Proceedings of the First International Convention Food Ingredients*, Cuneo, Italy, 1997; p 119.
[449] Sulaiman, M. Z., *et al. Chem. Eng. J.* **1998**, *69*, 145–148.
[450] Wilson, E. L., Burns, D. J. W. *J. Food Sci.* **1983**, *48*, 1101–1105.
[451] Chan, W. Y., Chaing, B. H. J. *Food Sci. Technol.* **1992**, *27*, 435–444.
[452] Jiraratananon, R., *et al. J. Membr. Sci.* **1997**, *129*, 135–143.
[453] Jiraratananon, R., Chanachai, A. *J. Membr. Sci.* **1996**, *111*, 39–48.
[454] Lue, S. J., Chiang, B. H. *Int. J. Food Sci. Technol.* **1989**, *24*, 395–401.
[455] Hernandez, E., *et al. J. Food Sci.* **1992**, *57*, 664–666.
[456] Ripperger, S., Altmann, J. *Sep. Purif. Technol.* **2002**, *26*, 19–31.
[457] Karlsson, H. O. E., Trägardh, G. *J. Food Eng.* **1997**, *34*, 159–167.
[458] Downes, J. W. In *Production and Packaging of Noncarbonated Fruit Juices and Beverages*; Blackie Academic and Professional: Glasgow, 1990; pp 158–181.
[459] Sulc, D. *Confructa* **1984**, *28* (3), 258–318.
[460] Bartolome, A., *et al. Food Chem.* **1995**, *53*, 75–79.
[461] Carvalho, C. A. B., *et al. Desalination* **2002**, *148*, 61–65.
[462] Asenjo, C. F. In *Tropical and Subtropical Fruits: Composition, Properties and Uses*;, AVI Publishing: Westport, CT, 1980; pp 341–374.
[463] Vaillant, F., *et al. J. Food Eng.* **1999**, *42*, 215–224.
[464] Carneiro, L., *et al. Desalination* **2002**, *148*, 93–98.
[465] Carvalho, C., et al. In *XVII Congress Brasileiro de Ciencia e Tecnologia de Alimentos*, Fortaleza, Ceara, Livro de Resumos, 2000.
[466] Petrotos, K. B., *et al. J. Membr. Sci.* **1998**, *150*, 99–110.
[467] Calabro, V., *et al. Ind. Eng. Chem. Res.* **1994**, *33* (7), 1803–1808.
[468] Bailey, A. F. G., *et al. J. Membr. Sci.* **2000**, *164*, 195–204.
[469] Padilla, O. I., McLellan, M. R. *J. Food Sci.* **1989**, *54*, 1250–1263.
[470] Giovanelli, G., Ravasini, G. *Lebensm. Wiss. Technol.* **1993**, *26*, 1–12.
[471] Bartsch, R. A., Maeda, M., Eds. *Molecular and Ionic Recognition with Imprinted Polymers*; ACS Symposium Series 703; American Chemical Society: Washington, DC, 1998.
[472] Mosbach, K., Mayes, A. G. *Trends in Analytical Chemistry*; Elsevier: Amsterdam, 1997.
[473] Wang, H. Y., *et al. Langmuir* **1996**, *12*, 48–50.
[474] Kobayashi, H. Y., *et al. Anal. Chem. Acta* **1998**, *365*, 381–391.
[475] Trotta, F., *et al. J. Membr. Sci.* **2002**, *201*, 77–84.
[476] Ptitchkina, N. M., *et al. Carbohydrate Polym.* **1994**, *23*, 265–273.
[477] Li, W., *et al. J. Membr. Sci.* **2004**, *245*, 123–129.
[478] Goulas, A. K., *et al. J. Membr. Sci.* **2002**, *209*, 321–331.
[479] Li, W. Y., et al. In *Proceedings of the 4th National Membrane Science and Technology Conference Report*, Nanjing, People's Republic of China, 2002; p 10.
[480] Wang, X. L., *et al. J. Membr. Sci.* **2002**, *204*, 271–286.
[481] Sulaiman, M. Z., *et al. J. Chem. Eng.* **1998**, *68*, 145–148.
[482] Bowen, W. R., *et al. Chem. Eng. Sci.* **1996**, *51*, 4321–4332.
[483] Lipnizki, F., *et al. Desalination* **2002**, *144*, 179–186.
[484] Urtiaga, A., *et al. Desalination* **2002**, *148*, 115–120.
[485] Feuillat, M., *et al.* In *Oenologie: Fondements Scientifiques et Technologiques*;, Lavoisier Tec et Doc: London, 1998; pp 596–620.
[486] Mietton-Peuchota, M., *et al. Desalination* **2002**, *148*, 125–129.
[487] Goncalves, F., *et al. Sep. Purif. Technol.* **2001**, *22*, 423–429.
[488] Gomez Benýtez, J., *et al. J. Food Eng.* **2003**, *58*, 373–378.
[489] Goncalves, F., *et al. J. Food Eng.* **2003**, *59*, 229–235.
[490] Goertges, S., Stock, R. *Deutsche-Weinmagazin* **2000**, *2*, 24–28.
[491] Mourgues, J. *Revue des Oenologues* **1993**, *69S*, 51–54.

[492] Maujean, A., *et al. Cahier Scientifique* **1986**, *104*, 34–41.
[493] Maujean, A. In *Les acquisitions récents dans les traitments physiques du vin*; Doneche, B., Ed., Lavoisier Tec & Doc.: Paris, 1994; pp 85–102.
[494] Dunsford, P., Boulton, R. *Am. J. Enol. Vitic.* **1981**, *33*, 106–110.
[495] Correa-Gorospe, I., Rodriguez-Clemente, R. *Anales de Quimica* **1991**, *8*, 435–438.
[496] Dunsford, P., Boulton, R. *Am. J. Enol. Vitic.* **1981**, *32*, 100–105.
[497] Maujean, A., *et al. Revue Francaise d_Oenologit* **1986**, *104*, 34–41.
[498] Tanahashi, H., *et al. J. Chem. Eng. Jpn.* **1992**, *25*, 342–344.
[499] Gerbaud, V., *et al. Trans. I. Chem. E.* **1996**, *74*, 782–789.
[500] Vernhet, A., *et al. Am. J. Enol. Vitic.* **1999**, *50*, 391–397.
[501] Guitard, A. In *Proceedings of the Journeee de rencontres oenologiques de l'association des oenologues de la Facultee de Pharmacie de Montpellier*, Montpellier, Francia, 1983; pp 17–31.
[502] Perez Rodrýguez, L. *Vitivinicultura* **1991**, *9*, 19–22.
[503] Magerstadt, M. *Filtr. Sep.* **1988**, *35* (6), 513–514.
[504] Peynaud, E., Allard, J. J. *Compterendus Academie d'Agriculture* **1970**, *56* (18), 1476–1478.
[505] Aubert, I., Caron, S. *Viti* **2000**, *255*, 21–35.
[506] Delfini, C., Nicolini, G. J. *Int. Sci. Vigne Vin.* **1991**, *25* (1), 1–35.
[507] Urtiaga, A., *et al. J. Filtr. Sot.* **2001**, *3*, 4–7.
[508] Vernhet, A., *et al. J. Membr. Sci.* **2002**, *201*, 103–122.
[509] Urtiaga, A., *et al. Alimentacion, Equipos y Tecnologia* **2001**, *156*, 95–104.
[510] Ferrando, M., *et al. J. Agric. Food Chem.* **1998**, *46*, 15–23.
[511] Hernandez, P., *et al. Revue Francaise d'Oenologit* **1997**, *162*, 32–35.
[512] Escudier, J. L., Saint Pierre, B., Batlle, J. L., Moutounet, M. Proced_e et dispositif automatique de stabilisation tartrique de vins. French Pat. FR 2709308-A1, 1993.
[513] Mourgues, J. *Rev. des Oenologues* **1993**, *19*, 51–54.
[514] Wucherpfennig, K. *Industria delle Bevande* **1976**, *5*, 97–113.
[515] Ribereau-Gayon, P., *et al. Traitee d'oenologie.T2. Chimie du vin. Stabilisation et traitments.*; Dunod: Paris, 1998.
[516] dos Santos, C. *Anal. Chim. Acta* **2002**, *458*, 257–261.
[517] Moutounet, M. *Revue Franc_aise d_Oenologie* **1997**, *162*, 15–17.
[518] Uitslag, H., *et al. Aust. N.Z. Grapegr. Winemaker* **1996**, *390*, 75–78.
[519] Belleville, M. P., *et al. Vitic. Enol. Sci.* **1992**, *46*, 100–112.
[520] Czekaj, P., *et al. J. Food Eng.* **2001**, *49*, 25–31.
[521] Su, T. J., *et al. J. Membr. Sci.* **1999**, *163*, 265–274.
[522] Vernhet, A., *et al. Am. J. Enol. Vitic.* **1998**, *50*, 51–65.
[523] Belleville, M.-P., *et al. J. Food Sci.* **1990**, *55* (6), 1598–1602.
[524] Vernhet, A., *et al. J. Membr. Sci.* **1997**, *128*, 163–174.
[525] Barth, R. *BIOS Int.* **2000**, *1* (2), 46–48.
[526] Bamforth, C. W. *J. Am. Soc. Brewing Chem.* **1999**, *57* (3), 81–90.
[527] Moll, M. *Bières and Coolers: Définition, Fabrication et Composition*,; Lavoisier Tech. & Doc.: Paris, 1991.
[528] Howell, J. A., *et al*. In *Proceedings of the EuroMembrane Conference*; Bath, UK, 1995; Vol. 2, pp 25–30.
[529] Freeman, J. G., McKechinie, M. T. In *Fermented Beverage Production*; Blackie Academic and Professional: London.
[530] Takahashi S., In *European Brewery Convention, Proceedings of the Symposium on Separation*, Leuven, Belgium, 1990; pp 214–227.
[531] Kiefer, J. In *Proceedings of the European Brewery Convention Congress*, Lisbon, 1991; pp 657–664.
[532] Lüdemann, A. *Am. J. Enol. Vitic.* **1987**, *38* (3), 228–235.
[533] René, F., Maingonnat, J. F. *Revue Bibliografique IAA* **1993**, *110*, 721–729.
[534] Bomben, J. L., *et al. Adv. Food Res.* **1973**, *2*, 1–20.
[535] Lipnizki, F., *et al. J. Food Eng.* **2002**, *54*, 183–195.
[536] Baudot, A., *et al. J. Membr. Sci.* **1999**, *158*, 167–185.
[537] Ramteke, R. S., *et al. J. Sci. Food Agric.* **1990**, *50* (3), 399–405.
[538] Piggott, J. R., *et al. J. Food Sci. Technol.* **1993**, *28* (6), 629–637.
[539] von Sydow, E., Karlsson, G. *Lebensmittel Wissenschaft und Technologie.* **1971**, *4*, 54–58.
[540] von Sydow, E., Karlsson, G. *Lebensmittel Wissenschaft und Technologie,* **1971**, *4*, 152–157.
[541] Lazarides, H. N., *et al.* 'Advanced Processes: Engineering. and Food', Elsevier, Barking, UK, **1990**; Vol. 3, pp 96–195.
[542] Sulc, D. In *Lebensmitteltechnologie*; Heiss, R., Ed., Springer: Berlin, 1991; pp 209–227.
[543] Bengtson, G., Boeddeker, K. W. In *Proceedings of the Third International Conference on Pervaporation Processes in the Chemical Industry*; Bakish, R. A., Ed. Bakish Material Corporation: Englewood, NJ, 1988; pp 439–448.
[544] She, M., *et al. J. Membr. Sci.* **2004**, *236*, 93–202.
[545] Jiraratananon, R., *et al. J. Membr. Sci.* **2002**, *210*, 389–397.
[546] Sampranpiboon, P., *et al. J. Membr. Sci.* **2000**, *174*, 55–67.
[547] Curcio, S., *et al. J. Food Eng.* **2001**, *48*, 235–241.
[548] Kollmansberger, H., Berger, R. G. *Deutsche Lebensmittel-Rundschau,* **1994**, *90* (3), 69–71.
[549] Rajagopalan, N., Cheryan, M. *J. Membr. Sci.* **1995**, *104*, 243–255.
[550] Karlsson, H. O. E., Tragradh, G. *J. Membr. Sci.* **1994**, *91*, 189–198.
[551] Pereira, C. C., *et al. Desalination* **2002**, *148*, 57–65.
[552] Baudot, A., Marin, A. *Food Bioprod. Process.: Trans. IChE Part C* **1997**, *75*, 117–142.
[553] Lamer, T., *et al. Process. Biochem.* **1996**, *31*, 533–542.
[554] Cláudio, P., *et al. J. Membr. Sci.* **2004**, *238*, 9–19.
[555] Mannheim, C. H., Passy, N. *Process Biochem.* **1975**, *10*, 3–14.
[556] Matsuura, T., Blais, A., Baxter, A. G., Sourirajan, S. US Pat. 4322448, 1980.
[557] Kane, L., *et al. J. Food Sci.* **1995**, *60* (1), 190–194.
[558] Pepper, D., *et al. Desalination* **1985**, *53* (1–3), 157–166.
[559] Rodrigues, R. B., *et al. Alimentaria, enero-febrero* **2001**, 131–134.
[560] Sheu, M. J., Wiley, R. C. *J. Food Sci.* **1983**, *48*, 422–435.
[561] Kubota, K., *et al. Agric. Biol. Chem.* **1986**, *50* (11), 2867–2873.
[562] Lin, C. Y., Chiang, B. H. *Int. J. Food Sci. Technol.* **1993**, *28*, 453–460.
[563] Kubota, K., *et al. Food Aci. Technol. Int.* **1996**, *2* (3), 163–166.
[564] Sekiwa, Y., *et al. J. Agric. Food Chem.* **1997**, *45*, 826–830.
[565] Le Guen, S., *et al. J. Chromatogr. A* **2000**, *896*, 361–371.
[566] Le Guen, S., *et al. J. Agric. Food Chem.* **2001**, *49* (3), 1321–1327.
[567] Lee, G. H., *et al. J. Agric. Food Chem.* **2001**, *49* (9), 4324–4332.
[568] Jayarajah, C. N., Lee, C. M. *J. Food Sci.* **1999**, *64* (1), 93–98.

[569] Mahmud, H., *et al. J. Membr. Sci.* **2002**, *209*, 207–219.
[570] Souchon, I., *et al. Desalination* **2002**, *148*, 87–92.
[571] Souchon, I., *et al. Desalination* **2004**, *163*, 39–46.
[572] Pierre, E. X., *et al. J. Membr. Sci.* **2001**, *187*, 239–253.
[573] Spinnler, H. E., Production de γ-décalactone par Bioconversion. Pat. FR 53939 C, 1993.
[574] Girard, B., Fukumoto, L. R. *Crit. Rev. Food Sci. Nutr.* **2000**, *40* (2), 91–157.
[575] Jørgensen, R. B., *et al. J. Food Eng.* **2004**, *64*, 23–31.
[576] Lagana, F., *et al. J. Membr. Sci.* **2000**, *166* (1), 1–11.
[577] Decloux, M., *et al. Zuckerindustrie* **2000**, *125*, 106–123.
[578] Gratius, M., *et al. Int. Sugar J.* **1995**, *97*, 296–312.
[579] Djuri, M., *et al. J. Food Eng.* **2004**, *65*, 73–82.
[580] Ghosh, A. M., Balakrishnan, M. *J. Food Eng.* **2004**, *58*, 143–150.
[581] Balakrishnan, M., *et al. Sep. Purif. Technol.* **2000**, *19*, 209–220.
[582] Verma, S. K., *et al. Indian J. Chem. Technol.* **1996**, *3*, 136–143.
[583] Ghosh, A. M., *et al. J. Membr. Sci.* **2000**, *174*, 205–216.
[584] Balakrishnan, M., *et al. Int. Sugar J.* **2000**, *1213*, 21–25.
[585] Cartier, S., In *Proceedings of SPRI Workshop on Separation Processes in the Sugar Industry*, New Orleans, LA, USA, October 1996; pp 55–68.
[586] Kishihara, S., *et al. J. Membr. Sci.* **1986**, *41*, 103–114.
[587] Kwok, R. J. *Int. Sugar J.* **2000**, *98* (1173), 490–512.
[588] Eringis, A., Jaferey, I. In *Proceedings of the International Society of Sugarcane Technologists*; 2001; Vol. 24, pp 151–152.
[589] Bhattacharya, P. K., *et al. Sep. Purif. Technol.* **2000**, *21*, 247–259.
[590] Nene, S. N., In *The 8th World Filtration Conference*, Brighton, UK, 3–7 April 2000.
[591] Kochergin, V., *et al. Int. Sugar J.* **2000**, *102* (1223), 568–578.
[592] Nielsen, W. K., *et al. Sugar Technol. Rev.* **1982**, *9*, 59–117.
[593] Willett, C. C. *Int. Sugar J.* **1997**, *99*, 48–51.
[594] Gyura, J. *Desalination* **2002**, *148*, 49–56.
[595] Hamachi, M., *et al. Purif. Technol.* **2003**, *30*, 229–239.
[596] Karode, S. K., *et al. Sep. Sci. Technol.* **2000**, *35*, 2473–2490.
[597] Tragardh, G., Gekas, V. *Desalination* **1988**, *69*, 9.
[598] Cartier, S., *et al. Desalination* **1997**, *113* (1), 7–17.
[599] Wadley, S., *et al. J. Membr. Sci.* **1995**, *102*, 163–175.
[600] Lutin, F., In *Proceeding of Euromembrane*, Bath, UK, 1995; Vol. 2, pp 75–84.
[601] Sarode, A. D., *et al. Chem. Eng. Commun.* **2001**, *188*, 179.
[602] Dornier, M., *et al. J. Food Eng.* **1995**, *24*, 213–224.
[603] Decloux, M., Tatoud, L. *J. Food Eng.* **2000**, *44*, 119–126.
[604] Balakrishnan, M., *et al. Sep. Sci. Technol.* **2001**, *36* (4), 619–637.
[605] Barhate, R. S., *et al. J. Food Eng.* **2003**, *60*, 49–54.
[606] Itoh, S., In *Proceedings of the International Congress on Membranes and Membrane Processes*, ICOM-96, Yokohama, p 867.
[607] NHB *Ultrafiltered Honey*.; National Honey Board: Longmont, CO, 1991.
[608] Meindersma, G. W. *Starch/Starke* **1980**, *32* (IO), 329–334.
[609] Eriksson, G., Sivik, B. *Potato Res.* **1976**, *19*, 279–287.
[610] Oosten, B. J. *Die Stärke* **1976**, *28* (4), 135–137.
[611] von Meuser, F., Smolnik, H. D. *Die Stärke* **1976**, *28* (8), 271–278.
[612] Harmen, J., *et al. Desalination* **2002**, *144*, 331–334.
[613] Duxbury, D. D. *Food Process.* **1992**, *53*, 55–56.
[614] Vose, J. R. *Cereal Chem.* **1980**, *57*, 406–410.
[615] Sumner, A. K. *J. Food Sci.* **1981**, *46*, 364–366.
[616] Bramsnaes, F., Sejr Olson, H. *J. Am. Oil Chem. Soc.* **1979**, *56*, 450–454.
[617] Nickel, G. B. Process for Preparing Products From Legumes. Can. Pat. 1,104,871, **1981**.
[618] Basha, S. M. M. During Seed Development and Germination. PhD Thesis, University Of Oklahoma: Norman, OK, 1974; pp 79.
[619] Gao, L., *et al. Lebensm.-Wiss. u.-Technol.* **2001**, *34*, 149–158.
[620] Ulloa, J. A., *et al. J. Food Sci.* **1988**, *53*, 1396–1398.
[621] Yanagi, C., *et al. Desalination* **1994**, *98*, 161–170.
[622] Young, F. V. K., *et al.* Processing of Fats and Oils. In *The Lipid Handbook*Gunstone, F. D., Harwood, J. L., Padley, F. B., Eds. Chapman and Hall: London, 1994; pp 249–318.
[623] Vlyssides, A. G., *et al. J. Cleaner Product.* **2004**, *12*, 603–611.
[624] Owen, R. W., *et al. Clin. Chem.* **2000**, *46* (7), 976–988.
[625] Ergüder, T. H., *et al. Process Biochem.* **2000**, *36*, 243–248.
[626] Vlyssides, A. G., Iaconidou, K. *Olive Oil Production in Greece. EU IMPEL Olive Oil Workshop*, Cordoba, Spain, 2003.
[627] Cormenzana, A. R., *et al. Int. Biodeterior. Biodegrad.* **1996**, *38* (3/4), 283–290.
[628] Rozzi, A., *et al. Process Chem.* **1988**, *23*, 86–90.
[629] World Bank *Pollution Prevention and Abatement Handbook World Bank Group*,.; World Bank: Washington, DC, 1998.
[630] German Federal Ministry for Economic Cooperation and Development (BMZ) *Environmental Handbook, Documentation on Monitoring and Evaluating Environmental Impacts*, Bonn; Vol. 2, 1995.
[631] Cormenzana, A. R., *et al. Int. Biodeterior. Biodegrad.* **1995**, *35* (1–3), 249–268.
[632] Chatjipavlidis, I., *et al. Int. Biodeterior. Biodegrad.* **1996**, *38* (3–4), 183–187.
[633] López, M. J., *et al. Water Res.* **2001**, *35* (7), 1828–1830.
[634] Kima, I.-C., *et al. J. Membr. Sci.* **2002**, *205*, 113–123.
[635] Ochoa, N., *et al. Sep. Purif. Technol.* **2001**, *22–23*, 417–422.
[636] Cheryan, M. *Ultrafiltration and Microfiltration Handbook*; Technomic: Lancaster, 1998.
[637] Sen Gupta, A. K. Process for Refining Crude Glyceride Oils by Membrane Filtration; US Pat. 4062882, 1977.
[638] White, L. S., Nitsch, A. R. J. *J. Membr. Sci.* **2000**, *179*, 267–274.
[639] Koseoglu, S. S., *et al. J. Am. Oil Chem. Soc.* **1990**, *67* (5), 315–322.
[640] Koseoglu, S. S., In *Proceedings of World Conference on Edible Fats and Oils Processing: Basic Principles and Modern Practices*, Erickson, D. R., Ed.; American Oil Chemists' Society: Champaign, IL, 1990, pp 182$\pm$188.
[641] Raman, L. P., *et al. J. Am. Oil Chem. Soc.* **1996**, *73* (2), 219–224.
[642] Musale, D. A., Kumar, A. J. *Appl. Poly. Sci.* **2000**, *77*, 1782–1793.
[643] Lencki, R. W., Williams, S. J. *J. Membr. Sci.* **1995**, *101*, 43–51.
[644] Machado, D. R., *et al. J. Membr. Sci.* **1999**, *163*, 93–102.
[645] Hayashi, Y., *et al. J. Membr. Sci.* **2000**, *177*, 233–243.
[646] Iwama, A. *J. Am. Oil Chem. Soc.* **1987**, *64* (9), 1258–1267.
[647] Koseoglu, S. S., *et al. J. Membr. Sci.* **1997**, *134*, 101–108.
[648] Sridhar, S., *et al. J. Membr. Sci.* **2002**, *205*, 83–90.
[649] ISTAT, *Italian Statistical Yearbook 2000. Production of Wood Cultivation, Oil and Wine per Country*, Year 1998; pp 326–358.
[650] Chian, E. S. K., Dewalle, F. B. *Water Res.* **1977**, *11*, 295–312.
[651] Noble, R. D., Stern, S. A. *Membrane Separations Technology: Principles and Applications*; Elsevier: Amsterdam, 1995.

[652] Rautenbach, R., Albrecht, R. *Membrane Processes*; Wiley: Chichester, 1989.
[653] Cereti, C. F., *et al. Bioresource Technol.* **2004**, *91*, 135–140.
[654] Hamdi, M. *Bioprocess Eng.* **1993**, *8*, 209–214.
[655] Quemeneur, F., *et al. Entropie* **1980**, *93*, 22–29.
[656] Belkacem M., Thèse de Doctorat, INSA, Toulouse, 1995.
[657] Belkacem, M., *et al. Chem. Eng. J.* **1995**, *56*, 27–32.
[658] Lindau, J., Jonsson, A. S. *J. Membr. Sci.* **1995**, *87*, 71–82.
[659] Swientek, B. *Prepared Foods* **1997**, *166* (12), 104–108.
[660] Ahmad, A. L., *et al. Desalination* **2003**, *157*, 87–95.
[661] Cheryan, M., Rajagopalan, M. *J. Membr. Sci.* **1998**, *151*, 13–28.
[662] Argüello, M. A., *et al. J. Membr. Sci.* **2003**, *216*, 121–134.
[663] Hambraeus, L. Nutritional Aspects of Milk Proteins. In *Advanced Dairy Chemistry: Proteins*; Fox, P. F., Ed. Elsevier: London, 1992; Vol. I, pp 457–490.
[664] Scott, K. *Handbook of Industrial Membranes*; Elsevier: Oxford, 1995.
[665] Dẏaza, O., *et al. Food Hydrocolloids* **2004**, *18*, 601--610.
[666] Kinsella, E., Whitehead, D. M. *Adv. Food Nutr. Res.* **1989**, *33*, 343–438.
[667] Karleskind, D., *et al. J. Food Sci.* **1995**, *60*, 731–737.
[668] Karleskind, D. *J. Food Sci.* **1996**, *61*, 54–58.
[669] Marijana, D., *et al. J. Membr. Sci.* **2000**, *165*, 83–88.
[670] Al-Akoum, O. *Sep. Purif. Technol.* **2002**, *28*, 219–234.
[671] Mercier-Bonina, M., *et al. Chem. Eng. Sci.* **2004**, 2333–2341.
[672] Cheang, B. L., Zydney, A. L. *J. Membr. Sci.* **2004**, *231*, 159–167.
[673] Pearce, S. C., *et al. Int. Dairy Fed.* **1991**, *9201*, 118.
[674] Saboya, L. V., Maubois, J. L. *Le Lait* **2000**, *80* (6), 541–553.
[675] Eckner, K. F., Zottola, E. A. *J. Food Protect.* **1991**, *54*, 793–797.
[676] Madec, M. N., *et al. Lait* **1992**, *72*, 327–332.
[677] Gesan-Guiziou, G., *et al. J. Dairy Res.* **1999**, *66* (2), 225–236.
[678] Mehra, R. K., Donnelly, W. J. *J. Dairy Res.* **1993**, *60*, 89–97.
[679] Samuelsson, G., *et al. Int. Dairy J.* **1997**, *7* (4), 237–242.
[680] Rodriguez, J., *et al. J. Agric. Food Chem.* **1999**, *47* (2), 558–565.
[681] Lawrence, R. C. *Int. Dairy Fed. Bull.* **1989**, *240*, 2–15.
[682] Sprangler, P. L., *et al. J. Dairy Sci.* **1991**, *74*, 2809–2819.
[683] Kosikowski, F. V. *Food Technol.* **1986**, *6*, 71–76.
[684] Zall, R. R. In *Whey and Lactose Processing*; Zadow, J. G., Ed. Elsevier: Barking, 1992; pp 1–72.
[685] Cheryan, M., *et al. J. Membr. Sci.* **1990**, *48*, 103–114.
[686] Ennis, B. M., Higgins, J. J. *Dairy Sci. Technol.* **1982**, *16*, 27–34.
[687] de Boer, R., , *et al.*Ed. *Progress in Food Engineering*; Forster-Verlag AG: Küsnacht, Switzerland, 1983; pp 393–403.
[688] Houldsworth, D. W. *J. Soc. Dairy Technol.* **1980**, *33*, 45–54.
[689] Evenson, M. L., *et al. Int J. Food Microbio.* **1988**, *25*, 311–316.
[690] Sharpe, A. N., *et al. J. Food Prot.* **2000**, *63*, 126–130.
[691] Blysick-McKennal, D. N., Schainer, D. W. *J. Food Prot.* **1994**, *57*, 1052–1056.
[692] Yu, L. S. L., *et al. J. Food Prot.* **1995**, *58*, 943–945.
[693] Carroll, S. A., *et al. J. Food Prot.* **2000**, *63*, 347–353.
[694] Entis, P., Lerner, I. *J. Food Prot.* **2000**, *63*, 354–363.
[695] Daufin, G., *et al. Trans. I. Chem. E.* **2001**, *79*, 89–102.
[696] Koyuncu, I., *et al. Water Sci. Technol.* **2000**, *41*, 213–221.
[697] Delbeke, R. *Milchwissenschaft* **1981**, *36* (11), 669–672.
[698] Balannec, B., *et al. Desalination* **2002**, *147*, 89–94.
[699] Greiter, M., *et al. J. Membr. Sci.* **2002**, *210*, 91–102.
[700] Dresch, M. Membrane Processes for the Recovery of Dairy Cleaning-in-Place Solutions. PhD Thesis, ENSA, Rennes, France, 1998; p 199.
[701] Henck, M. A. Recycling of Caustic Cleaning Solutions Using Cross-Flow Filtration in the Dairy Industry. PhD Thesis, University of Zurich, Switzerland, 1993.
[702] Kristic, D. M., *et al. J. Membr. Sci.* **2002**, *208*, 303–314.
[703] Rao, H. G. R. *Desalination* **2002**, *144*, 319–324.
[704] Krsitic, D. M., *et al. Desalination* **2004**, *163*, 297–309.
[705] Heinemann, P., *et al. Desalination* **1988**, *68*, 243–250.
[706] DeWit, J. N. *Netherland Milk Dairy J.* **1984**, *38*, 71–84.
[707] Koltuniewicz, A. B., *et al. J. Membr. Sci.* **1995**, *102*, 193–207.
[708] Bohner, H. F., Bradley, R. L. *J. Dairy Sci.* **1992**, *75* (3), 718–724.
[709] Lee, H., *et al. Water Res.* **2001**, *35* (14), 3301–3308.
[710] Cheryan, M. *Ultrafiltration Handbook*,; Technomic: Lancaster, 1986.
[711] >Renner, E., Abd El-Salam, M. H. *Application of Ultrafiltration in the Dairy Industry*,; Elsevier: London, 1991.
[712] Kulozik, U. M., Kessler, H. G. In *Proceedings of the Third International Conference on Fouling and Cleaning in Food Processing*; Kessler, H. G., Lund, D. B., Eds.; Federal Republic of Germany: Prien-Chiemsee, 1989; pp. 248–257.
[713] Argüello, M. A., *et al. J. Agric. Food Chem.* **2002**, 1951–1965.
[714] Quebriac¸ O. Bourgeois, C. Valorisation du sang animal, ActualiteÂs et techniques en industries agroalimentaires, Edition APRIA, 35, 1985.
[715] Sattelee, L. D., *et al. J. Food Sci.* **1973**, *38*, 306–309.
[716] Cowan, J. A. C., *et al. Water Sci. Technol.* **1992**, *25*, 137–148.
[717] Ohno, S., Koyama, K., Fukuda, M. Toyo Soda Manufacturing Co. Ltd., Japan, US Pat. 4 347 138, August 1982.
[718] Tessier, J. P., Louveau, V. C. R. *Seances Acad. Agric. Fr.* (in French) **1979**, *65* (18), 1533–1544.
[719] Fransen, N. G., *et al. Bioresour. Technol.* **1988**, *65*, 145–150.
[720] Russel, J. M., *et al. Bioresour. Technol.* **1993**, *43*, 41–46.
[721] Fernando, T. *Biotechnol. Bioeng.* **1981**, *23* (1), 19–28.
[722] Torres, M. R., *et al. J. Food Eng.* **2002**, *54*, 215–219.
[723] Belhocine, D., *et al. J. Membr. Sci.* **1988**, *142*, 159–171.
[724] Rendueles, M., *et al. Res. Environ. Biotechnol.* **1996**, *1*, 193–206.
[725] Fachnrich, A., *et al. Desalination* **1998**, *119*, 213–216.
[726] Mavrov, V., *et al. Desalination* **2001**, *150*, 65–74.
[727] Cowan, J. A. C., *et al. Water Sci. Technol.* **1992**, *25*, 137–148.
[728] Afonso, M. D., *et al. Desalination* **2002**, *151*, 131–138.
[729] Afonso, M. D., *et al. Desalination* **2002**, *142*, 29–45.
[730] Vandanjon, L., *et al. Desalination* **2002**, *144*, 379–385.
[731] Pavia, E. H., Tyagi, A. D. *Safe Economical Rescue of Transport Water in the Fish Meal and Oil Industry*; ASME: New York, 1972.
[732] Abu, M. Y. B., *et al. J. Environ. Sci. Health B* **1984**, *19* (1), 67–78.
[733] Matthiasson, E., Sivik, B. *Livsmedelsteknik* **1978**, *20*, 241–256.
[734] Korhonen, R. W., Lanier, T. C. *A Research Abstract*; North Carolina State University: Raleigh, NC, 1991.
[735] Huang, L., Morrissey, M. T. *J. Membr. Sci.* **1998**, *144*, 113–123.
[736] Shokuhin Sangyo MAK, Japan. Pat. 251438, 1983.
[737] Hood, L. F., *et al. Food Product. Develop.* **1976**, *10*, 86.

[738] Senstad, C., Almas, K. A. In *Proceedings of the 3rd International Conference on Chitin/Chitosan*; Ancona, Italy; Muzzarelli, R. A. A., Ed.; 1985.
[739] Grossman, S., Bergman, M. Process for the Production of Gelatin from Fish Skins; US Pat. 5,093,474, 1992.
[740] Simon, A., *et al. Desalination* **2002**, *144*, 313–318.
[741] Singh, D. P. *Desalination* **1990**, *78*, 279–286.
[742] Leuenherger, B. H. *Food Hydrocolloids* **1991**, *5*, 353–361.
[743] Ledward, D. A. *Food Sci. Today* **1992**, *6* (4), 236–241.
[744] Greenlaw, D. B., *et al. Imaging Sci. J.* **1997**, *45*, 256–259.
[745] Almas, K. A. *Desalination* **1985**, *53*, 167–178.
[746] Jacobsen, F. *Meeting of the Scientific Committee of the International Association of Fish Meal Manufacturers*; London, 1984.
[747] Mameri, N., *et al. J. Chem. Technol. Biotechnol.* **1996**, *67* (2), 169–182.
[748] von Bockelmann, I., *et al.* In *Reverse Osmosis and Synthetic Membranes*; Sourirajan, S., Ed. National Research Council: Ottawa, 1977, p 445.
[749] Eriksson, C. E. *Proceedings of the 5th International Congress of Food Science and Technology*, Kyoto, Japan, 1978, p 72.
[750] Swafford, T. C. Separation–recovery of soluble/insoluble proteins from surimi processing washwaters. In *Proceedings of the Pacific Fisheries Technology Meeting*, Monterey, CA, USA, 1987.
[751] Mohr, C. M., *et al*. Noyes Data Corp., NJ, USA, 1989.
[752] Chao, A. C., *et al.* In *Proceedings of the 35th Industrial Waste Conference*; Purdue University: Lafayette, IN, USA, 1980; pp 560–570.
[753] Chao, A. C., *Proceedings of the 38th Industrial Waste Conference*, Purdue University, Lafayette, IN, USA, 1983; pp 829–837.
[754] Chao, A. C., *et al*. *Proceedings of the Triangle Conference on the Environment and Technology*, Chapel Hill, NC, USA, 1983.
[755] Chao, A. C., *Proceedings of the 39th Industrial Waste Conference*, Purdue University, Lafayette, IN, USA, 1984; pp 555–563.
[756] Chao, A. C., *et al.*Tojo, S. *J. Environ. Eng.* **1987**, *113*, 383.
[757] Lin, T. M., *et al. J. Food Sci.* **1994**, *60*, 4–9.
[758] Pedersen, L. D., *et al*. *Final Report Phase II*, *National Food Processors Association*, Dublin, CA, USA, 1989.
[759] Nitto Electric. Ind. K.K. Japan. Pat.. 151862, 1981.
[760] Nitto Electric. Ind. K. K., Japan. Pat. 061907, 1984.
[761] Montecinos, H., Borquez, R. In *Proceedings of the II Congresso de Engenharia de Processos do MERCOSUL*, Florianopolis-Santa Catarina, Brazil, 1999.
[762] Watanabe, H., *et al. Bull. Jpn. Soc. Sci. Fish.* **1982**, *48*, 869–876.
[763] Nishioka, F., Shimizu, Y. *Bull. Jpn. Soc. Sci. Fish.* **1983** *49*, 795–814.
[764] Jaouen, P., Quemeneur, F. In *Fish Processing Technology*; Hall, G. M., Ed., Blackie Academic and Professional: London, 1992; pp 212–248.
[765] Paulson, D. J., *et al. Food Technol.* **1984**, *38*, 77–85.
[766] Welsh, F. W., Zall, R. R. *J. Food Protect.* **1983**, *46*, 1026–1034.
[767] Egorova, N. I., *et al. Rybnoe Khozyaistvo* **1986**, *2*, 75–89.
[768] Patterson, J. W. *Industrial Wastewater Treatment Technology*, 2nd edn.; Butterworths: Stoneham, MA,, 1985.
[769] Li, F., Marks, D. W., Larock, R. C., Otaigbe, J. U. *SPE ANTEC Technol. Papers* 1999, *3*, 3821–3825.
[770] Faust, R., Shaffer, T. D. *Cationic Polymerization: Fundamentals and Applications*; ACS Symposium Series; American Chemical Society: Washington, DC, 1997.
[771] Kramer, O. *Biological and Synthetic Polymer Networks*; Elsevier,: New York, 1988.

Biographical Sketch

Andrzej B. Koltuniewicz graduated from the Wroclaw University of Technology, where he received his PhD as well. He was professor in Chemical Engineering Department, director of Chemical Engineering Institute of Wrocław University of Technology, and co-editor of *Chemical Engineering and Processing*, the quarterly of Polish Academy of Science PAN since 1985. He is ECC expert for evaluation and assessment of proposals and research projects in RTD ECC and national programs. His area of experience, lecturing, and consulting includes membrane processes, hybrid processes, clean technologies, sustainable development, and chemical and bioprocess engineering. He is author of the book *The Yield of Pressure-Driven Membrane Processes in the Light of Surface Renewal Theory*, and more than 150 publications, and has seven patents to his credit. He is reviewer of several international journals, including *Journal of Membrane Science*, *Desalination*, *The Chemical Engineering Journal*, *Industrial and Engineering Chemistry Research*, *Separation Science and Technology*. He has chaired several Polish and international conferences. He interacts with several universities in UK, Netherlands, France, Italy, Portugal, Spain, Germany, and Egypt. Since 2009 he is professor at Warsaw University of Technology, Faculty of Chemical and Process Engineering.

4.06 Basic Aspects and Applications of Membrane Processes in Agro-Food and Bulk Biotech Industries

F Lipnizki, Alfa Laval Copenhagen A/S, Søborg, Denmark

Glossary

Biological oxygen demand (BOD) Measure to determine the quality of water by defining the quantity of dissolved oxygen consumed during the decomposition of the organic compounds in the water.

Chemical oxygen demand (COD) Measure to determine the quality of water by defining the quantity of dissolved oxygen consumed during the decomposition of organic compounds and the oxidation of inorganic compounds in the water.

Concentration polarization Concentration profile of a solute having a higher concentration at the feed-side membrane surface compared to the bulk feed stream.

Dextrose equivalent (DE) Measure of the degree of conversion of starch into dextrose. This is defined as the sum of reducing sugars expressed as dextrose and is calculated as a percentage of the dry substance.

Diafiltration (DF) Membrane separation process to remove/reduce small molecular components, for example, salts or antibiotics from a feed stream. Therefore, the permeate removed from the feed is replaced by diafiltration water added to the feed.

Dialysis Liquid-phase separation process in which solutes are transferred under the driving force of a concentration gradient from one solution to another through a membrane.

Electrodialysis (ED) Liquid-phase separation process in which ions are driven through an ion-selective membrane under the influence of an electric field.

Membrane bioreactor (MBR) A unit in which a biological reaction and membrane-based separation are carried out simultaneously. The membranes can be either submerged directly into the reactor or operated in a side stream.

Membrane contactor (MC) Process in which a gas/liquid or liquid/liquid mass transfer of one phase to another occurs without dispersion of the phases on both sides of a porous membrane. MC units include, for example, membrane distillation (MD), osmotic distillation (OD), membrane emulsifiers, and membrane crystallizers.

Membrane crystallizers Process in which two liquids are separated by porous membrane. The volatile solvent of the crystallizing solution diffuses through the membrane driven by the vapor pressure gradient across the membrane.

Membrane distillation (MD) Distillation process in which the liquid and gas phases are separated by a porous membrane, the pores of which are not wetted by the liquid phase.

Membrane emulsifiers Process in which the dispersed phase is pushed through the pores of a membrane driven by the pressure gradient across the membrane.

Microfiltration (MF) Liquid-phase separation process in which particles and dissolved macromolecules larger than 1 μm are rejected by a membrane.

Milk protein concentrate (MPC) Concentrated milk consisting of 40–90% milk protein.

Molecular weight cutoff (MWCO) Molecular weight of a solute which is 90% rejected by a membrane.

Nanofiltration (NF) Liquid-phase separation process in which dissolved molecules smaller than about 2 nm are rejected by a membrane.

Osmotic distillation (OD) Concentration process in which water diffuses from the feed stream through a porous membrane driven by the vapor pressure gradient across the membrane.

Pervaporation (PV) Membrane separation process in which the feed and retentate streams are both liquid phases, while the permeate stream emerges from the downstream surface of the membrane as vapor.

Reverse osmosis (RO) Liquid-phase membrane separation process in which the applied transmembrane pressure causes selective movement of solvent against its osmotic pressure difference.

Transmembrane pressure (TMP) Pressure difference between feed and permeate pressure. In pressure-driven membrane, it is defined as the driving force of the process.

Ultrafiltration (UF) Liquid-phase separation process in which particles and dissolved macromolecules smaller than 1 μm and larger than about 2 nm are rejected by a membrane.

Vapor permeation (VP) Membrane separation process in which the feed is vaporized before contacting the membrane and the permeate stream

emerging from the downstream surface of the membrane is vapor phase.
Whey protein concentrate (WPC) Whey protein concentrate consisting of 29–89 wt.% protein.
Whey protein isolate (WPI) Purified whey protein concentrate consisting of more than 90 wt.% protein.

4.06.1 Introduction

Membrane filtration techniques have been used in the agro-food and bulk biotech industries for a long time, but the success story of today's membrane processes in these industries did not start until Sidney and Sourirajan invented the phase inversion membrane in the 1960s [1]. This invention changed the membrane market and since then the total markets excluding medical applications have developed to a combined size of 8–9 billion Euro worldwide and are still growing strongly with an average annual growth rate (AAGR) of 8–9%. Even though the largest membrane market is related to water and wastewater treatment including desalination, the membrane markets for the agro-food and bulk biotech industries (excluding the pharmaceutical industry) are both significant markets with worldwide volumes of 800–850 million Euro and 220–240 million Euro, respectively. The key membrane technologies in the agro-food and bulk biotech markets are microfiltration (MF) and ultrafiltration (UF) both with a market share of 30–35% each, and nanofiltration (NF) and reverse osmosis (RO) with a combined market share of 25–30%. Other membrane technologies such as membrane contactors (MCs), electrodialysis (ED), pervaporation (PV), and vapor permeation (VP) have a small but increasing market share of less than 5%. The success of membrane technology in the agro-food and bulk biotech markets can be directly linked to some of the key advantages of membrane processes over conventional separation technologies:

- operation at low to moderate temperature ensuring a gentle product treatment;
- use of unique and highly selective separation mechanisms, such as sieving, solution-diffusion, or ion-exchange mechanism;
- easy installation and extension due to modular design; and
- reduced energy consumption in comparison with evaporators and condensers.

One of the challenging aspects in utilizing membrane processes in the agro-food and bulk biotech industries is the control of membrane fouling. Depending on the application, membranes tend to foul less or more severely. Fouling is commonly observed as a reduction of plant capacity over time. A common approach to reduce fouling and thus its impact on the membranes are regular cleaning intervals. In the agro-food and bulk biotech industries, a cleaning interval of 24 h or after completion of a batch is common. The cleaning intervals can be integrated in the operation of the plant – for example, continuous back-flushing during operation or cleaning before plant shut down – and/or integrated in the plant design – for example, having some parts of the plant in production mode while other parts are in cleaning mode. If cleaning agents are required, caustic or acid cleaning agents are typically sufficient, but, for example, enzymatic cleaning agents are also applied. Further, optimized plant operation can reduce fouling and thus the need for cleaning. Operation below the critical flux – the flux under which no fouling occurs – is an approach to maximize the time intervals between cleanings. However, this approach is commonly related with low flux/low pressure operation which, in reverse, has a negative impact on the plant size and thus investment costs. Alternatively, operation in the turbulent flow regime minimizes the effect of concentration polarization and thus reduces fouling. This approach, on the other hand, is related to higher operation costs since it increases the pressure drop along the module compared to laminar operation. Fouling can also be related to blockage of the module channels by feed material, for example, suspended solids such as fibers. The impact of this can be reduced by correct module selection, that is, open-channel tubular or plate-and-frame modules in the presence of fibers. Further, pretreatment of the feed can help optimize the plant performance by reducing/adjusting the level of suspended solids. In addition, pretreatment can be an efficient way to control precipitation in the plant.

The first section of this chapter provides a brief overview of the main membrane processes used in the agro-food and bulk biotech industries. The following sections discuss successful applications of membrane technology in these industries. The final section of this chapter gives a brief outlook on future developments in membrane technology within both agro-food and bulk biotech industries. It should be noted that each of the sections in the chapter is self-contained and therefore can be read independently of the others. The reader is therefore encouraged to move directly to the sections of interest.

4.06.2 Membrane Processes in the Agro-Food and Bulk Biotech Industry

In the agro-food and bulk biotech industries, both conventional membrane processes (such as MF, UF, NF, and RO) and emerging membrane processes (such as membrane MCs and PV) are used. While the common aspect of all these processes is that separation is achieved by a semipermeable membrane, the driving forces achieving these separations can be divided into three groups:

1. membrane processes driven by hydrostatic pressure commonly described by the sieving mechanism including MF, UF, and, to a certain extent, NF;
2. membrane processes driven by an activity gradient, which are based on the solution-diffusion mechanism covering RO, PV, and VP; and
3. membrane processes based on other driving forces, such as ED (electrical potential) and dialysis (concentration gradient).

In **Table 1**, an overview of the most relevant membranes for the agro-food and bulk biotech industries is given.

4.06.3 Applications of Membrane Processes in the Agro-Food Industry

The agro-food industry is a diversified industry. This section covers membrane applications in key food industries: dairy, beverage, and food additive production as well as the sugar and starch industries. Since the food industry requires large amounts of water, the final part of this section is dedicated to water and wastewater applications in the food industry.

4.06.3.1 Dairy Industry

The dairy industry is one of the key food industries based on a worldwide milk production of 655 million tons per year [4]. Since the 1960s, membranes have been applied for the concentration, clarification, and fractionation of dairy products, that is, to obtain specific milk components without the use of heat as in evaporation or the supplement of additives such as enzymes. A breakthrough application of membrane technology in the dairy industry was the conversion of whey, a former waste by-product from the cheese production, into refined proteins for commercial use by UF. The key membrane processes in the dairy industry are MF and UF, followed by NF and RO. In the following section, the use of membranes in the processing of milk, whey, and cheese is discussed.

4.06.3.1.1 Milk products

In the treatment of raw milk either for consumption or for further processing, MF can be used as an alternative to ultra-pasteurization. MF removes bacteria and spores from the milk without altering the organoleptic and chemical properties of the milk. In the initial step of this process, the raw milk is preheated to around 60 °C and then separated into skimmed milk and cream (see **Figure 1**). After cooling to 50 °C, the skimmed milk is then further treated by MF at a constant/uniform transmembrane pressure (TMP). In the past, this was achieved by partial recirculation of permeate, whereas today special ceramic MF membranes with a permeability gradient in the support or selective layer are used. The bacteria content in the permeate is reduced by more than 99.5%, while the retentate contains nearly all the bacteria and spores. The retentate is then mixed with a standardized amount of cream before conventional heat sterilization for a few seconds between 120 and 130 °C. After cooling, this mixture is recombined with the permeate stream and pasteurized at about 70 °C. Since, in this approach, only 10% of the milk is heat-treated at high temperatures, this milk has improved sensory quality.

The fractionation of milk protein directly from skimmed milk is another interesting MF application (see **Figure 2**). By using ceramic MF at constant TMP, it is possible to separate micellar casein, which can be used in cheese manufacturing, from whey proteins. The resulting permeate, which is rich in whey protein, can then be concentrated by UF to produce whey protein concentrate (WPC). In a further step, the WPC can be separated by

Table 1 Membrane processes relevant to agro-food and bulk biotech industries

Membrane processes	*Definitions*[a]	*Examples of applications*
Direct pressure driven		
Microfiltration (MF)	Liquid-phase separation process in which particles and dissolved macromolecules larger than 1 μm are rejected by a membrane.	• Removal of bacteria and spores from milk • Clarification of wine and beer
Ultrafiltration (UF)	Liquid-phase separation process in which particles and dissolved macromolecules smaller than 1 μm and larger than about 2 nm are rejected by a membrane.	• Concentration of whey • Clarification of fruit juice • Concentration and purification of blood plasma
Nanofiltration (NF)	Liquid-phase separation process in which dissolved molecules smaller than about 2 nm are rejected by a membrane.	• Partial demineralization of whey • Concentration of enzymes • Recovery of alkaline brine from ion-exchange regeneration
Driven by activity gradient (solution diffusion mechanism applies)		
Reverse osmosis (RO)	Liquid-phase membrane separation process in which the applied transmembrane pressure causes selective movement of solvent against its osmotic pressure difference.	• Concentration of milk • Concentration of fruit juices • Diafiltration water preparation and recovery
Vapor permeation (VP)	Membrane separation process in which the feed is vaporized before contacting the membrane and the permeate stream emerging from the downstream surface of the membrane is vapor phases[b].	• Aroma and flavor recovery
Pervaporation (PV)	Membrane separation process in which the feed and retentate streams are both liquid phases while the permeate stream emerges from the downstream surface of the membrane as vapor.	• Aroma and flavor recovery • Dealcoholization of wine
Other driving forces		
Electrodialysis (ED) (electrical potential)	Liquid-phase separation process in which ions are driven through an ion-selective membrane under the influence of an electric field.	• Whey demineralization • Tartrate stabilization of wine • Concentration of lactic acid
Dialysis (concentration gradient)	Liquid-phase separation process in which solutes are transferred under the driving force of a concentration gradient from one solution to another through a membrane.	• Dealcoholization of beer and wine
Membrane contactors (MCs) (pressure/concentration/vapour pressure gradient)	Process in which a gas/liquid or liquid/liquid mass transfer of one phase to another occurs without dispersion of the phases on both sides of a porous membrane. MC units include, e.g., membrane distillation (MD), osmotic distillation (OD), membrane emulsifiers, and membrane crystallizers.	• Bubble-free carbonation of soft drinks • *In situ* extraction of fermentation productions • Alcohol reduction • Concentration of vegetable and fruit juices • Concentration of flavors

[a] All definitions based on [2] except vapor permeation and membrane contactors.
[b] Based on [3].

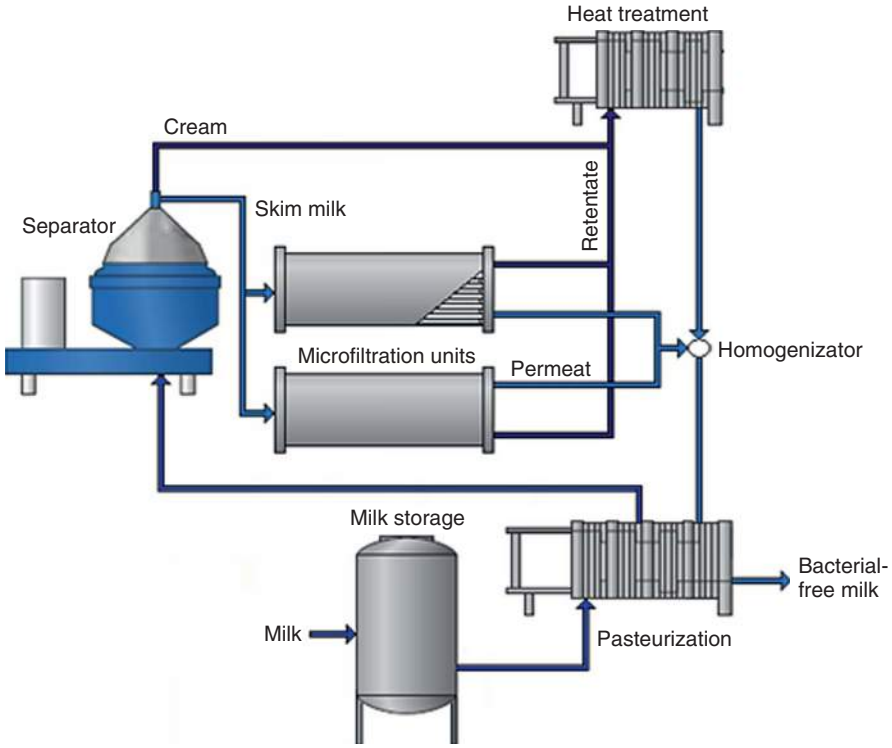


Figure 1 Simplified process concept for removal of bacteria from milk by MF.

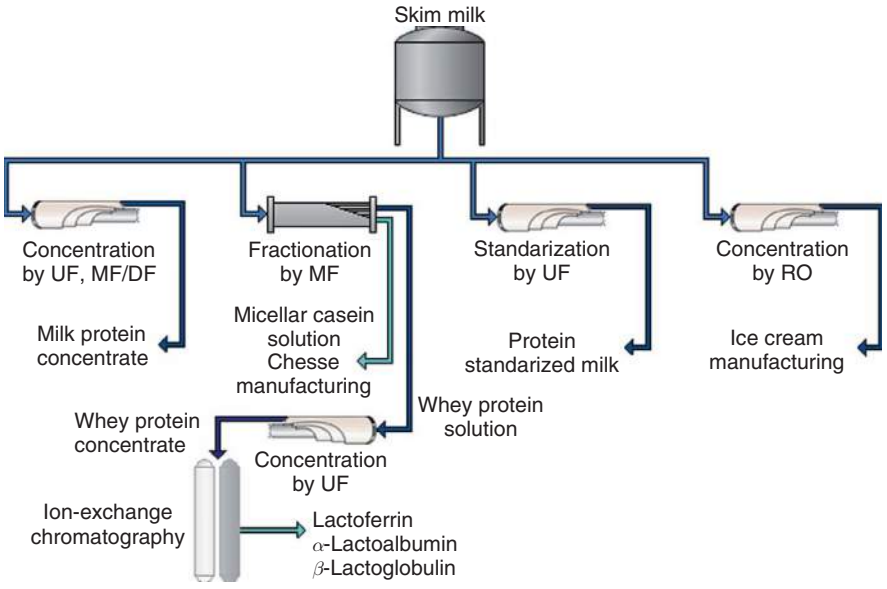


Figure 2 Membrane opportunities in the milk production.

ion-exchange chromatography into the three high-value products: lactoferrin, β-lactoglobulin, and α-lactoalbumin.

The standardization of milk is a method to improve the consistency and sensory quality of milk (**Figure 2**). Due to natural variations, the protein content of milk changes during the year. Applying UF, it is possible to increase or decrease the protein content of the milk without adding milk powders, casein, and whey protein concentrates. Generally, low-fat milk, for example,

skimmed milk or 1% milk, with increased protein content has a higher viscosity and an improved appearance (whiter milk). This results in an improved consumer appeal for this milk, since low-fat milk with increased protein content has a similar sensory quality as milk with higher fat content.

Concentrated milk is mainly used in the production of ice cream (see **Figure 2**) and contains all the solids but only 30% of the water. Conventionally, milk concentration is achieved by evaporation techniques, but can also be achieved in a more gentle way by RO. Alternatively, milk can be concentrated by MF and/or UF to produce milk protein concentrate (MPC) with 50–58% proteins. Since MPCs are commonly used as food additives, it is crucial to maintain the protein functionality. In order to produce MPCs for specific food applications, a combination of UF with MF and/or diafiltration (DF) is used at adjusted pH values and temperatures.

4.06.3.1.2 Whey processing

Whey is a residue from the production of cheese which remains after the milk has been coagulated with rennet and strained. Worldwide, the whey production in 2005 was approximately 150 million tons, which includes about 0.9 million tons of high-value proteins (adapted from Reference 5). Whey was earlier a major disposal problem for the dairy industry due to its low solids content and high biological oxygen demand (BOD), and it was either disposed of as sewage, sprayed on fields, or used as animal feed. Today, membrane technology is applied to concentrate whey to produce whey protein concentrate and whey protein isolate (WPI), and to fractionate and purify the whey to obtain purified α-lactoalbumin and β-lactoglobulin (see **Figure 3** for an overview of the different treatment options including membrane technologies).

A straightforward approach to produce WPC with a protein content of 35% to 85% TS (total solids) is concentration of the whey proteins by UF. In addition, WPI with up to 90% proteins in the total solids can be produced by the use of MF to remove bacteria and fat as pretreatment before UF.

Since the presence of fat in the whey decreases its functional properties and reduces its storage time,

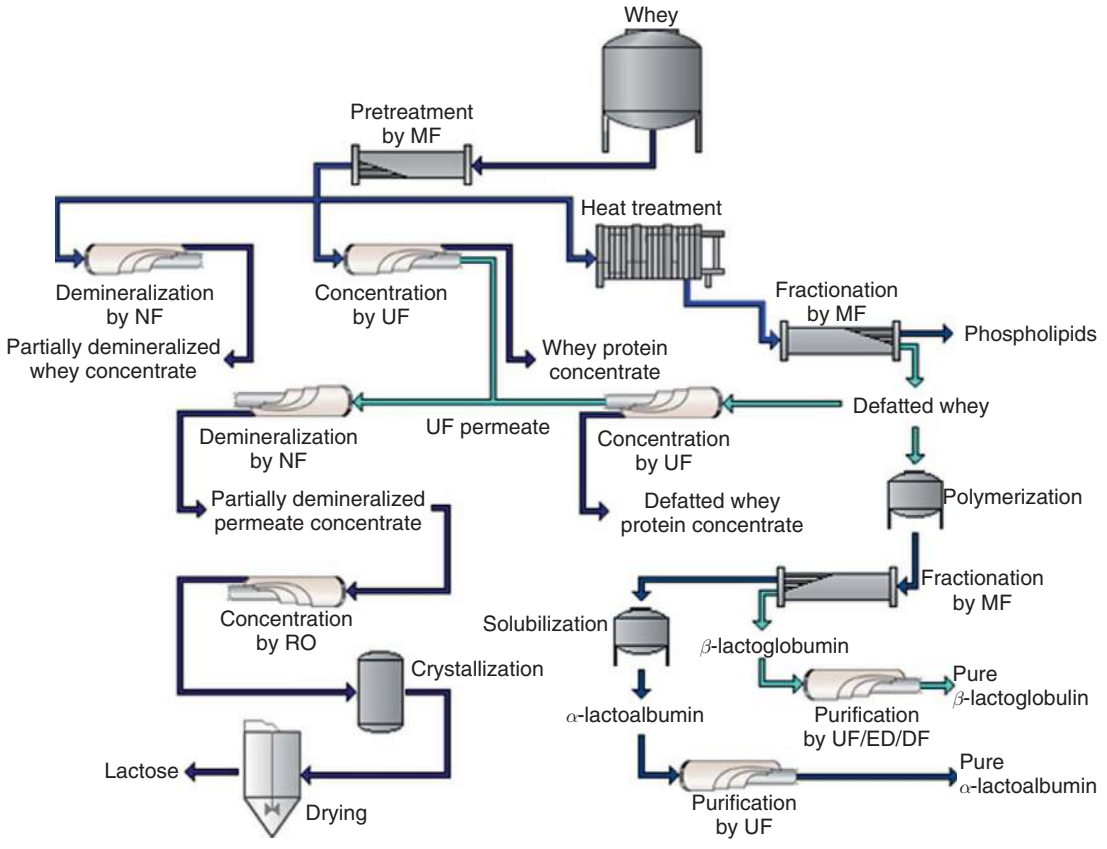


Figure 3 Whey processing with membrane applications.

different approaches to remove residual fat from whey have been developed. The most common approach involves thermocalcic precipitation, heat treatment, which exploits the ability of the phospholipids to aggregate by calcium binding at 50 °C [6, 7], followed by MF to remove the precipitate, which is used as emulsifier agent for food and cosmetic applications. The defatted whey is either concentrated by UF to produce WPC with the option to recover lactose from the UF permeate or it is further treated to obtain the purified proteins β-lactoglobulin and α-lactoalbumin. In the latter case, the defatted whey is pH-adjusted (pH 4–5) and the α-lactoalbumin is reversibly polymerized by heat treatment at 55 °C to entrap most of the residual lipids and the other whey proteins with the exception of β-lactoglobulin. Thus, by use of MF, the β-lactoglobulin can be fractionated from the other proteins. The MF permeate can then be purified by UF in combination with ED or DF [7]. Further, the α-lactoalbumin in the MF retentate can be purified by solubilization at neutral pH, followed by UF.

Demineralization of whey is another potential application for membrane technologies and depending on the desired degree of demineralization, either NF or ED can be applied. Moderate demineralization can be achieved by NF, whereas high demineralization degrees can be achieved by ED. An interesting aspect of NF is that it combines demineralization and concentration of whey. Further, whereas the typical demineralization degree with NF is 35%, which is equal to a concentration factor of 3.5–4, demineralization degrees of up to 45% can be achieved by combining NF with DF.

4.06.3.1.3 Cheese making

Every year about 17 million tons of different cheeses are produced worldwide [4], and membrane processes are used in the preparation of milk for cheese production. The application of membrane technology varies with the cheese type. UF is applied to concentrate cheese milk by a factor of 1.2–2 in its production and thus, the capacity of the cheese vats and whey draining equipment can be increased. However, the cheese yield is not significantly improved since the protein content is still only 4–5%. This approach is established in the production of Cheddar, Cottage, and Mozzarella cheeses and has also been successfully tested for parmesan cheese [8], but it can also be used to standardize cheese milk and manipulate the mineral composition to improve cheese consistency. Another approach to use membrane processes in the cheese production is partial concentration by UF. In this case, standardized cheese milk is concentrated by a factor of 2–6. In the production of Cheddar cheese, the APV-SiroCurd process can be applied. In this process, the milk is concentrated 5 times combined with DF to adjust the salt balance [9]. Similar processes are also applied in the production of, for example, Queso Fresco, structure Feta, Camembert and Brie and most recently in the production of Prato cheese with reduced fat [10]. A further approach to use UF in cheese production is total concentration of the cheese milk by which the standardized cheese milk is concentrated by UF to the final total solids content in the cheese. This approach offers the maximum yield and the cheese can be produced without cheese vats since no whey drain is required. Typical cheeses produced by this approach are, for example, cast Feta, quark, cream cheese, Ricotta, and Mascarpone. Another application related to the cheese manufacturing is the purification of cheese brine by UF for recycling.

4.06.3.2 Beer and Wine

Beer and wine are some of the oldest and most popular fermented drinks. Research in the use of membranes in beer and wine production started in the 1970s. The first successful application was dealcoholization of beer by RO in the 1980s. Other applications followed subsequently. In the following discussion, the different positions of membrane processes in the wine and beer industry will be presented.

4.06.3.2.1 Beer

Beer is the most popular alcoholic drink with an annual production of 1.5 billion hl, with China, the United States, and Germany as the key beer-producing countries [11]. The beer production process starts in the brew house with the wort production. Malt is steeped with hot water and mixed with hops to produce wort, which is then brewed in the wort boiler for up to 2 h before clarification and cooling. After this, the wort is combined with yeast and filled into the fermentation tanks, where the yeast converts the grain sugars to alcohol and thus produces beer. After the fermentation, the beer is clarified and transferred to the bright beer cellar for maturation. Before bottling, the beer is often sterile-filtered and/or pasteurized. The beer dealcoholization, if requested, is done before the final sterile

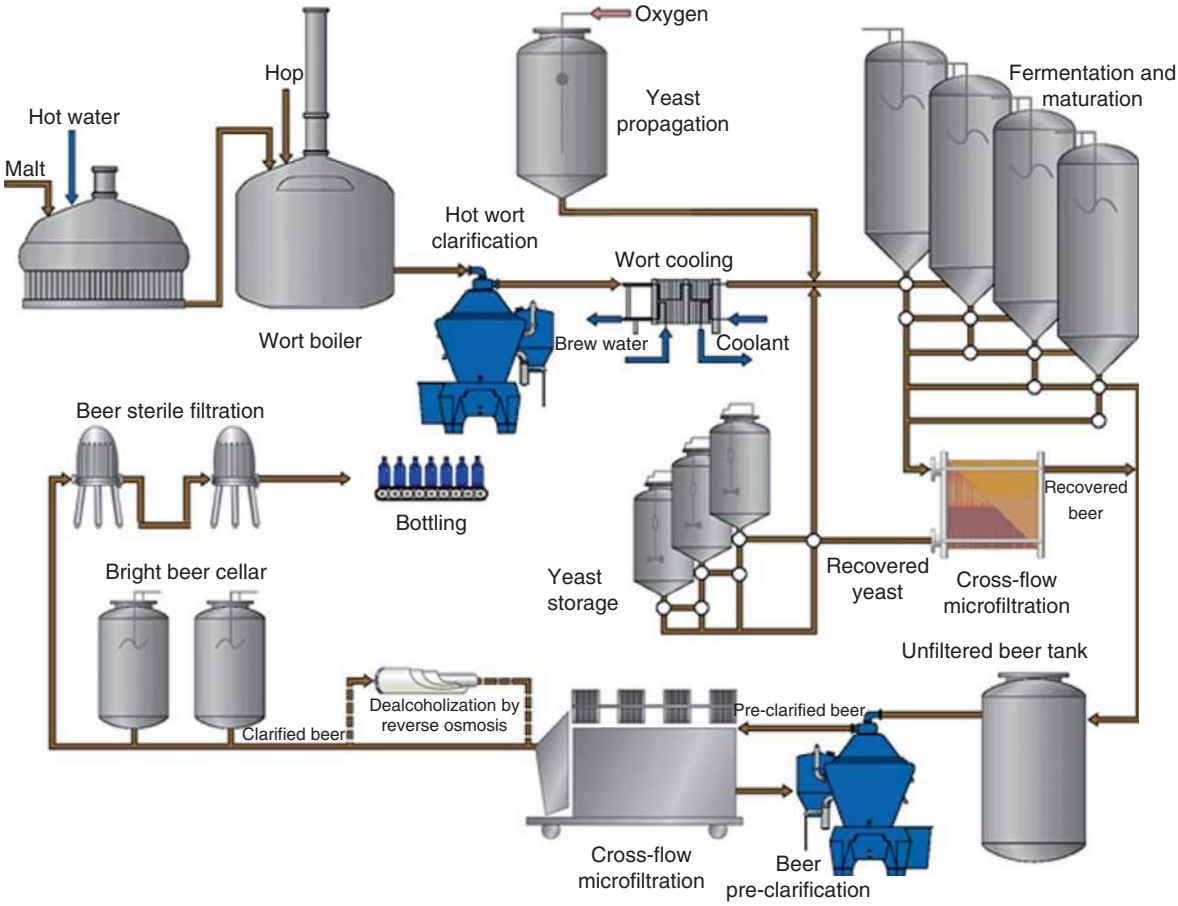


Figure 4 Beer production with membrane applications.

filtration/pasteurization. In **Figure 4**, the overall beer production process is shown.

The first potential membrane application is the recovery of beer from tank bottoms. After fermentation, yeast settles at the bottom of the fermentation vessels. The settled tank bottoms account for 1.5– 2% of the total beer volume and, apart from the yeast, they contain a high proportion of beer, which is lost if not recovered. In order to recover the beer and concentrate the yeast up to 20% dried matter (DM), a continuous MF can be used to separate the beer from the yeast. The recovered beer is virtually sterile without any oxygen pickup and therefore it can be added directly to the beer going to the bright beer cellar. Hence, by using this process, it is possible to boost the annual production of a brewery by 1% without major investments. Another membrane application in the beer production is clarification of the beer after fermentation and maturation. In the traditional brewing process, clarification is generally achieved by a separator followed by kieselguhr (diatomaceous earth) filtration. However, the handling of kieselguhr is considered a health risk and its disposal and related effluent costs are increasing. In the membrane concept, a continuous MF process is used. In this process, yeast, microorganisms, and haze are removed from the beer without affecting the taste of the beer. Apart from achieving high and consistent beer qualities in every batch, the cost of this process typically matches those of conventional kieselguhr filtration.

Beer dealcoholization by RO membranes is a technology, which has been available in the market for more than 15 years, and today about 2% of the total beer production is low alcohol or alcohol-free beer. Applying RO, the alcohol content in the beer can be reduced by 8–10 times. Hence, a standard beer with 4–5% alcohol by volume can be converted to low-alcohol beer with 0.4–0.5% alcohol and most of the flavor components. The dealcoholization of beer

typically starts with pre-concentration of the beer followed by DF using demineralized water to adjust the alcohol level. In order to compensate for any flavor losses resulting from the removal of the taste carrier alcohol, hops, and syrups are added to the beer. Before bottling, the partially dealcoholized beer is clarified. Further, the permeate from the low-alcohol beer production can be used for other alcoholic drinks such as alco-pops. Alternatively to RO, dialysis can be applied for the dealcoholization of beer.

Another application of membranes in the brewing industry is the sterile filtration prior to packing instead of pasteurization. In 2007, approximately 115 million hl of beer worldwide, mainly in Asian countries, were cold-filtered [12]. In some countries such as China cold-filtered beer – beer produced without heat impact – is even sold as premium beer. A typical cold sterilization system consists of a series of two filters, for example, dead-end pre-filters of 0.7 µm followed by sterile filters with 0.45 µm. Two autonomously operated sets of these filters are typically placed in parallel, one set in beer filtration mode and one set in cleaning mode.

Most recently, MCs have also entered the brewing industry. In the production of high gravity beer – beer with 9–10% alcohol – MCs are used during the deoxygenation of water for dilution of the beer. Further, MCs are used for CO_2 removal followed by nitrogenation to obtain a dense foam head, and oxygen removal to preserve the beer flavor [13]. Another application under discussion is the use of MF for separation of wort and mash. This can be achieved either by drainage and leaching with water or by use of diaphragm pressure filters. By integrating MF, this discontinuous process could become continuous [14].

4.06.3.2.2 Wine

The annual wine production is approximately 270 million hl with the European countries France, Italy, and Spain in the lead followed by the United States and Argentina [11]. Red wine accounts for 50% of the market, while white wine has a market share of 25%. The remaining 25% is shared between rosé and sparkling wines. The classical wine production starts with crushing and pressing of the grapes to obtain wine must (see **Figure 5**). This wine must is then centrifuged and, if required, the sugar content is adjusted before fermentation. During fermentation, yeast is added to the wine must, which turns fructose into ethyl alcohol and thus converts must into wine. The traditional fining process after the fermentation consists of filtration and sedimentation aided by clarifying agents, followed by separation to improve the color and flavor of the wine. The wine is then stored in casks or large tanks for maturation. Finally, the wine is stabilized and sterile filtered before bottling. Must correction by RO is the first potential application in the wine production. Compared to alternative methods such as chaptalization, RO increases the sugar content in the must without addition of nongrape components at ambient temperature. The use of RO leads to enrichment in tannins and organoleptic components by water reduction between 5% and 20%. This method is particularly suitable to reverse the dilution of the must quality due to rain during the harvest by the selective removal of

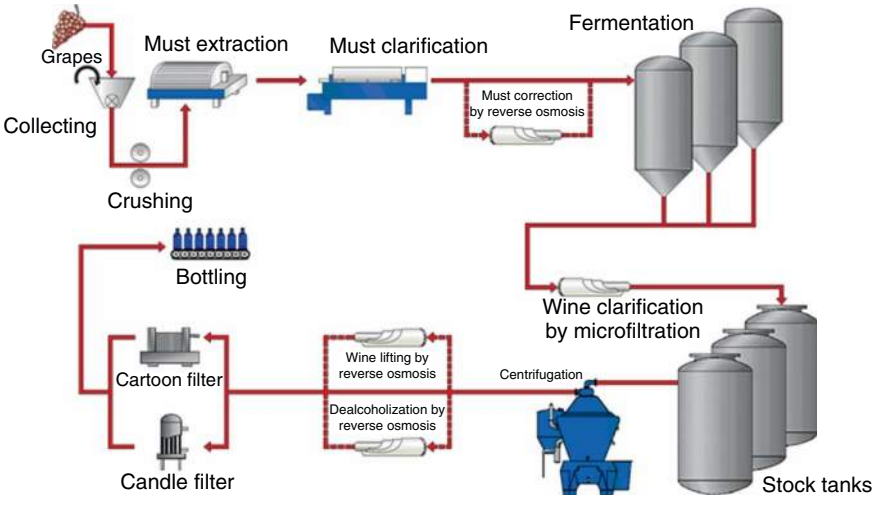


Figure 5 Wine production with membrane applications.

excess water. Further, the use of RO is accepted by the International Code of Oenological Practices [15], which states that the must volume should not be reduced by more than 20% and the initial potential alcohol volume of the must should not be increased by more than 2%. It should be noted that NF can also be applied, which allows some acid to be removed at minimum sugar loss. The use of MF for clarification of wine after fermentation was introduced in the 1970s and has subsequently gained more and more interest. In this position, MF combines clarification, stabilization, and sterile filtration in one step and thus eliminates the need for fining substances and filter material used in the conventional approach. In order to increase productivity and minimize the need for cleaning, the fouling behavior has to be optimized as a function of the process conditions (transmembrane pressure, flow regime, temperature, etc.), membrane (material, pore size, module configuration, etc.), and wine (type, solids content, turbidity, etc.). One of the key parameters is the pore size of the membrane which, on the one hand, should not be too small and thereby lead to reduction in color and aroma, and, on the other hand, should be small enough to reject undesired compounds, for example, large suspended solids, yeasts, etc., and to operate close to the critical flux. Often, more open MF membranes with pore diameters between 0.2 and 0.45 μm are used for white wines, while tighter MF membranes with pores smaller than 0.2 μm are used for red wines. For the tartaric stabilization, ED is an established technology to remove potassium, calcium cations, and tartrate anions from wine. The ED stack consists of a wine and a brine compartment, and by application of an electrical potential tartrate anions migrate toward the anode and potassium and calcium cations toward the cathode. The degree of removal can be adjusted for each wine by conductivity and pH measurements before treatment. This process is widely commercialized and recognized by the International Wine office as good practice [16].

The rejuvenation/lifting of old wine with RO and DF is another application for membrane technology in the wine industry. Not all wines are suitable for long aging and, over time, their tastes might deteriorate. By applying a DF process with RO, the negative aroma can be removed with the permeate by slightly concentrating the wine and thus removing water, some alcohol, and the negative aroma components. The removed permeate volume is replaced by addition of demineralized water to avoid remineralization of the wine. Since this process does not change the composition and structure of the wine, this lifted wine – due to its improved quality – can be either sold at a higher price or blended with a younger wine.

In the wine industry, there is also a trend toward low-alcohol or alcohol-free products. Attempts to produce thermally dealcoholized wine can be dated back to 1908 [17], whereas the use of RO for alcohol reduction in wine started in the 1970s. In recent years, both NF and RO have established themselves in the production of high-quality wines with reduced alcohol content due to improved aroma retention. The applied polymeric membranes have high alcohol and water permeability but low permeability for aromatic, gustatory, froth, and color components. In the initial step, water and ethanol are removed through the membrane, while the major components of the wine matrix are rejected and concentrated. After this, water is added to restore the original matrix of the wine. Alternatively, the process can be run in the DF mode with constant addition of DF water until the desired reduction is achieved. Thus, this technology can also be applied to adjust the alcohol level in the wine. An optimum, rich flavor of the grapes is often combined with a high sugar level, which results in a high alcohol content during fermentation. These alcohol aromas might suppress other wine flavors. Hence, the wine can be improved by slight concentration by RO, removing water and a fraction of the alcohol. This technology allows the winemakers to harvest the grapes independent of their sugar content based on the grape flavor ripeness. As an alternative to RO, OD has been applied in the wine industry for alcohol removal. By passing wine on one side of a microporous hydrophobic membrane and degassed water on the other side, some of the alcohol evaporates from the wine, diffuses through the membrane, and condenses in the water at low temperature and low pressure [18].

PV for recovery of wine aromas is under investigation in the wine industry. Karlsson *et al.* [19] tested a concept for the direct recovery of aromas from wine, while Schäfer *et al.* [20] investigated the removal of aroma components during wine fermentation without influencing the final wine quality.

4.06.3.3 Fruit Juices

Among the different types of juices, orange and apple juice are the most produced juices worldwide. The production of concentrated orange juice at 65° Brix reached 2.2 million tons in 2007 with Brazil and the United States as the key producing countries, while 2 million tons of concentrated apple juice were

produced worldwide in 2007 with major productions in China, the United States, and Poland [21, 22]. For processing of juices, membrane technology has established itself as part of the production process starting from the 1970s. In the following discussion, membrane opportunities for the apple and orange juice production are discussed as examples for membrane opportunities in the fruit juice production in general.

4.06.3.3.1 Apple juice

Freshly pressed apple juice consists of 85–90% water and contains disaccharides, monosaccharides, polysaccharides, such as starch and pectin, acids, and minerals. The cloudy apple juice is normally sold as a clarified apple juice concentrate with approximately 30% water. The original technology for production of apple juice consists of grinding or crushing the fruits into small uniform pieces generally followed by the pressing of the fruit mash in a discontinuous press. The pressing is followed by the clarification/fining of apple juice using settling tanks and kieselguhr filtration. This traditional approach of clarification/fining is not only time consuming but also involves the consumption of large quantities of enzymes, gelatin, and chemicals.

Alternatively, UF has established itself as an attractive substitute for the traditional fining process (see **Figure 6**). Before entering the UF unit, the juice undergoes an enzymatic treatment to degrade pectic substances. The UF unit removes suspended solids and high-molecular-weight solids such as proteins and starch from the juice resulting in high-quality juice at high capacities. Commonly, tubular membrane modules are used for the clarification of apple juice in combination with DF. Alternatively, the combination of a high-speed separator with a spiral-wound membrane module can be applied and thus the need for DF can be

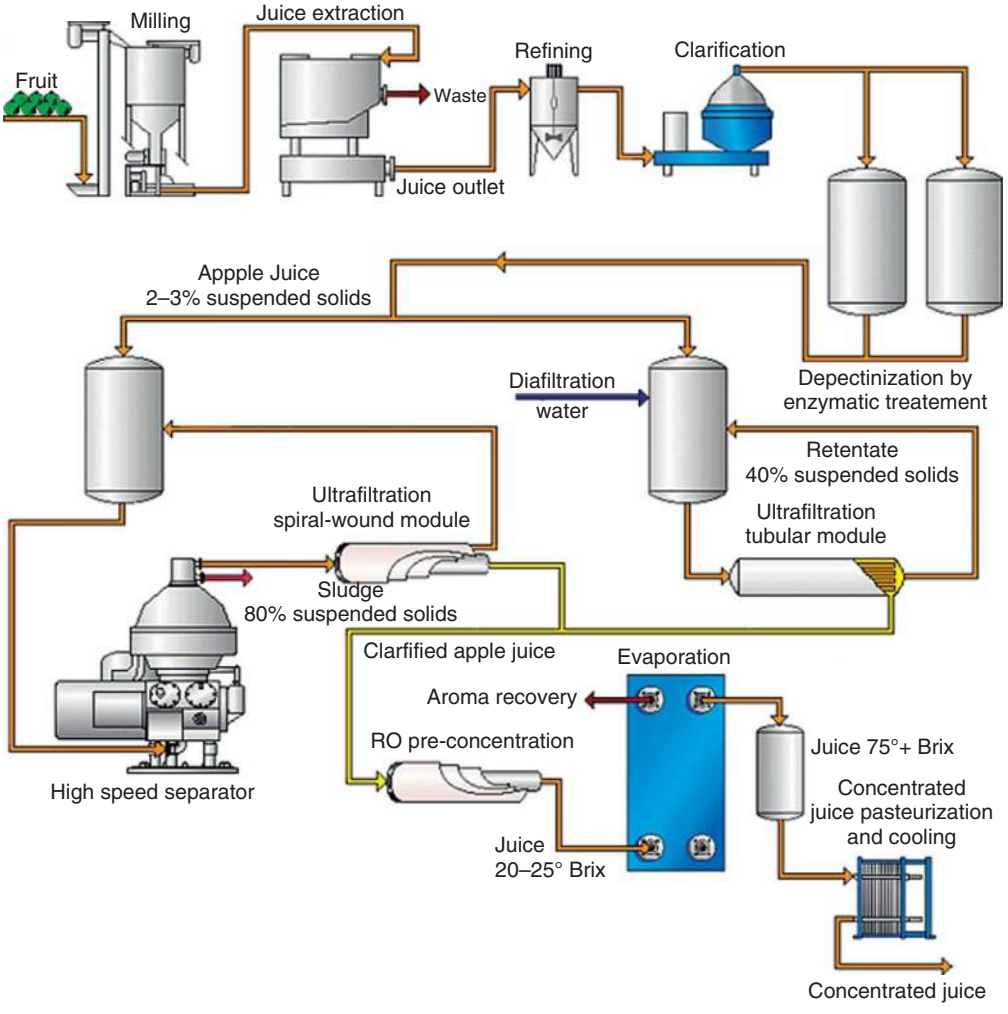


Figure 6 Fruit-juice production with membrane applications.

eliminated. After clarification, the juice is typically concentrated by evaporation from 11–12° to above 70° Brix in order to reduce storage and transportation costs. In this step, the combination of RO and evaporation can be an interesting alternative. RO can remove more than 50% of the water prior to evaporation as initial step, thus reducing the overall energy costs by 25–40% compared to direct evaporation and minimizing the residence time in the evaporator. In this concept, the RO concentrates the juice to 20–25° Brix, while the subsequent evaporation can boost it to above 70° Brix. As alternative to conventional evaporation, OD has been successfully tested to concentrate apple juice up to 64° Brix [23]. Further, hydrophobic PV has been suggested as an alternative to recover parts of the apple juice aroma prior to evaporation. Details on an overall concept for the integration of membrane processes including UF, RO, and hydrophobic PV can been found in Reference 24. It should be noted that these concepts are also suitable for grape, cranberry, and other colored juices.

4.06.3.3.2 Orange juice

In the production of orange juice, the fresh oranges are washed, inspected, and sized before the extraction. After extraction, the juice is passed through a finisher and centrifuges for deoiling and partial clarification. After centrifugation, the juice is further clarified by UF to remove all suspended solids prior to optional debittering by ion exchange to avoid contamination of the ion-exchange resins. After debittering – that is, removal of polyphenols, limonin, hesperidin, and naringin – the juice is then further concentrated in an evaporator up to 65° Brix. In order to increase the yield of the process in some countries, the pulp from the finisher and from the discharge of the centrifuges is collected to recover the remaining juice from it. This pulp is then flushed with water resulting in a pulp wash that can contain high levels of bitter substances, which are unwanted in the final juice. Again, the combination of UF followed by ion exchange to remove the bitter components is used prior to concentration by evaporation and blending. These concepts can also be adopted for other citric juices such as lemon, lime, and grapefruit.

4.06.3.4 Food Additives

Additives are widely used in the food industry to enhance the taste and flavor of food as well as to improve and stabilize its appearance. Membrane processes are successfully integrated in the production of food additives, in particular those of natural origin. In this section, some of the most common and well-established applications of membrane technology in the production of food additives are described. The focus is first on animal blood plasma and gelatine as representatives for animal proteins and then on carrageenans and pectins as examples of natural polysaccharides and food gums, respectively.

4.06.3.4.1 Animal blood plasma

The annual production of blood from pigs and cattle is approximately 10 million tons. In the past, blood from slaughterhouses was simply dried and then sold as animal fodder. Even though this is still the common approach, an alternative is to collect blood in a special collection system and to convert it into a food additive. This alternative is used for approximately 150 000–200 000 tons of animal blood per year.

Animal blood consists of two fractions: the light blood plasma fraction accounting for 55–65% of the total volume with 7–8% proteins and the heavier viscous fraction of the blood cells with about 35% proteins. After collection, the blood is separated by a blood separator into these two fractions, the blood cell and the blood plasma fraction. The blood plasma fraction can be concentrated by UF to about 29–30% proteins before spray drying (see **Figure 7**). One of the key advantages of using UF is that the proteins are not only concentrated but also clarified since low-molecular-weight compounds (LMWCs), that is, salt and minerals, will pass through the membranes. In addition, the protein purity can be further adjusted by the use of DF. If it is desired to minimize losses of LMWCs, it is possible to use NF or alternatively RO. In case the blood plasma is concentrated by UF and NF, the UF/NF permeate can be further polished by RO to obtain a high-quality water which can be recycled to the slaughterhouse. Alternatively, if RO is used for the concentration, the RO permeate can be directly recycled. The above approach is typically used for blood from pigs and cattle but research also investigated concentration of, for example, chicken blood plasma by UF [25].

The blood cell fraction is commonly not used but it is possible to produce soluble proteins by enzymatic hydrolysis. In this setup, UF can be used to separate the proteins from the blood cell mass. Applying DF, the protein yield can be up to 90%.

4.06.3.4.2 Gelatine

Gelatine is a protein which forms a firm gel in aqueous media. Due to its high gelling strength, it is used not only in the food industry but also in the bulk biotech industry as a protective coating for drugs.

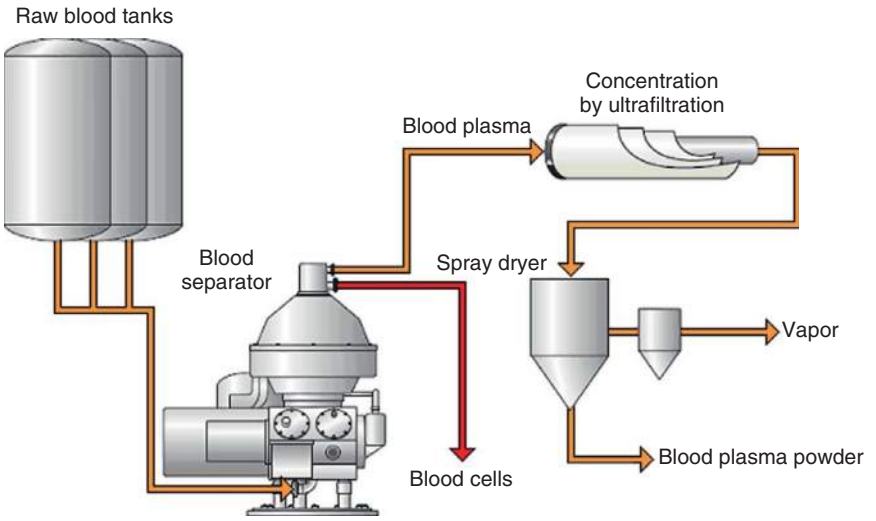


Figure 7 Animal blood processing with membrane applications.

Further, gelatine is used in the photographic industry as coating of films and photo paper. The annual worldwide production of gelatine was 326 000 tons in 2007 [26]. About 50% of the gelatine product is based on pig skin, while the remaining 50% is split between bovine hides and bones.

The initial step in the gelatine production is the pretreatment of the protein containing collagens (see **Figure 8**). The pig skin and bovine hides are dehaired, washed, sized, and degreased, while the bones are placed in diluted acid for removal of minerals followed by degreasing. In the next step, the cross-linking collagens are reduced. For less cross-linked collagens as in pig skin, commonly an acidic pretreatment for 24–48 h is required to produce A-type gelatine. In the case of more complex collagens such as bovine hides and bones, an alkaline treatment is used, which can last several weeks and

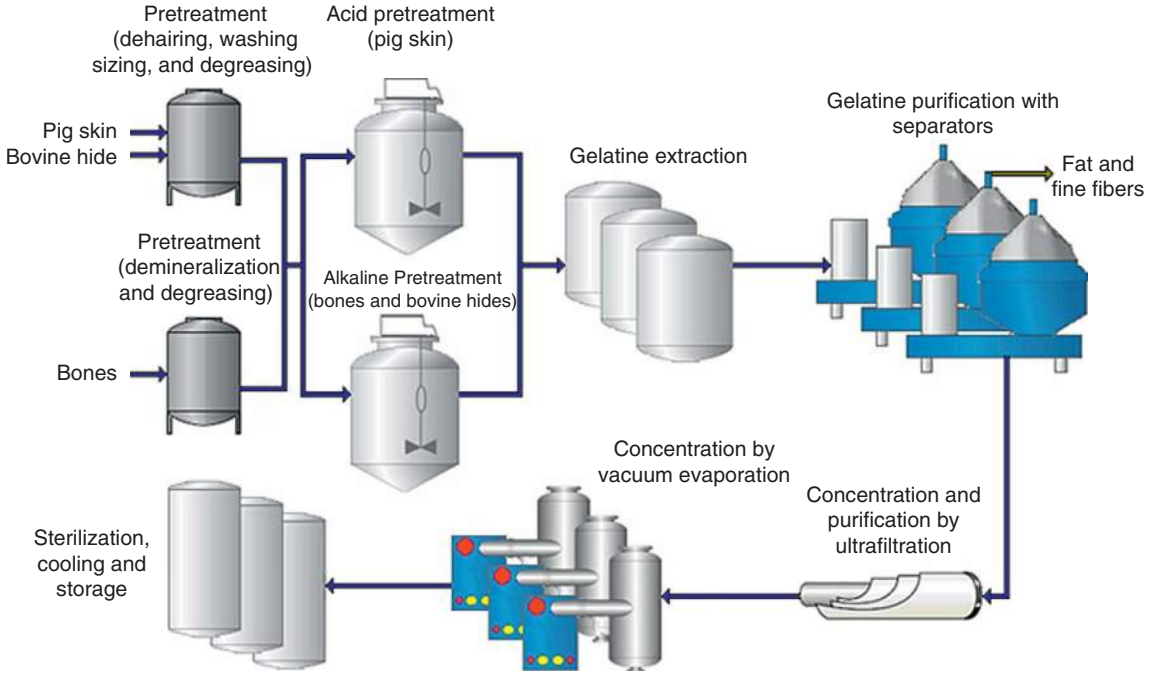


Figure 8 Gelatine production with membrane applications.

results in B-type gelatine. Most recently, enzymatic treatments are used, resulting in shorter residence time and higher yields. In the next step, the gelatine is extracted from the pretreated collagens in either water or acid solution. The temperature of the extraction bath defines the jelly strength–bloom value. While higher temperature supports the extraction, it leads to lower bloom value of the final product. The extracted gelatine is then further purified by, for example, separation or leaf filter before further purification and pre-concentration by UF. UF concentrates the gelatine from approximately 4 to 12 wt.% and thus reduces the load on the final concentration step by evaporation by 2/3. Further, UF allows impurities such as salts, residue acid, and amino acids to pass into the permeate, thus improving the quality of the gelatine and reducing the load on the optional ion exchanger. In order to minimize water consumption, the UF permeate can be purified by RO. The pre-concentrated gelatine from the UF plant might be further demineralized by ion exchange. In the final steps, the gelatine is evaporated, sterilized, cooled, and dried.

4.06.3.4.3 Carrageenan and other seaweed extracts

Carrageenan is a generic description of a group of sulfated polysaccharides, which are extracted from certain species of seaweed. It is typically sold as powder ranging from white to beige depending on its grade. Carrageenan is used in food products to stabilize and gelatinize proteins such as casein in water. Utilizing this feature, carrageenan is found in products such as yoghurt, ice cream, cottage cheese, milk pudding, or whipped toppings. Additional applications can be identified in the cosmetic and bulk biotech industries, for example, as stabilizer in toothpaste or gelling agent in air fresheners. The worldwide production of carrageenan in 2007 was approximately 40 000 tons per/year, with a market value of US$350 million (adapted from Reference 27).

Carrageenan is produced from different genera and species of red algae, for example, *Chondudrus cripus*, *Eucheuma,* and *Gigartina stellata.* This results in specific types of carrageenan, which are blended to obtain a uniform product. The seaweed is typically harvested by ranking and then dried before being shipped to a processing plant, where the seaweed is cleaned by water and hammer-milled to expose the inner surface of the seaweed prior to extraction. During the initial extraction step, the carrageenan is dissolved in 70–75 °C hot water containing alkaline reagents such as calcium and sodium hydroxide. The resulting paste is then stored for 2–24 h in holding tanks at 90–95 °C and finally mixed with filter aids such as diatomite or expanded perlite. By using a filter press for clarification, the hydrocolloids are removed from the soluble impurities, which results in a pale syrupy liquid containing 0.8–1.0% of carrageenan. The carrageenan is then pH-adjusted and concentrated by UF at approximately 90 °C. At this high temperature, carrageenan concentrations of up to 3–5% can be achieved, which is equivalent to 3–5 times volume reduction. In addition, salts, color, sugar, and other low-molecular-weight components (LMWCs) are removed from carrageenan with the permeate leading to high purities. The energy consumption of UF is 20–30 kW h m^{-3} lower than for evaporation requiring for the same duty 30–50 kW h m^{-3}. The subsequent steps in the carrageen production depend on the desired final product. The carrageen can be either directly dried in a drum or roll-drier or be further purified by precipitation in either water or alcohol followed by pressing and drying before blending.

Agar and alginates are two other important groups of seaweed extracts, which are mainly used as gelling agents and stabilizers in the food industry. The worldwide production of agar in 2007 was approximately 10 000 tons per year with a market value of US$ 180 million and for alginates it was approximately. 40,000 tons per year with a market value of US$ 290 million. (adapted from Reference 27). Both production processes are very similar to carrageenan and here UF has established itself as the method of choice for concentration after extraction.

4.06.3.4.4 Pectin

Pectin is a natural polymer containing galacturonic acid units, which is widely used in the food industry due to its ability to increase viscosity and bind water. Therefore, pectin is used, for example, in the dairy industry to stabilize milk drinks and yoghurt or in the confectionary industry as gelling agents for jams. In 2007, the worldwide production of pectin was 35 000 tons per year/ [28]. The most common raw materials for pectin production are apple pomace and dried citrus peel, which are both by-products from fruit juice production. In addition, residues from sugar beets are used but to a small extent.

The raw materials for pectin production – apple pomace and citrus peel – are typically delivered from a number of fruit-juice producers in a washed and dried stage to a central pectin production unit. The raw materials are then treated with hot water

typically containing an extraction aid such as mineral acids or enzymes. The extraction step separates the pectin and solids such as starch. The extracted pectin is then separated and purified.

In case of apple pectin, the extracted pectin is passed through a filter press, further filtered, and then clarified by enzymes before being concentrated and purified by UF with DF. The apple pectin is concentrated from approximately 1% to 3–6% TS, which corresponds to a volume reduction of 3–6 times. In addition, this step removes sugars and salts from the apple pectin and further achieves a certain degree of decolorization. The purified and concentrated apple pectin is then spray-dried and milled before being blended with sugar or dextrose to a standardized gelling powder. Further, it is possible to apply RO on the UF permeate and to separate it into a purified water stream, which can be recycled to the process, and a retentate stream, which can be further treated by UF. UF divides the RO retentate into colored by-product on the retentate side and a stream containing fructose/glucose, which can be further purified and concentrated by evaporation, on the permeate side.

After extraction, the citrus pectin is clarified in a decanter or high-speed separator before being concentrated and purified by UF. The citrus pectin is concentrated from 0.7–1% to 3–4% TS combined with a reduction in low-molecular-weight impurities such as salts. The concentrated citrus pectin is then either precipitated with alcohol (e.g., 1-propanol) to remove further impurities to produce high-molecular-weight citrus pectin or de-esterified by the addition of ammonia to produce low-molecular-weight citrus pectin. In the final step, the citrus pectin is spray-dried, milled, and blended similar to the apple pectin. Further, in the citrus pectin production, it is also possible to recover the water from the UF permeate by purification using RO.

4.06.3.5 Beet and Cane Sugar Industry

In over 130 countries worldwide, beet and cane sugars are produced at an annual rate of approximately 140 million tons, of which about 70% is cane sugar. Even though research on membrane applications in the sugar industry started in the beginning of the 1970s with the work of R. F. Madsen on the opportunities of membrane processes in the beet-sugar industry, most of the processes for the sugar industry are still under development. In the first part of this section, the membrane applications in the beet-sugar industry are reviewed followed by a discussion on the cane sugar industry. It should be noted that this section focuses only on selected key applications and a complete review can be found in Reference 29.

4.06.3.5.1 Beet sugar

The production of beet sugar starts with the washing and slicing of the sugar beets into very thin V-shaped beet slices called cossettes (see **Figure 9**). The sugar-beet cossettes are then passed to the diffusion tower in which the sugar is separated by extraction with the addition of hot water into raw juice and beet pulp. The pulp, which is rich in nutrients, is dewatered with a filter press resulting in beet pulp and press water. The beet pulp is commonly used as cattle feed but the isolation of pectin from beet pulp has also been investigated using UF combined with DF [30]. Further, RO has been tested for the recycling of press water [31].

The raw juice from the extraction is commonly purified by liming followed by carbonation and demineralization to remove proteins, pectins, inorganic salts, and coloring substances. Various approaches to replace this step by membranes have been investigated. Generally, tight MF or open UF membranes have been identified as suitable technologies to achieve the desired purities. The different approaches vary in the pretreatment of the juice. Even though some approaches using membranes directly on raw juice have been reported [32, 33], most approaches propose either a clarifier and/or partial liming combined with a screen filter as pretreatment before the membrane unit. In addition, ED has been proposed as an alternative or addition to the conventional demineralization and decalcification of the purified raw juice and the first successful integration of ED into the sugar industry was started in 1996 [33]. The key advantage of ED compared to conventional demineralization techniques, that is, ion exchange, is its continuous operation without the need for regeneration. After purification, the clarified thin juice has a sugar content of 14–16° Brix and is then conventionally concentrated by multistage evaporation to thin juice with 60–75° Brix. This concentration step takes about 50% of the total energy required for the production of sugar. Since the beginning of the 1970s, NF and RO have been considered as interesting alternatives from an energy point of view. Since 25° Brix is equivalent to an osmotic pressure of 40 bar, the need for evaporation generally remains. NF and RO might be used as capacity boosters for an existing installation if there is not sufficient steam available. In the final stage of the sugar production, the white sugar and the sugar syrup (molasses) are separated by several steps of boiling and crystallization before storage.

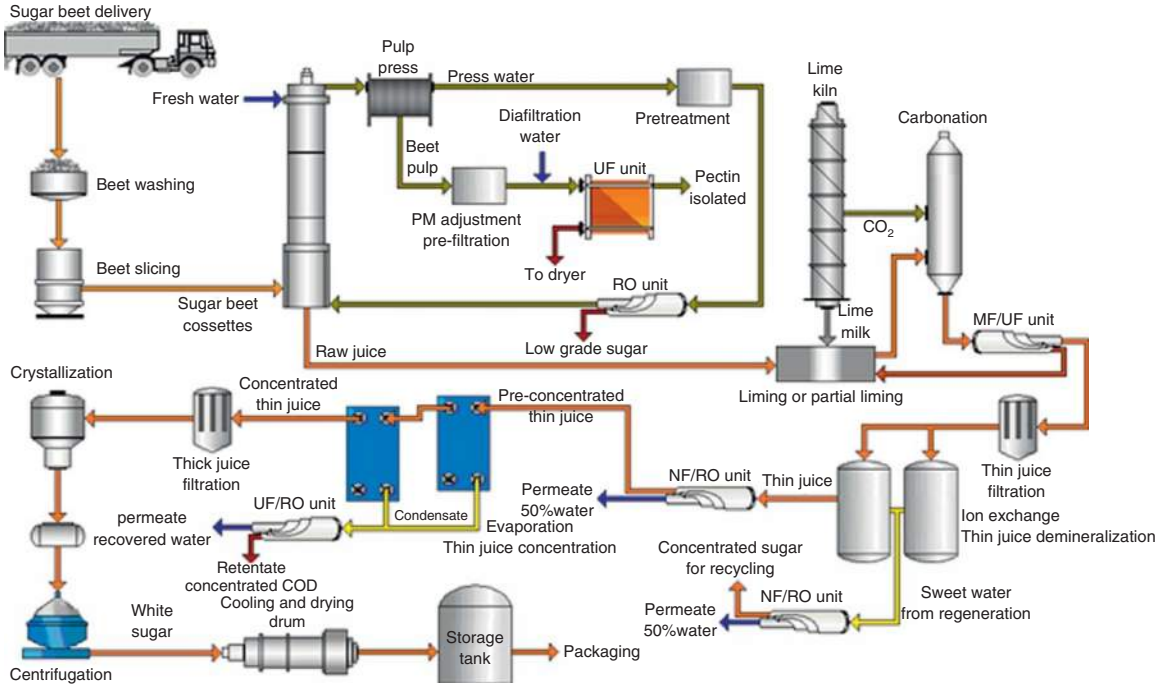


Figure 9 Beet-sugar production with membrane opportunities.

4.06.3.5.2 Cane sugar

Within the first 24 h after the delivery of cut cane bundles to the cane sugar mill, they are chopped, shredded with rotating knifes, and hammer-milled (see **Figure 10**). The cane sugar is then extracted either by roller mills using a counter-current process with fresh hot water through a chain of multiple roller mills or by continuous diffusion. In the conventional process, the dark-green juice is then clarified under the addition of heat and lime as clarifying agents to obtain a clear juice. Another concept is to apply sulfitation and/or carbonation to produce low-color cane juices. As alternative to these conventional methods, different clarification concepts including UF have been developed. The new Applexion process (NAP) [34] integrates two steps to treat limed clear juice after a clarifier. In the first step, UF is applied to remove high-molecular-weight components including starch, dextran, wax, and gum from the cane juice followed by juice softening by ion exchange to remove magnesium and calcium salts. The resulting juice is suitable to produce very low color sugar. A modification of the NAP process is the so-called SAT process, which is also built around UF [35]. In this concept, the raw cane juice is passed through a clarification step using processing aids. The overflow from this clarifier is passed directly through a UF unit, while the underflow is treated in a vacuum drum filter before being mixed with UF retentate and then passed through a second clarifier. The overflow from the second clarifier is mixed with UF permeate for further low-color sugar production, while the underflow is recycled in front of the vacuum drum filter. The clarified juice is then concentrated by multi-stage evaporation to obtain raw syrup with 60–70° Brix. As an alternative to evaporation, MD has been tested for concentration of the clear juice [35]. In the next step, the raw syrup is boiled and crystallized in several steps to separate the raw sugar and the remaining sugar syrup and molasses. The refining of the cane sugar is often divided between the cane sugar mill and the sugar refinery. In the sugar refinery, the crystallized raw sugar from the sugar mill is remelted and further decolorized and purified. MF and UF have been reported to be successful as an initial decolorizing step before final decolorization by ion exchange. Thus, MF and UF are reducing the load on the ion exchange leading to longer production cycles [36]. The purified sugar is then stored.

4.06.3.5.3 Common membrane applications in the beet and cane sugar industry

One of the key operation units in the sugar industry is evaporation. Even though RO or other membrane technologies have not succeeded in replacing the

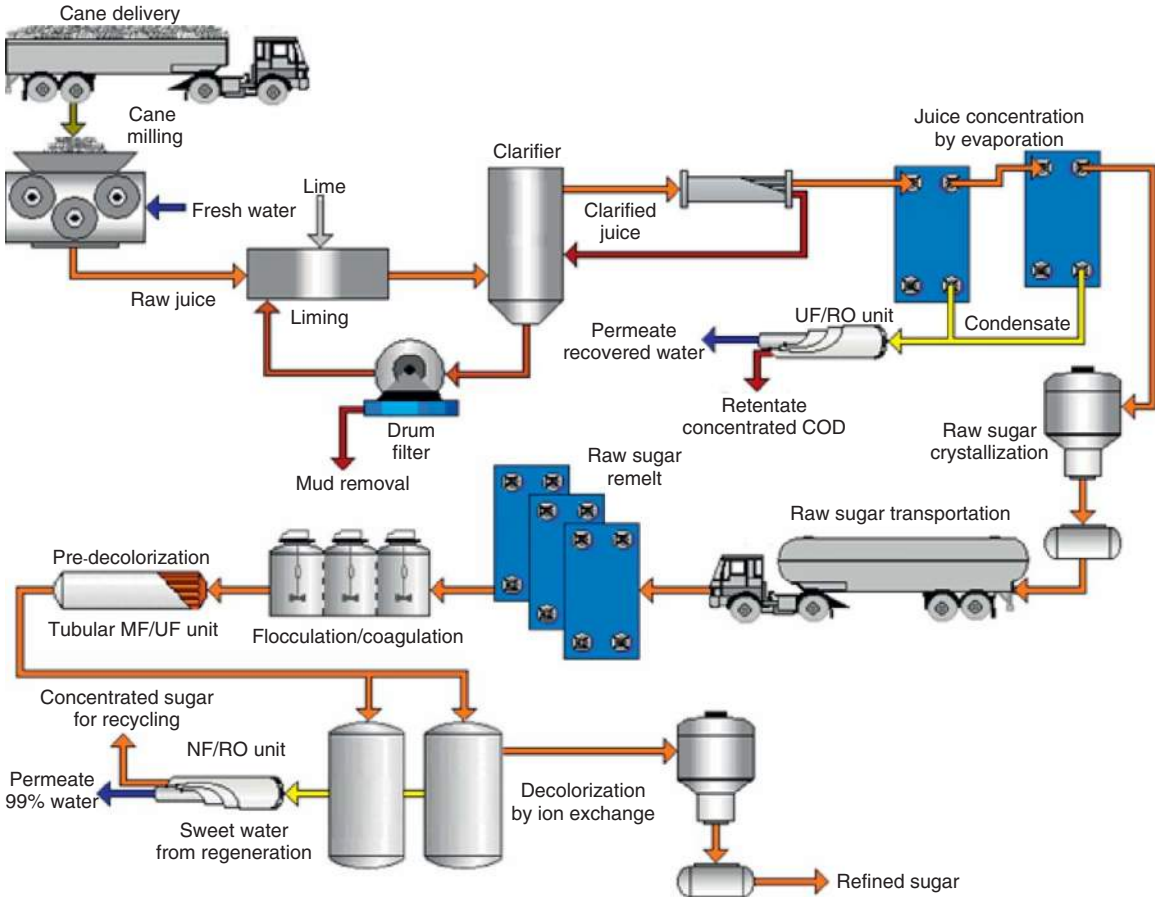


Figure 10 Cane-sugar production with membrane opportunities.

evaporation step, RO has been found to be very suitable for the polishing of evaporator condensate, which might contain chemical oxygen demand (COD)/BOD as carry-over. RO can reduce the COD/BOD in the permeate, typically by a factor of 10.

Furthermore, RO can be applied to treat waste streams containing sugar from the cleaning of tanks and other equipment in the sugar industry. The problem with wastewater streams from the sugar industry is that even 1° Brix of sugar is equivalent to a COD of 5000 mg l^{-1}. By applying RO, it is possible to obtain a purified water stream as permeate and a concentrated sugar stream as retentate.

Finally, NF can be integrated in the regeneration of ion-exchange resins. During the regeneration, the ion-exchange columns are flushed with alkaline brine to desorb the colorants from the resin. By NF, it is possible to remove the colorants from the alkaline brine to produce purified brine for recycling and thus significantly reduce the waste stream before further treatment. Hence, this approach can be used to reduce the waste discharge and salt and water consumption of a sugar factory.

4.06.3.6 Starch and Starch-Based Sweetener Industry

Starch is one of the most widely found polysaccharides in our diet and it is either consumed directly as part of the diet, for example, as potatoes, cereals etc., or extracted and then added to food, for example, as thickener for soups. Apart from the food industry, starch is also used in the paper, textile, and oil industries due to its gluing and viscosity-increasing characteristics. The worldwide starch production is about 60 million tons per year, with the United States as the main starch-producing country. About 85% of the starch processed worldwide is based on corn followed by other sources such as rice, wheat, tapioca, taro, and potato. The most important starch

derivatives are starch-based sweeteners, which are produced by acid and/or enzymatic hydrolysis of the starch carbohydrates. These sweeteners are nutritive sweeteners, which are used as a low-cost replacement of sucrose extracted from sugar cane and beets. The two key groups of starch-based sweeteners are glucose/dextrose syrup and high fructose syrups. The annual production of glucose/dextrose syrups is about 17 million tons worldwide. Most of the glucose/dextrose syrups are based on corn starch with the largest production in the United States. The worldwide production of high fructose syrups (HFSs) is about 16 million tons per year of which over 90% is related to high fructose corn syrups (HFCSs). Over 75% of all HFSs are currently produced in the United States. In the following section, the main focus will therefore be on membrane opportunities in the production of corn-based starch and corn-based sweeteners.

4.06.3.7 Corn Starch Production

Wet-milling is a flexible process to produce starch slurry and to obtain valuable by-products, for example, oil and gluten. Wet-milling starts with the steeping process, in which the corn is softened by soaking in a weak sulfurous acid solution with lactic acid bacteria – the so-called steeping water – for up to 48 h. The steeping water from this step is commonly concentrated by evaporation and used as a protein supplement to animal feed. Various combinations of MF, UF, and RO with and without evaporation as the final concentration step have been investigated for the concentration of the steeping water [37], but they have not established themselves in this step as an alternative. Degermination follows steeping. In this step, the oil-rich germs, a valuable by-product, are freed from the corn by grinding and separated from the starch by hydrocyclones. The overflow from the hydrocyclones contains the germ which is washed and then pressed to extract the oil. The remaining germ cake from the oil pressing can be added to animal feed. The underflow from the hydrocyclones containing starch, protein, and fibers is then fine milled. The resulting slurry is separated into a starch and a fiber fraction by starch extraction combined with counter-current fiber washing. After the extraction step, the crude starch milk is concentrated and the gluten (insoluble proteins) is separated from the starch. The light gluten from the separator is commonly thickened by a separation to heavy gluten and concentrated by rotary vacuum filter and then dried. MF has been investigated as an alternative to concentrate both light and heavy gluten [37] but has so far not established itself as a standard unit of operation for gluten concentration. The starch phase from the separation is then finally washed in a multistage hydrocyclone system before dewatering by a separator and drying.

4.06.3.7.1 Corn-based sweetener production

Corn-based sweetener production can be divided into three stages according to the three different products: (1) corn/dextrose syrup, (2) 42-HFCS, and (3) 55/90-HFCS.

The production of corn/dextrose syrup starts with the liquefaction of the starch (see **Figure 11**). The starch is suspended in water and liquefied by either enzyme–enzyme liquefaction or acid–enzyme liquefaction to reach a liquefaction product with 10–20 dextrose equivalent (DE), a measure for the degree of starch hydrolysis where a complete conversion of starch into dextrose equals a DE of 100. In the subsequent saccharification step, the complete conversion of starch into dextrose is achieved under the addition of enzymes, such as amyloglucosidase and pullanase, and might take up to 48 h. In order to separate the mud fraction consisting mainly of proteins and fats from the corn/dextrose syrup, a separator and/or a pre-coated rotary vacuum filter (RVF) are commonly used. An alternative option for mud removal is the combination of a separator with MF/UF. This combination achieves higher purities than the RVF and thus reduces the posttreatment of the dextrose. At this stage, the corn/dextrose syrup can be either further processed by decolorization, deionization, concentration, etc., and sold as syrup or maltodextrine or further converted to 42-HFCS.

In the following dextrose refining step, the corn/dextrose syrup is prepared for the isomerization of 42-HFCS. The syrup is pH-adjusted and passed through a carbon treatment to remove soluble proteins and color followed by leaf filters to remove the carbon. The decolorized syrup is then passed through ion exchange to remove ionic materials. The regeneration of these ion-exchange units commonly starts by water flush. The resulting sweet water contains a high COD/BOD from the sweeteners and can be concentrated by RO resulting in a concentrated sweetener stream and a purified water stream, which can be recycled. In the next step, the syrup is concentrated about 1.5 times by evaporation. The condensate from the evaporation step contains

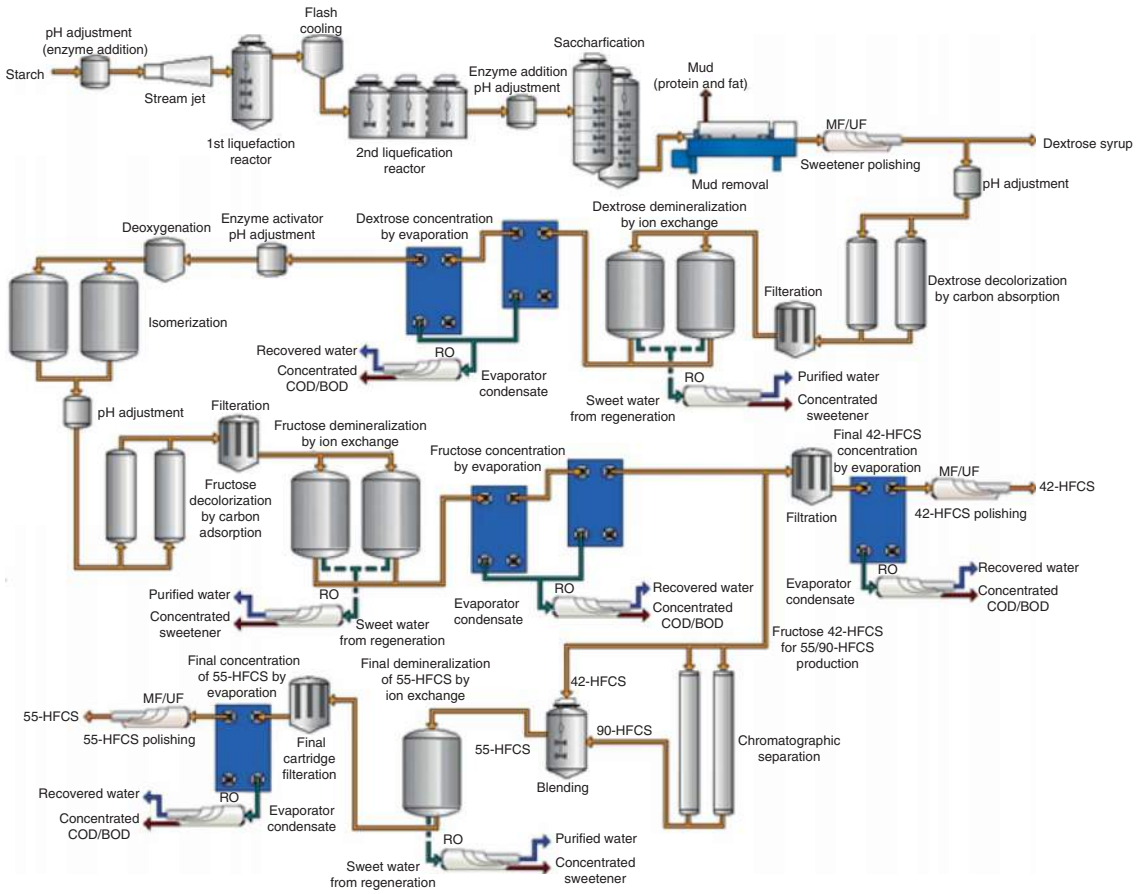


Figure 11 Corn-based sweetener production with membrane applications.

carry-over resulting in a high BOD/COD. This evaporator condensate might be treated similar to the sweet water from the ion-exchange units by RO. Before isomerization, the syrup is deoxygenated and adjusted to neutral/slightly basic pH. Further, magnesium is added to the syrup as enzyme activator. The isomerization process itself takes place in packed-bed reactors with immobilized glucose isomerase converting dextrose to 42% fructose. Carbon treatment and ion exchange purify fructose in a manner similar to dextrose. The resulting stream is then concentrated by evaporation to provide a stream, which is either used for the production of 55/90-HFCS or passed through cartridge filters and a final evaporation step to produce 42-HFCS. After evaporation, MF/UF can be applied as final polishing step to produce pyrogen-free high-quality 42-HFCS. In addition, an ion-exchange step might be added before filtration in the 42-HFSC production to increase the purity of the product. In this case, RO can also be used for the purification of the sweet water from the ion-exchange and the polishing of evaporator condensate.

In the final stage, the 42-HFCS is concentrated by chromatographic separation beyond the equilibrium point of the isomerase reaction. The concentration of 90% fructose is achieved in a multi-stage moving bed chromatographic system with a calcium ion-exchange resin, which has strong affinity to fructose. The resulting 90-HFCS is then purified by passing it through a final ion-exchange stage to remove ionic contents and impurities followed by a cartridge filter before final concentration by evaporation. Alternatively, the 90-HFCS can be blended with 42-HFCS to obtain 55-HFCS and then be purified. Again, RO can be used for polishing of the sweet water from the ion exchange and of the evaporator condensate. Further, MF/UF can be applied for the final polishing of the 55-HFCS.

4.06.3.7.2 Other starch productions

Apart from corn-based starch and sweetener production, membranes have also been investigated for the

potato and wheat starch production. Potato fruit water contains highly valuable protein. In the potato starch production, the cleaned potatoes are disintegrated and the fruit water is removed by a decanter before the extraction and concentration of the starch. Generally, two approaches to handle the potato fruit water can be distinguished: (1) concentration of solubles in the fruit water – proteins, ash, and sugar – by RO and (2) concentration and classification of proteins by UF. In the first approach, RO recovers all solids in the retentate, which can then be concentrated by evaporation, dried, and used as fertilizer. The high-quality RO permeate can be recycled to the process. In the second approach, high-purity proteins can be recovered in the concentrate. The proteins might be further purified and concentrated by evaporation, chromatography, and drying. The UF retentate can be either purified by RO as in the first approach or sent to sewage treatment. The UF approach is an interesting alternative to the conventional protein recovery by, for example, acid-thermal coagulation followed by purification by a separator, and drying. In the wheat starch industry, the use of UF and RO for the concentration of solubles instead of evaporation has been investigated but this is not economically viable due to low fluxes and short membrane life cycles [38, 39]. Further, the combination of UF and RO was studied for the treatment of wastewater from the production of vital wheat gluten [40]. Based on pilot trials, it is possible to recover gluten from the wastewater stream for further concentration by drying. In order to achieve highly purified water to be recycled to the process, treatment of the UF permeate by RO was suggested. Overall, it should be noted that the approaches to use membranes in the potato and wheat starch industry are still in their infancy and further investigations are required.

4.06.3.8 Water and Wastewater in the Food Industry

Water is widely used in the food industry either directly as food ingredient or for product cleaning and plant sanitation. Despite efforts to reduce the water consumption in the food industry, consumption rates are still relatively high, for example, in the brewing industry 8–15 l of water are used for each liter of beer, while, in the dairy industry, the water consumption is between 9 and 18 l for each kilogram of dairy product.

In the water loop of the food industry, generally two positions of membrane processes can be distinguished: (1) pretreatment of the in-take water to fulfill the requirements for the specific application, and (2) posttreatment of the wastewater either as part of internal water recycling or as end-of-pipe treatment.

The requirements for the pretreatment of in-take water vary widely with its application. Generally, three classes of water can be distinguished in the food industry:

1. Process water is potable water, which can be used as a food ingredient or is in contact with the food as part of a production step. Typically, the membrane processes UF, NF, and RO are integrated in the production of process water. Particularly, UF membranes with a molecular weight cutoff (MWCO) of less than 10 kDa can be applied for pyrogen removal. On the other hand, NF and RO do not only remove pyrogen but can also be used for demineralization of water and removal of bacteria. The membrane processes applied vary with the in-take water quality and the usage of the water.
2. Boiler and cooling water is demineralized soft water to avoid scaling and fouling of the cooling and heating equipment. Depending on the in-take water quality, typically NF and RO are applied.
3. General purpose water is often chlorinated potable water to rinse raw ingredients and clean equipment. NF and RO can be used in the preparation of this water but it is important to note that the chlorination of water should be positioned after the NF/RO step since free chlorine can destroy NF/RO membranes.

After usage, the different water streams have to be posttreated for recycling or discharge. In the initial step of posttreatment, membrane processes can be used to recover valuable components from the wastewater streams, for example, RO can be used for the concentration of sugars to reduce the BOD in the wastewater and directly recover sugar, while UF can be used to recover food proteins. Most recently, membrane bioreactors (MBRs) have been introduced in the wastewater-treatment plants of the food industry. MBRs are MF/UF modules, which are either submerged into the ternary treatment of the wastewater-treatment plant or operated as a side stream to ternary treatment. The permeate of the MBR is free of suspended solids and can be either discharged or upgraded with NF/RO for recycling.

4.06.4 Membrane Processes in the Bulk Biotech Industry

The roots of biotechnology can be dated to more than 5000 years ago, when considering the fermentation of fruits to alcoholic beverages as the first controlled biotechnological process. Nowadays, the term biotechnology covers a wide range of processes based on reactions using either microorganisms or enzymes. In the following section, the focus is on bulk products such as antibiotics, enzymes, organic and amino acids, vitamins, and biopolymers. In the final part, the production of purified water, a key for many bulk biotech processes, and treatment of wastewater will be discussed.

4.06.4.1 Antibiotics

Antibiotics are active pharmaceutical ingredients (APIs) produced by fermentation with antimicrobiological activities and are therefore used to reduce growth or completely inactivate other microorganisms. The development of antibiotics started with the discovery of penicillin in 1928 followed by major discoveries of other antibiotics during the 1950s. The introduction of membrane technology in the antibiotics industry started at the end of the 1960s. The total market for antibiotics is approximately US$12 billion [41]. China, followed by India and European countries, leads in the production of antibiotics. About 65% of the market is related to β-lactam antibiotics, mainly penicillins and cephalosporins followed by tetracyclines. The main usage of antibiotics is in human but also in animal treatment.

Antibiotics are produced by fermentation and involve further processing, that is, separation, purification, and concentration. Membrane processes can be integrated in the production of both natural and semi-synthetic antibiotics due to their efficiency and high selectivity in comparison with conventional technologies such as rotary vacuum filtration, centrifugation, solvent extraction, and evaporation/distillation. In **Table 2**, a selection of antibiotics, which are produced with the help of membrane technology, is given.

The production of antibiotics starts with purification of the substrates and addition of the seed culture to start the fermentation (see **Figure 12**). Following the fermentation, MF or UF can be directly used to separate the antibiotic from the biomass. This is often done in combination with DF. This can either be done directly if the product is extracellular or followed by cell disruption if it is an intracellular product. The MF/UF retains the biomass including cell debris on the retentate side, while the antibiotics pass into the permeate. This process can be supported by DF to maximize yield and purity. NF and RO can then be applied to concentrate the clarified antibiotics stream – the UF permeate. Further, it is possible to recycle the NF/RO permeate as DF water to the DF stage. Also, by using NF, it is possible to further purify the antibiotics by allowing inorganic salts and other low-molecular-weight impurities to be removed with the permeate. The antibiotics are then further purified by either solvent extraction, absorption, or precipitation.

Table 2 Selection of antibiotics produced with membrane technology

Main class	*Sub classes*
Lactames	Cephalosporin, 7-ACA, penicillin, 6-APA
Aminoglycosides	Streptomycin, neomycin, lincomycin, amikacine, gentamycin
Polypeptides	Bacitracin, polymixin, acitomycin
Tetracyclines	Tetracycline, fusidin
Macrolides	Tylosin, erythromycin

After solvent extraction, the antibiotics are recovered in a separation step with a disk centrifuge combined with recovery of the solvents. After the disk centrifuge, UF can be used as a polishing step to remove pyrogens and other impurities before crystallization and thus improve the quality of the final bulk antibiotic product, which is recovered by using a decanter.

In case of absorption, RO can be applied to recover and pre-concentrate the antibiotics from the adsorption eluate before further concentration by evaporation. This includes the possibility to use RO to polish the evaporator condensate. Further, the concentrate from the evaporator can be polished by UF before crystallization and recovery by a decanter. When using precipitation, only a decanter is required to recover the bulk antibiotics.

4.06.4.2 Enzymes

Enzymes are proteins produced by fermentation. These proteins have partly metallic side groups and can catalyze chemical reactions. Enzymes were discovered by Mitscherlich in 1826 and were originally

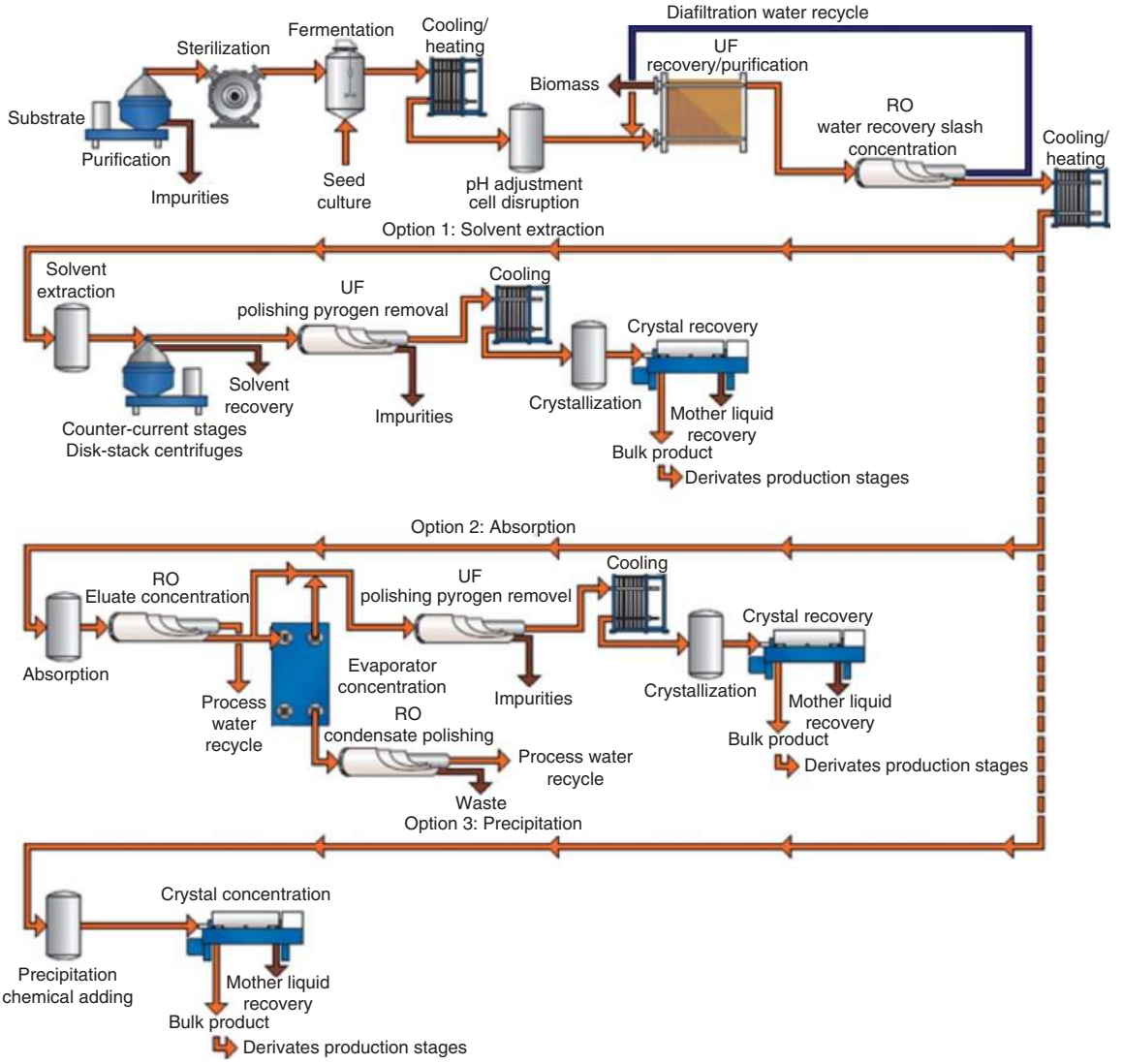


Figure 12 Antibiotics production with membrane applications.

called ferments until Buchner in 1897 suggested referring to them as zymase. The first large-scale installations of membrane processes in the enzyme industry can be found from the 1970s. The worldwide production of enzymes accounts for a market value of about US$2 billion [41]. The main production sites of enzymes are in Europe and in the United States with rapidly increasing production in China and India. Applications of enzymes can be found in the production of food and food ingredients related to, for example, corn syrups, bread, vegetables, eggs, and dairy products, in the production of beverages such as beer, wine, fruit juices and in the production of a wide range of other goods, including detergents, animal food, and pharmaceuticals. Most recently, enzymes gained a lot of attention as key components in the production of bioethanol, that is, for the second-generation cellulosic-based bioethanol production. In Table 3, a selection of enzymes, which can be produced with the help of membranes, is given.

Table 3 Selection of enzymes produced with membrane technology

Origin	*Examples*
Microbial	Protease, amylase, cellulase, lipase, amyloglucosidase (AMG), pectinase, lactase, glucose oxidase/isomerase
Animal	Rennet, trypsin, pepsin
Plant	Bromelain, papain
Other	Lysozyme

Enzymes can be produced either by extraction from plant or animal tissues or by microbial fermentation, which is today the most common approach. The use of membrane filtration in enzyme processing is well established, being both a non-destructive technology and able to combine molecular separation, purification, and concentration.

The production of enzymes typically starts with either extraction/adsorption of enzymes from plant or animal tissues or with microbial fermentation (see **Figure 13**). Depending on the enzymes, they can be found either retained in the cells (intracellular) or between the cells (extracellular). In case the enzymes are intracellular, the cells are separated from nutrient broth and concentrated in a decanter. After this, the cells are disrupted by either autolysis or mechanical methods resulting in the cell juice containing the enzymes and the cell debris, which are then separated in an additional decanter step. The result is a liquid enzyme solution. Alternatively, if the enzymes are extracellular, the biomass consisting of the cells and nutrient broth are separated from the enzyme solution by a decanter. The resulting enzyme solutions from both the intracellular and extracellular production are rich in LMWCs, such as salts and metabolic products. MF can be used as pretreatment before enzyme concentration stages to remove some of these impurities. The enzymes can then be either used directly or further purified and concentrated by crystallization, precipitation, adsorption, or UF/NF. By UF, the enzyme strength can typically be concentrated 25 times without hardly any loss of enzyme activity. The initial concentration can be done by UF/NF with spiral-wound elements and since the viscosity increases with increasing enzyme concentration, UF plate-and-frame modules are often used in the final concentration step. This process also allows control

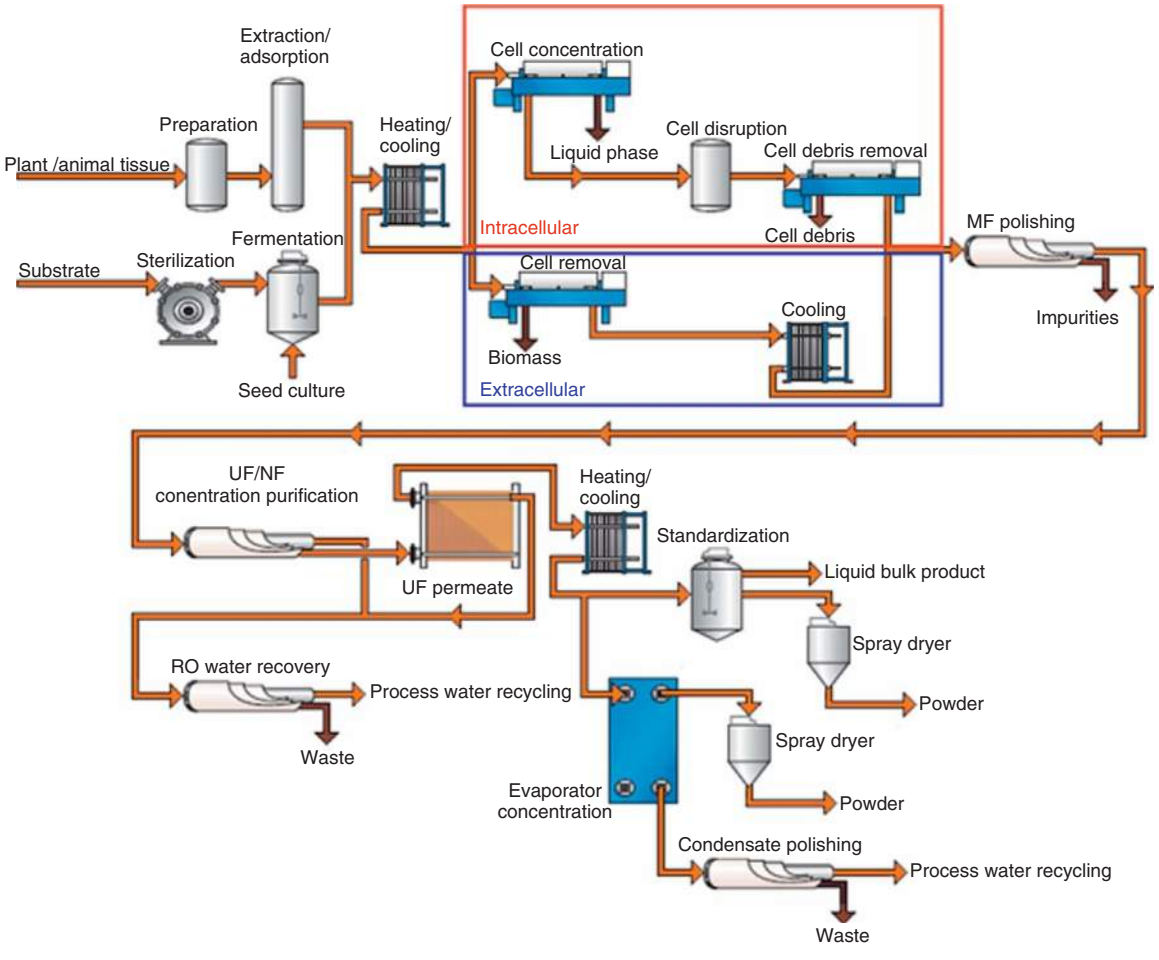


Figure 13 Enzyme production with membrane applications.

of the LMWCs in the enzyme solution, since the components will pass partially through the membranes. The purification effect can be further enhanced by using DF, thus increasing the purity by reducing color and endotoxins. The DF/washing step is also used to remove excess salt when the enzyme is recovered by salt extraction. The enzymes are then typically standardized and either directly used as liquid bulk product or spray-dried with an optional pre-concentration step by evaporation to be used as powder. Further, RO can be used to recover purified water from the UF permeate and from the evaporator condensate.

4.06.4.3 Organic Acids

The main organic acids obtained from fermentation are acetic acid, citric acid, lactic acid, gluconic acid, and itaconic acid. The worldwide production of organic acids represents a value of US$1.4 billion. Among the different organic acids, citric acid with a production of 1.4 million tons [42] is by far the most widely produced organic acid with China as the key producing country, followed by lactic acid with a production of approximately 150 000 tons [43]. The focus of this section is on citric and lactic acid and they are therefore used as examples of organic acid processes with membrane opportunities.

4.06.4.3.1 Citric acid

The fermentation-based production of citric acid on a large scale started in 1923. Citric acid is a widely used preservative in the food and beverage industry, for example, carbonate beverage accounting for approximately 50% of its production. Other applications of citric acid can be found in the pharmaceutical and the detergents industries in which citric acid is used, for example, for membrane cleaning. One production route to manufacture food-grade citric acid is by fermentation combined with lime/sulfuric acid precipitation. After the fermentation, UF combined with DF can be used to separate the citric acid from the biomass. To purify the citric acid and reduce impurities such as remaining biomass, salts, and sucrose, the UF permeate can then be treated by RO/NF, thus reducing the posttreatment processes. Calcium carbonate is then added to the citric acid in the RO permeate to form neutral, insoluble precipitated calcium citrate containing approximately 75% of citric acid. The calcium citrate is passed through various washing and filtration steps, using, for example, plate or rotary filters to remove all impurities, and is finally dissolved with sulfuric acid. The addition of sulfuric acid results in free citric acid and precipitated calcium sulfate, which is removed from the process. The citric acid solution is then deionized and preconcentrated by evaporation before crystallization. The final product is citric acid crystals in either monohydrate or anhydrous form.

4.06.4.3.2 Lactic acid

Lactic acid is a natural organic acid which can be found not only in milk but also in other food products such as meat and beer. Today, lactic acid is widely used in the food industry as a preservative, flavor enhancer, and an acid adjustment. The future potential of lactic acid is also in the production of polylactic acid (PLA), a biopolymer, and ethyl lactate, a biodegradable solvent. Generally, lactic acid can be produced biologically or synthetically. The disadvantage of chemical synthesis is that it produces both L(+)-lactic acid and D(−)-lactic acid, while microbial fermentation with appropriately selected microorganisms produces only one isomer at a time.

Lactic acid production starts with the fermentation of typically corn starch, cane sugar, or milk whey with, for example, lactic acid bacteria (LAB) or filamentous fungi. In connection with the fermentation, ED has been considered for continuous removal of lactic acid/lactate to overcome product inhibitions [44, 45]. One of these approaches includes the use of reverse electro-enhanced dialysis (REED) with anion-exchange membranes separating the fermentation broth and an alkaline dialysate in alternating compartments. By direct electrical current, lactate is extracted from the broth into the alkaline solution where the charge is mainly carried by hydroxide ions, which migrates into the next broth compartment. The symmetric setup of the membranes allows for regular reversal of the current, which removes fouling and hereby prolongs operation. The resulting fermentation broth containing sugars and proteins is returned to the fermenter, while the dialysate with lactate is further treated by bipolar ED separating the alkaline solution for recycling and lactate, which is concentrated and acidified. Lactic acid can be further purified and concentrated by conventional methods such as ion exchange and evaporation.

Alternatively, the use of UF was proposed in combination with milk whey batch fermentation [46]. The UF concentrates bacteria and proteins for recycling to the fermenter, while lactate from the permeate is purified by cation and anion exchangers

to reach high lactic acid purities before being concentrated by RO followed by evaporation.

4.06.4.4 Amino Acids

Amino acids are the fundamental building blocks of proteins and are produced by either chemical synthesis or fermentation. The worldwide market for amino acids is US$2.3 billion [41]. The key amino acids from a volume point of view are glutamic acid with an annual production of 1.7 million tons and L-lysine with 800 000 tons, which are both mainly produced in Asia with China and Japan as main producing countries. The following section focuses on these two amino acids as examples for all amino acids.

4.06.4.4.1 Lysine

Lysine is an important amino acid in human and animal nutrition and can be found in high concentrations in meat, poultry, and dairy products, while plant proteins contain only minor concentrations of this amino acid. The biologically active L-configuration of lysine is therefore used as an additive in human and animal food. The development of the industrial lysine production is closely related to the general development of the amino acid production by fermentation in the 1950s. Even though it is possible to produce lysine synthetically, the more economic biological method is used nearly exclusively.

The first step in the production of L-lysine is fermentation typically using strains of *Corynebacteria* or *Brevibacteria* as lysine-producing bacteria and molasses as the carbon source. After fermentation, UF can be used to effectively separate the fermentation broth into a retentate stream containing the concentrated microorganisms and a permeate stream with the purified L-lysine. The purified UF permeate can then be pre-concentrated by RO before evaporation and spray drying. Alternatively, to achieve higher purities, lysine can by recovered from the UF permeate by an ion-exchange step after which the ion-exchange eluate can be either directly crystallized or pre-concentrated by RO before evaporation and spray drying.

4.06.4.4.2 Glutamic acid

Glutamic acid is a nonessential amino acid, which is mainly used and produced in the form of its sodium salt as monosodium glutamate (MSG). Glutamic acid can be found in animal and plant proteins. In 1908, glutamic acid was identified as the key component in a seaweed extract, which is widely used in the Asian cuisine and was patented and marketed as flavor enhancer in its sodium salt form – MSG – by Ajinomoto Corp. in Japan. Initially, glutamic acid was produced synthetically but fermentation of glutamic acid was developed in 1957 and is today the common way of production.

The fermentation medium consists of strains of *Corynebacteria* or *Brevibacteria* producing the glutamic acid plus carbon sources (glucose and molasses), inorganic salts, and biotin. Similar to the production of lysine, UF can be used after the fermentation process for the initial separation of the microorganism and the glutamic acid followed by the pre-concentration of glutamic acid containing UF permerate by RO before evaporation and crystallization. Alternatively, ion exchange can be used for the recovery of glutamic acid and RO can be used as initial concentration step before further processing.

4.06.4.5 Vitamins

Vitamins are non-prescription medicine and account for a market of approximately US$900 million [41]. While most vitamins are produced synthetically, only vitamin B_2 (riboflavin), B_{12} (cyanocobalamin) and 2-keto-L-gulonic acid (2-KLG), a precursor for synthetic production of vitamin C, are microbially produced on a significant scale. The annual production of 2-KLG is about 80 million tons with nearly all production in China, while the production of vitamin B_2 and B_{12} is significantly lower, at 1000 and 10 000 kg, respectively. Even though there are opportunities to integrate membranes in the vitamin B_2 and B_{12} production, membranes are presently mainly established in the vitamin C production, which will be discussed in the following section.

4.06.4.5.1 Vitamin C

Vitamin C is an essential nutrient with antioxidizing properties and is used as a supplement to human and animal food or additive to pharmaceuticals and cosmetics. Natural vitamin C can be found in high concentration in many vegetables and fruits, for example, broccoli, cauliflower, kiwi fruit, and oranges. The recommended daily intake rate of vitamin C ranges from 45 mg to several thousand milligrams. The industrial production of vitamin C started in 1934 and was widely based on the Reichstein and Grüssner process combining one-step bacterial fermentation with chemical conversions. Today, the production is nearly exclusively

based on a two-step fermentation process which reduces the chemical conversion stages. This process was developed in China during the 1960s. The production of vitamin C starts with the catalytic hydrogenation of glucose to sorbitol. In the first fermentation step, L-sorbose is produced from the sorbitol by the use of various species of microorganisms. In the original Reichstein and Grüssner process, several chemical conversions would be used to produce ascorbic acid producing 2-keto-L-gulonic acid as intermediate precursor. In the alternative Chinese approach, a second fermentation step is employed to convert the sorbose to 2-keto-L-gulonic acid.

Previously, flocculation followed by centrifugation, ion-exchange demineralization, and crystallization would be applied to purify the 2-keto-L-gulonic acid before further processing. An alternative approach is to use UF with plate-and-frame modules directly after the second fermentation step to replace the flocculation and centrifugation, thus reducing the operating costs significantly [47]. Among various other approaches to optimize the vitamin C production, a method has recently been patented to produce L-ascorbic acid directly from D-glucose by application of yeast, which has been transformed by mannose epimerase [48]. MF, UF, and NF are considered as methods for isolating the L-ascorbic acid from the fermentation broth.

4.06.4.6 Biopolymers

The term biopolymer can be used generally for all macromolecules produced by plants or microorganisms consisting of repeating monomers connected by covalent bonds. In the bulk biotech industry, this term is used for polymers produced by microorganisms converting biomass such as sugar and starch to biopolymers. In recent years, these biopolymers have gained a lot of attention because they are produced from renewable sources and are often biodegradable. The market for biopolymers is approximately US$200 million [41] and xanthan gum accounts for about 80% of the market with an annual production of 20 000 tons.

4.06.4.6.1 Xanthan

Xanthan is an anionic biopolymer with repeated chains of cellulose monosaccharides and oligosaccharides. In the industry, xanthan gum is used for its thickening, stabilizing, suspending, and emulsifying properties. Applications can be found not only in the food and beverage industry, for example, in sauces, salad dressings, desserts, and fruit juices, but also in the pharmaceutical and cosmetic industries, for example, tablets and creams as well as in the oil industry as drilling liquid to enhance oil recovery. One of the key characteristics of xanthan gum is its high viscosity combined with a very high pseudoplasticity, which means that its apparent viscosity decreases with increasing shear force applied. In addition, xanthan gum is stable over a wide range of temperature and pH as well as water soluble but insoluble in a wide range of organic solvents. Originally, xanthan gum was discovered in 1959 as part of a US Department of Agriculture program and commercial production started in the 1960s.

The initial step in the production of xanthan gum is the fermentation using a strain of *Xanthomonas* bacteria and substrate with sugar as carbon source, nitrogen, and salts (see **Figure 14**). The resulting fermentation broth contains about 2–3% xanthan

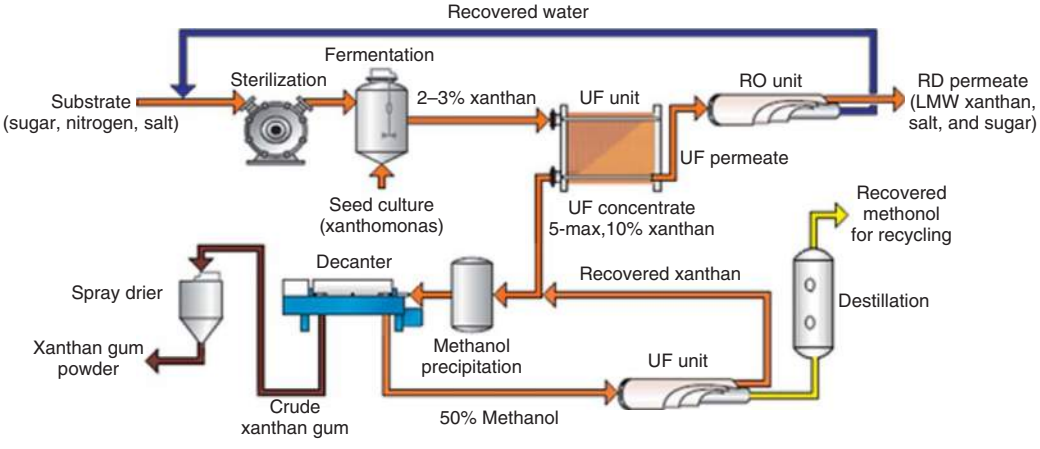


Figure 14 Xanthan gum production with membrane applications.

gum, which can be concentrated and purified by UF. This results in a UF retentate of 5–max. 10% concentrated high-molecular-weight xanthan gum and a UF permeate consisting mainly of water with some low-molecular-weight xanthan gum, salts, and sugars. This UF permeate stream can then be further treated by RO to obtain a pure water stream for recycling to the fermenter and a concentrated stream of low-molecular-weight xanthan gum, salts, and sugars. The concentrated xanthan gum in the UF retentate is further purified by precipitation in methanol. From the precipitation with methanol, the crude xanthan gum is recovered by decanter. The xanthan gum is then dried and milled resulting in a white to cream-colored free-flowing powder. The light phase of the decanter can be purified by UF recovering lost xanthan gum for recycling to the precipitation step and methanol for distillation recycling to the precipitation step.

4.06.4.7 Water and Wastewater in the Bulk Biotech Industry

The bulk biotech industry has grown significantly in recent years and so has its water demand. The in-take water requirements in the bulk pharmaceutical industry can be divided into different levels [49]:

1. Purified water is prepared by distillation, ion exchange, RO, or other processes and should not be used for the preparations used for parenteral administration;
2. Water for injections is pyrogen-free water, which is obtained by further purification of potable or purified water using distillation. It should be noted that water for injection is not necessarily sterile water.
3. Sterile water for injections is both sterile and pyrogen-free water. Filtration by MF membranes having a nominal pore diameter of 0.22 μm is one recognized sterilization method. It is important that these membranes can be heat sterilized.

The standards of the water are described in detail in, for example, the International Pharmacopoeia by the WHO, the EU Pharmacopoeia, or the US Pharmacopoeia. It should be further noted that water for injection and sterile water for injection are often produced by using cascades of different separation technologies, for example, RO followed by deionization and a second RO stage to maximize safety.

Apart from the in-take water, the wastewater from the bulk biotech industry might provide challenges because it might contain low levels of, for example, active ingredients, which must be removed before discharge to the environment. In recent years, MBRs have therefore also established themselves for wastewater treatment in the pharmaceutical industry [50]. These plants can be combined with RO to optimize the outlet quality.

4.06.5 Outlook

The continuous worldwide acceptance of membrane processes will ensure that the membrane market in the food and bulk biotech industry will grow by average annual growth rates of 5–8%. This will be supported by the development of new applications for the established membrane processes MF, UF, NF, and RO. The key drivers will be general economic and environmental targets but also the fast growth of new markets for functional food and bulk biotechnology. Additional growth can be expected from the emerging membrane processes ED, PV/VP, and MC. These processes have great potential, which has so far not been fully explored. Finally, integrated process solutions such as synergies and hybrid processes, including membranes, are still relatively new areas of process development. Further research in this area will not only provide economical benefits but also strengthen the understanding of membrane technology in the industry, a key factor to ensure long-term sustainable growth of membrane technology. The latest trend in the food and bulk biotech industry is biorefineries. Biorefineries are integrated biotech facilities aiming on full utilization of feedstock for the simultaneous production of food, biofuels, and biochemicals. One approach is the integrated production of sugar and biofuels from sugar beets, which is currently being investigated by the European Union [51], while major chemical companies, for example, Dow and DuPont, are working on biopolymers from corn and/or cellulose-based feedstock [52]. In all these concepts, membranes can play a significant role as highly selective and low-energy separation processes.

Overall, cross-flow membrane processes have established themselves in the food and bulk biotech industry and current research efforts will support their future growth.

References

[1] Loeb, S., Sourirajan, S. *Adv. Chem. Ser.* **1962**, *38*, 117–132.
[2] Koros, W. J., Ma, Y. H., and Shimidzu, T. *J. Membr. Sci.* **1996**, *120*, 149–159.
[3] Böddeker, K. W. *J. Membr. Sci.* **1990**, *51*, 259–272.
[4] International Dairy Federation, The World Dairy Situation 2007. In *Bulletin of the International Federation No 423*; International Dairy Federation: Brussels, 2007.
[5] Bylund, G. Ed. *Dairy Processing Handbook*; Tetra Pak Processing Systems: Lund, 1995.
[6] Fauquant, J., Vieco, E., Maubois, J.-L. *Lait* **1985**, *65*, 1–20.
[7] Maubois, J.-L. Current Uses and Future Perspectives of MF Technology in the Dairy Industry. In *Bulletin of the International Federation No 320;* International Dairy Federation: Brussels, 1997.
[8] Govindasamy-Lucey, S., Jaeggi, J. J., Bostley, A. L., Johnson, M. E., Lucey, J. A. *J. Dairy Sci.* **2004**, *87*, 2789–2799.
[9] Tamime, A. Y. Modern Cheese Making: Hard Cheeses. In *Modern Dairy Technology*; Robinson, R. K., Ed.; Elsevier Applied Science: New York, 1993; pp 49–220.
[10] Barros, C. M. V., Ribeiro, A. C. O., Viotto, W. H. *Desalination* **2006**, *200*, 555–556.
[11] Lipnizki, F., Nielsen, C.-E., Betcke, R., Carpio, J. *Filtr. Sep.* **2006**, *43*(2), 14–15; 18.
[12] Borremans, E., Modrok, A. *Drink Technology and Marketing* **2003**, *7*(4), off-print.
[13] Gabelman, A., Hwang, S.-T. *J. Membr. Sci.* **1999**, *159*, 61–106.
[14] Reed, R. *Membr. Technol.* **1998**, *101*, 5–8.
[15] International Organisation of Vine and Wine, Musts. In *International Code of Oenological Practices*; International Organisation of Vine and Wine: Paris, 2005; pp II. 2.1–2.24.
[16] Eurodia, Tartaric stabilisation of wine, 2002, http://www.eurodia.com (accessed February 2010).
[17] Jung, C. Verfahren, um aus Flüssigkeiten, die flüchtige Riechstoffe und Alkohole enthalten, durch Distillation den Alkohol und die Riechstoffe getrennt zu gewinnen. Swiss Pat. 44,090, 06 March 1908.
[18] Lipnizki, F., Nielsen, C.-E., Betcke, R., Carpio, J. *Filtr. Sep.* **2006**, *43*(2), 16–17.
[19] Karlsson, H. O. E., Loureiro, S., Trägårdh, G. *J. Food Eng.* **1995**, *26*, 177–191.
[20] Schäfer, T., Bengtson, G., Pingel, H., Böddeker, K. W., Crespo, J. P. S. G. *Biotechnol. Bioeng.* **1999**, *62*, 412–421.
[21] World markets and trade: Orange juice, Foreign Agricultural Service/USDA, April 2008.
[22] Global concentrated apple juice, Foreign Agricultural Service/USDA, April 2008.
[23] Laganàa, F., Barbieri, G., Drioli, E. *J. Membr. Sci.* **2000**, *166*, 1–11.
[24] Álvarez, S., Riera, F. A., Álvarez, R., *et al. J. Food Eng.* **2000**, *46*, 109–125.
[25] Torres, M. R., Marín, F. R., Ramos, A. J., Soriano, E. *J. Food Eng.,* **2002**, *54*, 215–219.
[26] Market data, Gelatine manufacturers of Europe, 2008, http://www.gelatine.org (accessed February 2010).
[27] McHugh, D. J. A Guide to the Seaweed Industry. In *FAO Fisheries Technical Paper No. 441*; Food and Agriculture Organization of the United Nations: Rome, 2003.
[28] Daniells, S. Pectin sourcing advances: 2007, 17 December 2007, http://www.foodnavigator.com (accessed February 2010).
[29] Lipnizki, F., Carter, M., Trägårdh, G. *Sugar Industry/ Zuckerindustrie* **2006**, *131*, 29–38.
[30] Hatziantoniou, D., Howell, J. A. *Desalination* **2002**, *148*, 67–72.
[31] Bogliolo, M., Bottino, A., Capannelli, G. *et al. Desalination* **1996**, *108*, 261–271.
[32] Tyndall, T. J. Recent Developments in Sugar Clarification with Tubular Polymeric Membranes. In *Proceedings of the Symposium on Advanced Technology for Raw Sugar and Cane and Beet Refined Sugar Production*, New Orleans, LA, USA, 8–10 September 1999.
[33] Lutin, F., Bailly, M., Barb, D. *Desalination* **2002**, *148*, 121–124.
[34] Lancrencon, X. *Int. Sugar J.* **2004**, *105*, 390–393.
[35] Chou, C. C. *First Biennial World Conference on Recent Developments in Sugar Technologies*, Delray Beach, FL, USA, 16–17 May 2002.
[36] Wilson, J. R., Percival, R. W. Ultrafiltration: A new alternative for the management of regenerant waste streams. In *Proceedings of the 1990 Sugar Processing Research Conference*, San Francisco, CA, USA, 29 May–1 June 1990; 116–125.
[37] Rausch, K. D. *Starch/Stärke* **2002**, *54*, 273–284.
[38] Meuser, V. F. Smolnik, H. D. *Starch/Stärke* **1976**, *28*, 421–425.
[39] Meuser, V. F., Smolnik, H. D. *Starch/Stärke* **1976**, *28*, 271–278.
[40] Fane, A. G., Fell, C. J. *AIChE Symp. Ser.* **1977**, *73*, 198–205.
[41] Chotani, G. K., Dodge, T. C., Gaertner, A. L., Arbige, M. V. Industrial Biotechnology: Discovery to Delivery. In *Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology*, 11th edn.; Kent, J. A., Ed.; Springer: Berlin, 2007; pp 1311–1374.
[42] Partos, L. Jungbunzlauer raises prices for citric acid, 2005, http://www.foodproductiondaily.com(accessed February 2010).
[43] Mirasol, F. *Chem.l Market Rep.* **1999**, *255*, 16.
[44] Nomura, Y., Iwahara, M., Hallsworth, J. E., Tanaka, T., Ishizaki, A. *J. Biotechnol.* **1998**, *60*, 131–135.
[45] Kim, Y. H., Moon, S. H. *J. Chem. Technol. Biotechnol.* **2001**, *76*, 169–178.
[46] González, M. I., Álvarez, S., Riera, F., Álvarez, R. *J. Food Eng.* **2007**, *80*, 553–561.
[47] Zhang, L., Wei, J., Wang, S. Plate & frame membrane system for recovery and concentration of 2-keto-L-gulonate. In *International Congress on Membranes and Membrane Processes*, Honolulu, HI, USA, 12–18 July 2008.
[48] Branduardi, P., Porro, D., Sauer, M., Mattanovich, D. Ascorbic Acid Production from D-Glucose in Yeast. Intl. Appl. WO 002006113147, 7 April 2006.
[49] The International Pharmacopoeia, 4th edn., 2008, http://www.who.int/phint (accessed February 2010).
[50] Noble, J. *Membr. Technol.* **2006**, *2006*(9), 7–9.
[51] Vaccari, G., Marchetti, G., Lenzini, G., Tamburini, E. New proposal for integrated production of sugar and biofuels from sugar beet. In *10th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction – PRES'07*, Ischia Island, Italy, 24–27 June 2007.
[52] Ritter, S. K. *Chem. Eng. News* **2004**, *82*(22), 31–34.

Biographical Sketch

Frank Lipnizki completed his BEng (Hons) in Manufacturing and Management at the University of Bath, UK in 1995; diploma in mechanical engineering (process engineering) at the University of Bochum, Germany, in 1996; PhD (hydrophobic pervaporation: process integration and optimization) in chemical engineering at the University of Bath, UK in 1999. He received a postdoctoral Druvan scholarship in food engineering at Lund University, Sweden, in 2000; and since 2001, he has been a part of Alfa Laval - Business Centre Membranes (previously Danish Separation Systems), Denmark. Further, in 2010 he was appointed Docent/Reader in food engineering at Lund University, Sweden. His main research interests are the integration and optimization of membrane process for the food, biotech, and process industry. Frank Lipnizki has authored over 25 publications in reviewed journals and books and has more than 40 presentations at international conferences on membrane technology to his credit.

4.07 Membrane Bioreactor in Water Treatment

G Wen, J Ma, L Zhang, and G Yu, State Key Laboratory of Urban Water Resource and Environment, Harbin, China

Glossary

Backwashing Reversing flow through a membrane to remove foulants.

Biofilm Film or layer of biological material.

Biomass Viable microorganisms used to achieve removal of organics through biotreatment.

Cake layer A layer matter composed of organic, inorganic, and biological foultant leading to membrane flux decrease.

cMBR MBR process, the combination of a traditional bioreactor with membrane filtration device into a single unit process.

Critical flux The flux below that level the increase of transmembrane pressure (TMP) or the decline of flux with time does not occur.
Flux The quantity of material passing through a unit area of membrane per unit time under specific pressure.
Food-to-microorganism (F/M) (ratio) Rate at which substrate is fed to the biomass compared to the mass of biomass solids.
Fouling Membrane contamination which causes reduction of permeate flux due to membrane pore constriction, pore blocking, and cake layer formation by sludge particles, colloids, and solutes.
HRT (hydraulic retention time) The measure of the average length of time that a soluble compound remains in a constructed reactor, which is equal to the volume of aeration tank/influent flowrate.
Hydrophilicity/hydrophobic The tendency of a molecule to be solvated by water: hydrophilicity is easily solvated, while hydrophobic is hardly solvated.
iMBR MBR process with the membrane module immersed into the bioreactor.
Membrane bioreactor A process of wastewater-treatment technology combining membrane separation process with conventional activated sludge treatment process.
Model A pattern, plan, representation (especially in miniature), or description designed to show the main object or workings of a system, or concept.
SRT (sludge retention time) The retention time of microbiological cells in the areated pool.
Transmembrane pressure (TMP) Pressure difference between membrane two sides when operation under constant flux.
UV_{254} Absorption value of some organic compounds in the 254-nm wavelength in water.
Zeta potential Potential at the shear plane of a solid and liquid interface.

4.07.1 Fundamentals of Membrane Bioreactor

4.07.1.1 Definition of Membrane Bioreactor

Membrane bioreactor (MBR) is a new type of wastewater treatment technology combining membrane separation process with conventional activated sludge (CAS) treatment process. Due to the fact that the membrane pore size may be below 0.1 μm, MBR can effectively produce a high-quality clarified effluent. The MBR process has received more and more attention because of its advantages such as high removal efficiency for pollutants, space saving, and less sludge production. Membrane filtration ensures that microorganisms are completely trapped into the bioreactor and this gives better control over the biological reactions and modifying the conditions of the microorganisms in the aerated tank. It enables long sludge retention time (SRT) and high mixed liquor suspended solid (MLSS) concentration. In general, the MBR process can be divided into three categories according to the working mechanism: rejection MBR, extractive MBR, and diffusive MBR of which the latter two are new processes still at a developmental stage.[1, 2]. In the past 20 years, most research work related to MBR has been focused on the rejection MBR for water and wastewater treatment with less attention being given to the other two types. Up till now, the MBR process has been successfully applied worldwide, including larger-scale municipal wastewater treatment plants (WWTPs) and small-scale industrial WWTPs. [3, 4].

4.07.1.2 Configurations of MBR

Most researchers usually refer to MBR as rejection MBR, which can be divided into three types according to their configuration.

1. *Submerged/immersed membrane bioreactor* (*referred to as iMBR*). In iMBR, membrane modules are immersed into the bioreactor directly (**Figure 1**). A suction pump is applied to draw the effluent through

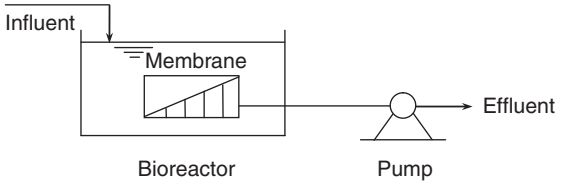


Figure 1 Schematic diagram of immersed membrane bioreactor (iMBR).

the membrane while the sludge is trapped into the bioreactor by the membrane. Air is usually utilized for providing oxygen to maintain aerobic conditions and scouring the membrane surface and clean the exterior of the membrane. The submerged membrane bioreactor (SMBR) is more commonly used than the cross-flow MBR due to less energy-intensive and lower fouling potential.

2. *Cross flow membrane bioreactor* (*referred to as cMBR*). cMBR is the combination of a traditional bioreactor with a membrane filtration device into a single unit process. The membrane module in the MBR is equivalent to the secondary settling tank of conventional biological treatment system, in which solid and liquid are separated, whilst the sludge is returned into the bioreactor and the permeate collected (**Figure 2**). This way, the membrane is easily cleaned *in situ* and operated with high sludge concentration in the MBR reactor.

3. *Hybrid membrane bioreactor*. This is similar to the iMBR system but is filled with some carriers in the reactor. This system is superior to the iMBR one as the carriers can stabilize the treatment process efficiently and reduce the membrane fouling (**Figure 3**).

4.07.1.3 Characteristics of MBR

The MBR process has obvious advantages over conventional wastewater treatment process [2]:

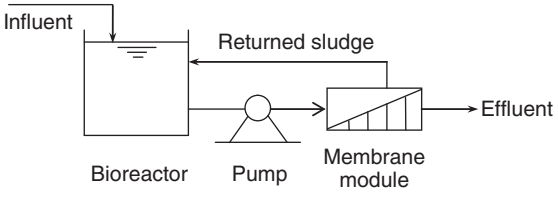


Figure 2 Schematic diagram of cross-flow membrane bioreactor (cMBR).

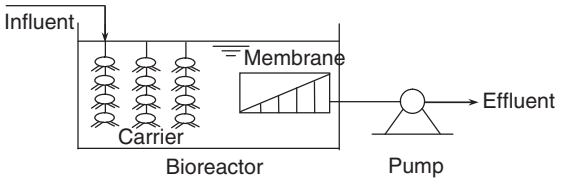


Figure 3 Schematic diagram of hybrid membrane bioreactor (MBR).

1. MBR produces clarified water with high quality. The indicative output quality of MBR systems (microfiltration or ultrafiltration) includes suspended solids (SS) $<1\,mg\,l^{-1}$, turbidity <0.2 NTU (depending on the membrane nominal pore size). Removal of organic matters in MBR comes from two aspects: one is the biodegradation of organic pollutants in the bioreactor; and the other is the membrane filtration of organic matters with high molecular weight.
2. MBR has a smaller footprint. The secondary settling and tertiary sand filtration processes are eliminated, thereby reducing the plant footprint. In certain instances, the footprint can be further reduced because other process units such as ultraviolet disinfection can also be eliminated or minimized.
3. The MBR process, compared with CAS process, enables independent hydraulic retention time (referred to as HRT) and sludge retention time (referred to as SRT), which is difficult to control in CAS system. Solid particles could be held by membrane module in the bioreactor, which can give a better control of SRT and HRT in the system and also improve MBR biodegradation efficiency.
4. MBR can be designed with a long sludge age; hence, low excess sludge production can be achieved, which also promotes the enrichment of nitrifying bacteria, thereby enhancing nitrogen removal.
5. MBR provides a barrier to certain chlorine-resistant pathogens, because the membrane has an effective pore size of less than 0.1 μm – smaller than the pathogenic bacteria and viruses in the sludge.

4.07.2 Design and Operation of Membrane Bioreactor

4.07.2.1 Design of Membrane Bioreactor

At present, there is no mature and systematic method for the design of MBR. For treating a special wastewater with MBR, selecting the design parameter is usually based on the results of bench scale and pilot scale experiment.[5, 6]. This section will summarize and introduce the design process of MBR.

The first step is to choose the configuration of MBR. MBR mainly has two kinds of configurations, SMBR and CMBR, that are normally used. SMBR is

characterized by a small, compact equipment, small work pressure, non-water cycle and low energy consumption. Sludge is difficult to accumulate in the membrane surface and it plugs the membrane pore due to the formation of shear and turbulence during aeration. In general, SMBR is used only for aerobic treatment. In the design, packing density, the use of aeration mode, as well as the location of aeration device placed become key factors. The SRT and HRT of CMBR can be effectively controlled to achieve a higher removal rate of organic matter, whereas, due to a longer SRT, nitrifying bacteria can be enriched. CMBR can be used for aerobic and anaerobic treatments.

There are three segments to be designed in MBR design [7, 8], which will be introduced as follows: the design of bioreactor, the design and selection of membrane module, and the design of aeration equipment will be discussed in that order.

4.07.2.1.1 The design of bioreactor

1. Determination of the organic matter. The sludge loading rate (Ns) in the bioreactor, Ns, referred as the removed amounts of organic matters per unit of sludge quantity and time, is an important control parameter in the process of activated sludge design and operation, which is significanct to guarantee the system treatment efficiency and confirm the reasonable size of the project. In the MBR process, due to the retention of the membrane modules, the bioreactor maintains a very high sludge concentration (5–10 times higher than the CAS process). If a lower Ns is selected, the treatment efficiency in the system is perfect, but there is a relative increase in the footprint of the treatment works and infrastructure investments. However, if a higher Ns is selected, although it reduces the area of treatment works and infrastructure investment, the treatment efficiency may increase. Therefore it is a key issue to choose a reasonable value of Ns in the MBR process design. Generally, Ns in the range of 0.3–0.4 kg COD/ (kg VSS d) is suitable.

2. Determination of the sludge concentration in bioreactor. What value of activated sludge concentration of X is more appropriate is often determined through experiment, due to the difficulty to obtain through theoretical calculations. Many studies suggested the range of X values from 6000 mg L^{-1} to 20 000 mg L^{-1}, depending on the concentration of organic matter in raw water. For treating low concentration organic wastewater, X value use the low value; on the contrary, X value use the high value.

3. Calculation of the volume of the bioreactor in accordance with established Ns and X values, as well as the influent quality and effluent requirements.

$$V = \frac{Q(S_0 - S_e)}{XN_S} \quad (1)$$

where S_o is the influent concentration (mg L^{-1}), S_e is the effluent concentration (mg L^{-1}), X is sludge concentration, Q is the flux, and V is the volume of bioreactor (m^3).

4.07.2.1.2 Membrane module selection and design

1. Selection of the type of membrane modules. In MBR, the membrane is contaminated rapidly because of the high concentration of wastewater passing through it. So, it is crucial to select appropriate antifouling membrane and membrane module.

   Based on the different membrane materials, the membrane is considered as an organic membrane or an inorganic membrane.[9] Common organic membrane materials include polysulfone (PS), polyether sulfone (PES), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyethylene (PE), polypropylene (PP), and so on. Inorganic membranes contain mainly metals, metal oxides, and ceramic materials. Inorganic membranes can overcome some shortcomings of organic membranes, such as chemical stability, excellent mechanical properties, high flux, and resistance to pollutants, ease with which these could be cleaned, etc.

   Nowadays, there are two types of membrane modules used for MBRs, hollow-fiber membrane and tubualr membrane. The former is mainly used for SMBR, while the latter is mainly used for CMBR. Hollow-fiber membrane has the advantage of high packing density, low cost, and high anti-pressure and the disadvantage that these could be easily blocked. With good hydrodynamic conditions, tubualr membrane modules have the advantage that they are not easy to plug, they are easy to clean, and have low pretreatment requirements for liquid, suitable for sewage treatment, but with the shortcoming of high cost.
2. Design of the required number of membrane modules. Calculate the number of membrane modules according to the size and membrane output of water per module and design membrane module package form.

3. Selection and design of the form of flux output. Two forms of flux output from membrane module are used: outside-in and inside-out. In fact, in practical engineering the outside-in MBR is normally used, as the inside-out MBR has the disadvantages of smaller flow channel and being easily blocked.

4.07.2.1.3 Aeration system design

The first component of an aeration system is the bioreactor demand, specifically, that of the mixed liquor required for (a) solids agitation and (b) dissolved oxygen (DO) for maintaining a viable microorganism population for biotreatment. The second component of the aeration system is the demand of membrane unit to scour solids from the membrane surface.

The oxygen requirement to maintain a community of microorganisms and degrade BOD and ammonia and nitrite to nitrate can be found by a mass balance on the system:[10]

$$m_0 = Q(S - S_0) - 1.42P_x + 4.33Q(NO_x) - 2.83Q(NO_x) \quad (2)$$

where m_o is the total oxygen required (g d^{-1}). The first term in Equation (2) refers to substrate oxidation, the second to biomass respiration, the third to nitrification, and the final term to denitrification.

The oxygen requirement to scour solids from the membrane surface is based on previous experience, in many cases the manufacturers recommend an appropriate aeration rate. There are three types of aerations used in MBR plants: coarse-bubble aeration, fine-bubble aeration, and, less commonly, jet aeration.[10]

Finally, an example of a brewery wastewater treatment that illustrates how to design a practical MBR process is presented.

To illustrate the design of an MBR for treating brewery wastewater, consider a brewery wastewater flow 5000 m^3 d^{-1}, influent COD of 1500 mg L^{-1}, and the required effluent COD concentration of less than 60 mg L^{-1}. The design process consists of the following steps:

1. Bioreactor design. In the MBR process, take the Ns as 0.35 kg COD/ (kg MLVSS d) and the sludge concentration as 10 000 mg L^{-1}. The volume (V) of the bioreactor can be calculated as follows:

$$V = \frac{Q(S_0 - S_e)}{XN_S} = \frac{5000 \times (1500 - 60)}{10000 \times 0.35} = 2057\,m^3 \quad (3)$$

The hydraulic retention time (HRT) in MBR is given by

$$HRT = \frac{V}{Q} = \frac{2057}{5000} = 0.41\,d = 9.9\,h \quad (4)$$

The sludge retention time (SRT) is calculated as follows:

$$SRT = \frac{X \times HRT}{0.4 \times (S_0 - S_e - 0.34X \times HRT)} = \frac{10000 \times 0.41}{0.4 \times (1500 - 0.34 \times 10000 \times 0.41} = 223 \quad (5)$$

Based on the calculated SRT, the excess sludge drained from the system should be 9.2 m^3.

2. Choice of membrane module. We consider the use of a polypropylene hollow-fiber membrane module. According to manufacturer information, the stable membrane flux is 0.01–0.012 m^3 m^{-2} h^{-1}, the required total area A of membrane modules calculated based on wastewater amounts is calculated as

$$A = \frac{5000}{24 \times 0.01} = 20833\,m^2 \quad (6)$$

We need 1736 modules, the individual membrane module area being 12 m^2 per module. Twenty-four modules comprising one group, made of frame construction, can be taken out from the bioreactor for cleaning and replacement.

3. Design of aeration system. The aeration system is crucial for MBR operation. In MBR, the aeration system at the bioreactor bottom should be designed for high-efficiency transfer and enough aeration intensity to prevent foulant deposit on membrane surface and lessen membrane fouling. So, a perforation pipe is normally used for aeration mode. The amount of aeration can be calculated in three ways: based on gas-to-water ratio; based on oxygen transfer efficiency; or based on aeration intensity and bioreactor surface area. The last of these is implemented for aeration amount calculation.

According to the experimental results, the aeration intensity of 0.01 m^3 m^{-2} s^{-1} is determined. On the assumption that the water depth is 5 m in the bioreactor, the surface for aeration is 411.4 m^2, and the required amounts of air is 247 m^3 min^{-1}.

Four blowers were selected, three were used and one was for preparation, with each blower gas volume 82.3 m^3 min^{-1}, air pressure 70 kPa, power 80 kW.

4.07.2.2 Operation of Membrane Bioreactor

The operational conditions of MBR play a key role, and optimized operational conditions and parameters

are very conducive to reduce and control membrane fouling. [11–13] The critical flux is an important concept in SMBR. Many researchers [14, 15] focused on the study of critical flux in MBR. Above the critical flux, fouling can be observed; and below that level, the increase of transmembrane pressure (TMP) or the decline of flux with time does not occur. Under subcritical operation, MBRs could achieve long-term stable operation without frequent membrane cleaning. In order to reach better understanding of the operational characteristics and optimize these factors for enhancing the performance and reduce membrane fouling, operational parameters including aeration intensity, the ratio of suction and nonsuction time (intermittent filtration), DO concentration, SRT, HRT, filtration modes, sludge concentration, and temperature were investigated. [16, 17, 18]

4.07.3 Performance of MBR

Compared with conventional water treatment processes, MBR, with high effluent water quality and treatment efficiency, is a more efficient technology and is more beneficial to society and the environment as well as commercially. The main application of MBR is the municipal wastewater treatment, especially the domestic wastewater treatment; however, it is also an attractive option for industrial wastewater treatment, especially in North America, where MBR has more commercial applications. In addition, the applications of MBR for polluted surface water supply have caught the attention of more researchers. Here, we focus on the performance of MBR in several main applications.

4.07.3.1 MBR for Municipal and Domestic Wastewater Treatment

4.07.3.1.1 Organic matter, SS, and other pollutants

In MBR systems, most of the organic matters are decomposed by microorganisms, and the membrane rejection enhances their removal efficiency. In general, the removal efficiencies of COD, BOD, SS, and UV_{254} in MBR systems, especially for the treatment of municipal wastewater, are more than 90%.

In an MBR process, almost all of the SS are removed. As a consequence, the removal of heavy metals and micro-pollutants attached to the SS is also improved. In the past, some work showed that the MBR process is extremely efficient in the removal of bacteria. Many studies demonstrated that viruses are generally much more resistant to disinfection than classical fecal indicator bacteria. However, there is relatively little literature and experience with regard to removal of viruses, which is becoming an important issue in recent years. Some studies indicate that the membrane can reject the virus, and also that the membrane pore size can affect removal efficiency. In addition, the cake layer or the gel layer can also work as a barrier.

4.07.3.1.2 Nitrogen transformation

With high biomass concentrations, better retention of slow-growing microorganisms, such as nitrifiers, can be obtained. MBR has enhanced nitrogen-removal ability and the results are often satisfactory.

Nitrogen-removal processes require both aerobic and anoxic stages. Simultaneous nitrification–denitrification (SND) can occur in the continuously fed MBR system by cyclical (on/off) aeration. Under low DO, diffusional limitation may create an anoxic zone within the biological floc where denitrification can take place. Furthermore, if SND is achieved through the shortened pathway, that is, through nitrites, it is advantageous over conventional nitrogen-removal processes. The advantages of SND via nitrite are reduced aeration, COD, alkalinity requirements, and lower biomass yield.

The factors that influence SND are primarily ambient DO concentration and floc size. The floc sizes in MBR are reported to be smaller than that in CAS despite its high operating MLSS concentration. Up to now, the reported SND studies in MBR are all in anoxic/oxic (A/O) systems operating under intermittent aeration mode. It was observed that the total nitrogen-removal efficiencies of 95% and 83% can be obtained in A/O MBR. In addition, extractive MBR has more potential for nitrogen removal.

4.07.3.1.3 Phosphorus removal

Phosphorus removal is more commonly achieved by dosing with chemicals such as metal coagulants or lime that can form sparingly soluble precipitates. However, biological technology without additional chemicals is a more environmental and economized technology. Most wastewaters treated by biological processes are carbon available, but phosphorus is not significantly removed. Membrane rejection may have little effect on phosphorus removal. Some improvements have been made for biological phosphorus removal, for example, anaerobic zone was added at

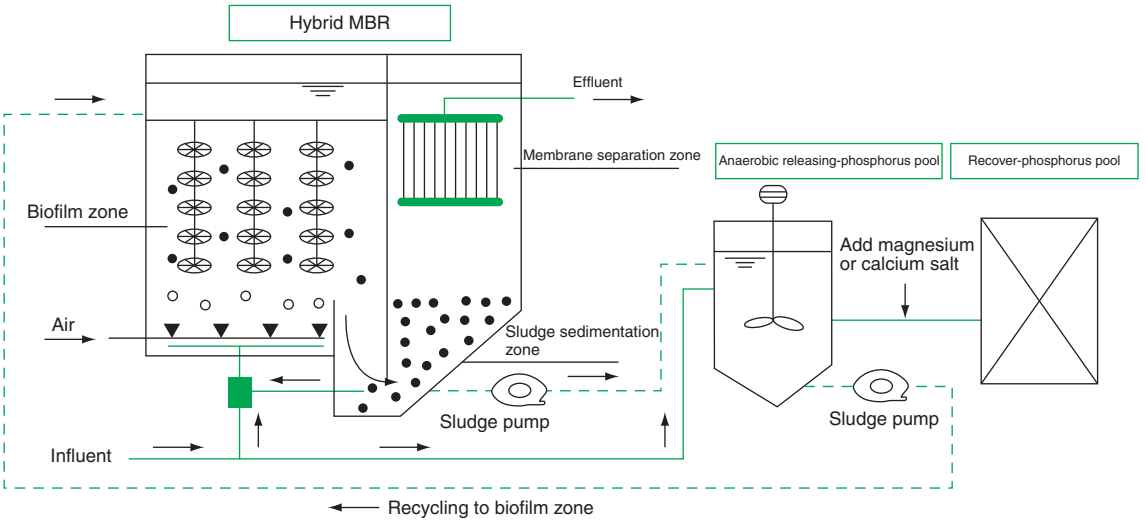


Figure 4 Extra-cycle sludge – hybrid membrane bioreactor (MBR) for nitrogen and phosphorus recovery process (Zhang, China patent, ZL200610009693).

the front of an activated sludge plant and nitrate-free sludge from the aerobic zone was the result [19].

The process of de-nitrification and phosphorus recovery by using hybrid MBR is based on MBR technology that, filling as biofilm carrier, is placed in the reactor, as shown in **Figure 4**. In this hybrid MBR system, it provides an anoxic microenvironment formed with biofilm and suspended and activated sludge Zoogloea in a high concentration. Nitrogen removal is accomplished by the process of synchronous nitrification and de-nitrification in the same reactor. Simultaneously, it transfers phosphorus-rich sludge to the anaerobic zone by extra cycling to achieve phosphorus release, and then the phosphorus is recycled by chemical precipitation or crystallization.

4.07.3.2 MBR for Industrial Wastewater Treatment

In the 1980s, a few researchers and system suppliers in North America investigated the MBR process for the treatment of industrial wastewater [3]. Due to the increased research and commercial applications of industrial wastewater treatment, MBR processes have been popular in industrial wastewater treatment particularly toxic and refractory wastewater [20], but the scale is much smaller. The type of MBR preferable for industrial wastewater treatment is the external configuration that is easy to clean and disassemble. Numerous MBR systems were applied in various industrial wastewater streams including food-processing wastewater, petrochemical wastewater, hospital wastewater, printing and dyeing wastewater, and slaughterhouse wastewater.

Apart from sharing some similar properties with municipal wastewater, industrial wastewater has more special properties, which include more difficult-to-dispose pollutants or some special pollutants such as heavy metals and micro-pollutants. In some actual cases, the MBR system showed higher removal efficiencies for these pollutants than that shown by CAS system [21, 22].

The MBR system was very efficient in removing pollutants from petrochemical wastewater. When it was used for olefin process wastewater treatment, 90% of total organic carbon (TOC) and COD removal was achieved. For complicated petrochemical wastewater, the removal of TOC and COD was up to 92% and 83%, respectively [21]. For heavy metal, the removal rate of chromium, zinc, and lead can be up to 95%, 60%, and 62%, respectively [22]. In the bioreactor, the ability of complete solid retention and the maintenance of a more diverse microbial culture could make MBR provide a suitable environment for endocrine disrupter chemical (EDC) biodegradation [3, 23].

4.07.3.3 MBR for Drinking Water Treatment

MBRs offer a more integrated approach so it is practical to develop this technology as an effective water

treatment process for polluted water supplies. MBRs could combine conventional water treatment operations including coagulation, flocculation, sedimentation, filtration, and disinfection, into one unit. For treating water of a specific quality, MBR could be combined with some special processes such as advanced oxidation processes (AOPs), bioactivated carbon, and PAC, although very limited literature could be found on this subject as such applications are fairly new.

4.07.3.3.1 Organic carbon and nitrogen

As a result of economic development and lack of enough supervision , domestic and industrial wastewaters have been discharged into natural water bodies without sufficient treatment, which has led to serious pollution of the surface water supplies in some areas, with organics and ammonia nitrogen (NH_3–N) as the main pollutants [24]. As nitrate is water soluble and does not bind to soil, it is more likely that it will migrate into drinking water sources. Worldwide, nitrate in groundwater used for drinking water exceeds the maximum contaminant limits. Therefore, nitrogen and pollutant removal become essential for safe water supply; and as an innovative and promising process, MBR technology should be availed so as to use its advantages on drinking water treatment.

From the literature in this field, it seems that the conclusions of some studies are controversial. By using submerged MBR for treating simulated polluted surface water, Li and Chu [25] achieved over 60% of TOC removal and 95% of ammonia removal; Tian *et al.* [24] achieved less than 50% TOC removal and near 90% ammonia removal. However, on the other hand, some studies have shown unfavorable results. Therefore, it can be concluded that MBR is not stable enough for drinking water treatment and can be improved with integrated technology. It does, however, have a good performance of near 100% for the elimination of turbidity. The application of MBR for drinking water de-nitrification is just at the research and development stage [2]. Like the MBR wastewater treatment, a novel extractive MBR has the potential to overcome the limitations of conventional biological de-nitrification systems for drinking water treatment.

4.07.3.3.2 Micro-pollutants

Micro-pollutants can be effectively removed by AOP, so MBR in combination with AOP can ensure the safety of water supply. Williams and Rirbazari [26] found that MBR was effective for the removal of biodegradable organic matter (BOM) and trihalomethane precursors when combined with ozone and PAC. With MBR treatment, Li *et al.* [25] achieved around 75% reduction of the 3-day trihalomethane formation potential (THMFP), and the biostability of the effluent improved considerably as the assimilable organic carbon (AOC) decreased by 80%. However, Tian *et al.* [24] were not able to obtain good results in their attempts at removing the AOC.

In addition, the membrane biofilm reactor (MBfR), which uses hydrogen as an electron donor, is ideal for treating oxidized compounds in drinking water. Nerenberg and Rittmann [27] tested a hydrogen-based, hollow-fiber MBfR for the reduction of perchlorate, chlorate, chlorite, bromate, chromate, selenate, selenite, arsenate, and dichloromethane, and the best removal efficiency it could achieve was >98%, >95%, >75%, >95%, >75%, 67%, 93%, >50%, and 38%, respectively.

4.07.4 Cause and Control of Membrane Fouling

MBR has many advantages over conventional wastewater treatment systems and enables high pollutant removal efficiency. It can produce much higher quality effluents through retaining soluble microbial products (SMPs) in the system. However, membrane fouling is a major obstacle to the wide use of MBR. Moreover, subsequent membrane cleaning and associated costs are also of high concern to MBR users. Membrane fouling has been related to sludge concentration, supernatant characteristics, and intermittent operation.

An understanding of the fouling mechanisms is important for controlling membrane fouling, including the characteristics of the constituents that cause membrane fouling in MBRs and the factors of fouling.

4.07.4.1 Fouling Cause of MBR

4.07.4.1.1 Mechanism of membrane fouling

Membrane fouling is a barrier to the wide implementation of MBR. It could be termed a reduction of permeate flux under conditions of constant transpressure. As shown in **Figure 5**, the membrane

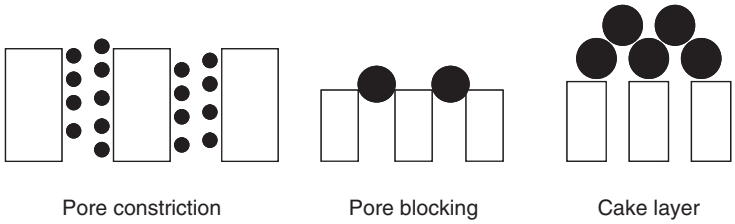


Figure 5 Membrane fouling in membrane bioreactor (MBR).

fouling in MBR is attributable to membrane pore constriction, pore blocking, and cake layer formation by sludge particles, colloids, and solutes.

MBR is usually operated under critical flux conditions because fouling rate increases almost exponentially operating above critical flux. But even subcritical flux operation can lead to fouling, according to a two-stage pattern: a low TMP increase over an initial period followed by a rapid increase after some critical time period, but an initial short-term rapid rise in TMP is observed. Therefore, a three-stage fouling process is proposed [28, 29]:

stage 1: an initial short-term rapid rise in TMP;
stage 2: a long-term weak rise in TMP; and
stage 3: a sharp increase in dTMP/dt, also known as TMP jump.

Figure 6 shows the schematic diagram of the TMP jump [28]. The TMP jump is believed to be the consequence of severe membrane fouling. Cho and Fane [30] attributed the TMP jump to the changes in the local flux due to fouling, which cause local fluxes to be higher than the critical flux. Zhang *et al.* [29] reported that the sudden jump was possibly not only due to the local flux, but also caused by sudden changes of the biofilm or cake layer structure. More EPS had been released from the biofilm due to limited oxygen transfer to it [31].

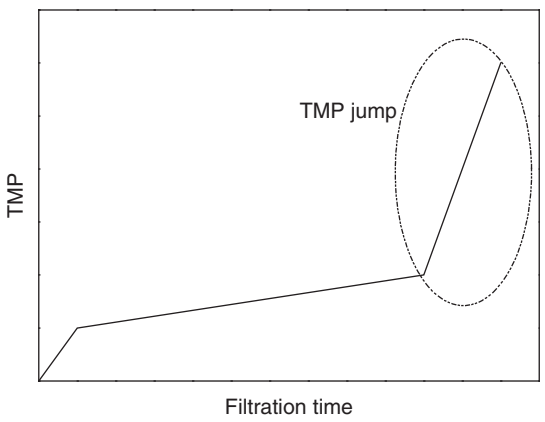


Figure 6 Schematic diagram of the transmembrane pressure (TMP) jump. Adapted from Meng (2009).

With respect to MBR, membrane fouling occurs due to the following mechanisms [28]:

1. adsorption of solutes or colloids within membranes;
2. deposition of sludge flocs onto the membrane surface;
3. formation of a cake layer on the membrane surface;
4. detachment of foulants attributed mainly to shear forces; and
5. the spatial and temporal changes of the foulant composition during the long-term operation.

4.07.4.1.2 Species of membrane foulants

Membrane fouling can be defined as the undesirable deposition and accumulation of microorganisms, colloids, and cell debris within membranes or on the surface of the membrane. Given the complex nature of the activated sludge, it is not surprising that the fouling behavior in MBR is more complicated than that in most membrane applications. Membrane fouling in MBR can be divided into two categories: physically reversible fouling which can be eliminated by physical membrane cleaning such as backwashing or surface cleaning, and physically irreversible fouling which cannot be eliminated by physical membrane cleaning. Although most of the recent research activities have been focused on the mechanism of membrane fouling, the control of irreversible fouling is the most important task for reducing the operation cost and keeping long-term and sustainable operation of MBR. Depending on the fouling components, the fouling can be classified into three major categories: biofouling, organic fouling, and inorganic fouling.

Biofouling refers to the deposition, growth, and metabolism of bacteria cells or flocs on the membranes, which has aroused a significant concern in membrane filtration processes [32]. For a low-pressure membrane, such as microfiltration and ultrafiltration for wastewater treatment, biofouling is a major problem because most foulants in MBR are much larger than the membrane pore size. Biofouling is derived from two situations – one is the deposition of individual cell or cell cluster on the membrane surface, another is the cells multiplying and forming a biocake. Many researchers suggest that SMP and EPS secreted by bacteria also play important roles in the formation of biological foulants and cake layers on membrane surfaces [33]. They also report that the microbial communities on membrane surfaces were quite different from those in the suspended biomass. The Betaproteobacteria, probably plays a major role in the development of mature biofilm, which leads to severe irremovable membrane fouling. Nevertheless, Jin [34] reported that γ-Proteobacteria is the more problematic species than other microorganisms and the deposited cells have higher surface hydrophobicity than the suspended sludge.

Organic fouling (main focus on EPS and SMP) in MBR refers to the deposition of biopolymers (proteins and polysaccharides) on the membranes. Metzger *et al.* [35] have done a more detailed study to characterize deposited biopolymers in MBR. After membrane filtration, the fouling layers were fractionated into upper, intermediate, and lower layers by using rinsing, backwashing, and chemical cleaning. The results showed that the upper fouling layer was composed of a porous, loosely bound cake layer with a similar composition as the sludge flocs. The intermediate fouling layer was contributed equally by SMP and bacteria aggregates and had a high concentration of polysaccharides. The lower layer, representing the irremovable fouling fraction and predominated by SMP, had a relatively higher concentration of bound proteins. This study revealed the spatial distribution of biopolymers on the membrane surface. Fourier transform infrared (FTIR) spectroscopy, ultraviolet–visible spectrometry, excitation emission spectroscopy (EEM), solid-state ^{13}C-nuclear magnetic resonance (NMR) spectroscopy, and high-performance size-exclusion chromatography (HP-SEC) are important analytical tools for the investigation of organic fouling. These studies confirm that SMP or EPS is the origin of organic fouling and plays important roles in the development of MBR fouling.

Inorganic fouling has been mentioned by only a few papers. Kang *et al.* [36] investigated the filtration characteristics of organic and inorganic membranes in a membrane-coupled anaerobic bioreactor, in which a thick cake layer composed of biomass and struvite formed on the membranes (specially on the inorganic membrane surface). The organic foulants coupled with the inorganic precipitation enhanced the formation of a cake layer. These findings indicate that inorganic fouling has become increasingly important in MBR. However, the understanding of inorganic fouling is still not clear and is a promising research problem.

4.07.4.2 Fouling Control of MBR

All the parameters involved in the design and operation of MBR processes have an influence on membrane fouling. However, the extent of fouling is strongly influenced by four factors (**Figure 7**): membrane characteristics, biomass characteristics, feedwater characteristics, and operational conditions [37].

TMP jump occurs inevitably during the long-term operation of MBRs under the mode of constant flux. Thus, the overall goal of fouling control is to alleviate the occurrence of the TMP jump.

Based on the factors influencing the membrane fouling, several methods have been proposed to control/alleviate membrane fouling.

4.07.4.2.1 Pretreatment of feedwater

Pretreatments of feedwater can alter the physical, chemical, and biological properties of feedwater and improve the performance of the MBR process. Three mechanisms have been summarized by Huang *et al.* [38]:

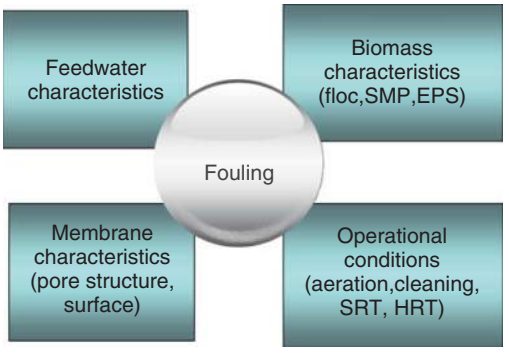


Figure 7 Factors influence membrane fouling.

- *Physical mechanisms*. Pretreatment can increase the size of aquatic substances to the level separable by the membrane, thereby enhancing their removal by the integrated membrane system. The size increase also shifts membrane fouling from pore constriction or blocking to cake filtration that is usually less severe and more reversible.
- *Chemical mechanisms*. Different chemicals (coagulants, oxidants, and adsorbents) can be added to the feedwater to alter water chemistry and reduce the affinity of foulants to membrane surfaces, thereby alleviating irreversible membrane fouling.
- *Biological mechanisms*. Pretreatment can remove biodegradable compounds relevant to membrane fouling or treated-water quality, or disinfect feedwater to reduce biofilm formation.

The major pretreatments of feedwater employed at full-scale filtration facilities include coagulation, adsorption, and oxidation. Huang *et al.* [38] has described the mechanism of different pretreatment methods, including advantages and disadvantages.

4.07.4.2.2 Modification of biomass characteristics

Bound EPS, SMP, and secretion from biomass exist in the MBR systems, which are regarded as the main foulants. SMP and EPS can accumulate on the membranes or penetrate into membrane pores. Accumulation and detachment of membrane foulants are determined by particle convection toward the membrane surface and the back transport rate of the deposited particles from membrane surface into the bulk. The back transport mechanisms in membrane filtration include inertial lift, shear-induced diffusion, and Brownian diffusion.

In addition, attempts have been made to modify biomass by using ultrasound, ozone, electric field, and magnetic enzyme carrier [39, 40]. Experimental results showed that ultrasound could control membrane fouling effectively, although membrane damage may occur under some operation conditions [41]. A magnetic enzyme carrier was applied to the lab-scale MBR in a continuous operation; it enhanced the membrane permeability to a larger extent compared with a conventional MBR with no enzyme [39]. Another interesting method is the use of an electric field, which could prevent the sludge flocs and colloids depositing onto the membrane surface [42].

Based on the characteristics of biomass, more and more methods may be developed in the future.

4.07.4.2.3 Optimization of operational conditions

Operation below the critical flux is an effective approach to avoid severe fouling, including reversible and irreversible fouling. This concept is called subcritical flux or nonfouling operation and is expected to lead to little irreversible fouling. The critical flux value depends on membrane characteristics, operating conditions (i.e., aeration intensity, temperature, etc.), and sludge characteristics. The concept of optimization of operation conditions in MBR, which could control the critical flux value, has been popularly used in the study of MBR fouling.

Since membrane fouling, especially irreversible fouling, plays an important role in long-term operation of MBRs, sometimes chemical cleaning is required to maintain MBR operation. However, chemical cleaning for the elimination of irreversible fouling should be limited to a minimum frequency because repeated chemical cleaning may shorten the membrane life span and the disposal of spent chemical agents will cause environmental problems.

Aeration used in MBR systems has three major roles: providing oxygen to the biomass, maintaining the activated sludge in suspension, and mitigating fouling by constant scouring of the membrane surface. The use of gas bubbling to enhance membrane processes, and MBRs in particular, has been thoroughly investigated and reviewed [43].

Additionally, SRT, HRT, F/M, and other operational parameters all have different influences on membrane fouling of MBR.

4.07.4.2.4 Exploration of new membrane materials

Membrane characteristics such as pore size, porosity, surface charge, roughness, and hydrophilicity/hydrophobicity have an impact on MBR performance, especially on membrane fouling. The membrane materials always show different fouling properties due to their different pore sizes, morphology, and hydrophobicity. Polyvinylidene fluoride (PVDF) membrane is superior to polyethylene (PE) membrane in preventing irreversible fouling of MBRs used for the treatment of municipal wastewater. The affinity capability of the three membranes was of the order: polyacrylonitrile (PAN) < PVDF < polyethersulfone (PES). It suggests

that among these membranes the PAN membrane is the most fouling-resistant of the three.

In general, membrane fouling occurs more readily on hydrophobic membranes than on hydrophilic ones because of the hydrophobic interaction between foulants and membranes. As a result, much attention has been given to reduce membrane fouling by modifying hydrophobic membranes into relative hydrophilic membranes.

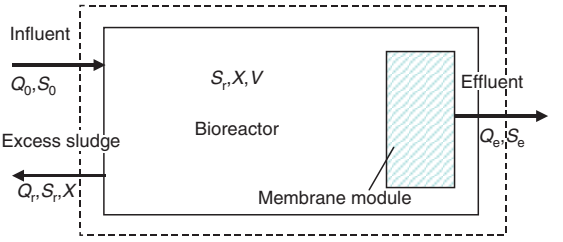


Figure 8 Material balance in submerged membrane bioreactor (SMBR).

4.07.5 Models of MBRs

Due to the emergence and popularity of MBRs, consisting of external configuration and submerged configuration for membrane modules, accurate prediction and simulation of the whole MBR process are becoming ubiquitous and significant for many membranologists, especially in water treatment systems. Models of membrane bioreactor could be an effective and accurate measurement to uncover MBR. Generally, the MBR models are classified into four categories: organics removal model, biomass kinetic models, membrane fouling models, and integrated models with the above couplings to describe the complete MBR [44].

4.07.5.1 Organics Removal Model

In an SMBR system, the kinetic characteristics of organic substrate degradation are different from that in CAS system because of the following reasons. First, an MBR can retain almost all microbes in the bioreactor, which leads to the retention of high sludge concentration, so the organic-sludge load is very low. In addition, the microorganisms in the reactor degrade the organic substrate mainly to maintain their activity due to high sludge concentration and low organic-sludge load. Moreover, the MBR can also retain the SMP in the reactor, which is degraded further as organic substrate. According to the practical characteristics of SMBR it is necessary to establish the model for removing organic substrate to give reference for the design of SMBR system.

The material balance in submerged membrane bioreactor is shown in **Figure 8**.

According to **Figure 8**, Equation (1) is used to describe the mass balance for the organic substrate in the reactor:

$$Q_0 S_0 = Q_e S_e + Q_r S_r + U_y V + V \frac{dS_r}{dt} \quad (1)$$

where Q_0 is the influent flow rate ($m^3\,d^{-1}$), S_0 is the influent organic substrate concentration ($mg\,l^{-1}$), Q_e is the effluent flow rate ($m^3\,d^{-1}$), S_e is the effluent organic substrate concentration ($mg\,l^{-1}$), Q_r is the excess sludge discharging rate ($m^3\,d^{-1}$), U_y stands for the organic substrate removal rate ($mg\,l^{-1}\,d^{-1}$), V is the effective volume of the bioreactor (m^3), and dSr/dt stands for the organic substrate variation rate in the reactor ($mg\,l^{-1}\,d^{-1}$).

The organic substrate variation rate in the reactor can be neglected when the system is in a steady-state condition. Associated with Equations (2) and (3), Equation (1) is equal to Equation (4), and Equation (4) can be changed to Equation (5). Equation (2)–(4) are shown as follows:

$$Q_0 = Q_e + Q_r \quad (2)$$

$$S_r = S_e + S_m \quad (3)$$

$$Q_0(S_0 - S_e) = Q_r S_m + U_y V \quad (4)$$

$$U_y = \frac{Q_0(S_0 - S_e)}{V} - \frac{Q_r S_m}{V} \quad (5)$$

where S_m stands for the organic substrate concentration removed by membrane module ($mg\,l^{-1}$).

With the following substitution

$$t_H = \frac{V}{Q_0}, t_S = \frac{V}{Q_r} \quad (6)$$

where t_H is defined as hydraulic retention time of the wastewater in the reactor and t_S is defined as SRT, Equation (5) can be changed to Equation (7), namely the model of removing organic substrate for SMBR system, and the abbreviation ROM model for short.

$$U_y = \frac{S_0 - S_e}{t_H} - \frac{S_m}{t_S} \quad (7)$$

According to the model developed by Wisniewski *et al.*, [15] the organic substrate removal rate in steady state for an SMBR system is determined only by organic substrate concentrations of the influent and

effluent and the HRT of the reactor. Wisniewski's model is based on the concept that the organic substrate concentration of the effluent is the same as that remaining in the reactor, but researchers have found that it is not so and can differ, sometimes significantly. However, according to the ROM model, the conclusion is that the organic substrate removal rate U_y is determined not only by the organic substrate concentrations of the influent and effluent and the HRT of reactor but also by the organic substrate concentration removed by membrane modules and SRT when the SMBR system is under a steady state.

4.07.5.2 Biomass Kinetics Models

Biomass kinetics models encompass the activated sludge model (ASM) family, SMP model, and a hybrid of ASM and SMP models [45].

The main difference between CAS biological system and MBR is the separation module of the effluent and activated sludge, which is the membrane for MBR separation while being the secondary clarifier for conventional biological treatment separation. Therefore, CAS systems from the ASM family model are suitable for the biomass kinetics in the MBR system.

The ASMs consist of ASM no.1, ASM no.2, ASM no.2d, and ASM no.3, according to the International Water Association (IWA). ASM no.1 was first introduced for the design and operation of the biological wastewater treatment process in 1987. The others are expanded and improved versions of the first model, devised in later years: ASM no.2 incorporated phosphorus removal from wastewater; ASM no.2d accounted for the ability of phosphorus-accumulating organisms to use cell internal substrates for de-nitrification and ASM no.3 did not include phosphorus removal but addressed problems found in ASM no.1.

Therefore, the four ASM models have their highlights individually. ASM no.1 is commonly used to simulate the process of organic matter removals, nitrification, and de-nitrification in activated sludge system, in which autotrophs and heterotrophs act as nitrifiers and de-nitrifiers accordingly. ASM no.2 incorporates a group of organisms, capable of accumulating phosphorus in the form of internal cell materials, into ASM no.1. The phosphorus-accumulating organisms (PAOs) are able to transform the external soluble phosphates into polyphosphates (X_{PP}) or polyhydroxyalkanoates (X_{PHA}) of internal cell materials. The growth of PAOs in aerobic conditions depends on the storage and consumption of X_{PHA}, while the hydrolysis of X_{PP} affords the energy for X_{PHA} storage. In contrast, ASM no.2d illustrates the growth of PAOs under anaerobic conditions, meanwhile including the denitrification. In ASM 3 model, heterotrophs focus on the storage, not hydrolysis of organic substrates, due to which heterotrophic growth is not determined by external compounds.

Due to higher concentration of activated sludge retained, higher SRT and lower F/M ratio in MBR, it is not wise to ignore the formation of SMPs in the effluents. SMPs are typically divided into two categories: biomass associated products (BAPs), associated with biomass decay, and utilization associated products (UAPs), associated with substrate uptake and biomass growth [46].

A model of SMPs formation–degradation may offer a reasonable approach for the performance of the MBR process [18]. The model accounts for the formation and exchange of SMPs between heterotrophs and nitrifiers, which are known to compete with each other for dissolved oxygen. Nitrifiers can also supply potential energy to heterotrophs. They chemically reduce inorganic carbon to organic carbon in the form of cell mass and SMPs and make organic substrate available for the growth of heterotrophs.

One advantage of the SMP model over ASMs is its capability to accurately model biomass in MBRs without the need for calibration using experimental data. Therefore, the hybrid of ASMs and SMP models are promising. The SMP concept has been incorporated into ASM no.1, ASM no.2, and ASM no.3 in MBR studies.

4.07.5.3 Membrane Fouling Models

According to the factors on membrane fouling, empirical hydrodynamic model, fractal permeation model, and sectional resistance model become the three important models in MBR system for wastewater treatment.

The empirical hydrodynamic model shows the correlation of various hydrodynamic parameters to membrane fouling rate and mixed liquor cross-flow velocity. Aeration is crucial for membrane fouling rate and cross-flow velocity, when bubbles rising in the reactor scour the membrane surface attenuating fouling layer formation.

The fractal permeation model [47] evaluates the permeability of the cake formed from the filtration of

activated sludge. The microstructure of a cake layer is usually disordered and complicated, which cannot be described by traditional geometry. Fractal theory can be applied to characterize the irregular object in terms of its average, self-similar properties.

By dividing the membrane into different sections and considering the resistance in each section, the sectional resistance model accounts for uneven cake formation stemming from varying shear distribution along the membrane surface. In this model, the total resistance comprises pore fouling resistance, sludge layer formation, and dynamic sludge film coverage. The dynamics of biomass attachment and detachment from membrane surface are incorporated in this model.

4.07.5.4 Integrated Models

MBR biochemical conditions have an effect on membrane fouling and biomass materials (SMP, etc.) have been attributed to be the main MBR foulants. The integrations of biomass kinetics models and membrane fouling models are ubiquitous and reasonable. ASM no.1-SMP hybrid/resistance-in-series model and ASM no.3/resistance-in-series model have been reported. The resistance-in-series model is adapted to account for the influence of the biomass on membrane fouling.

Models that can accurately describe the MBR process are valuable for the design, prediction, and control of MBR systems.

4.07.6 Further Challenges of Membrane Bioreactor

Although the exploration of MBRs has proceeded substantially in the past 20 years, MBR is also facing several challenges, including MBR market share, MBR standardization, membrane fouling, membrane life-span, costs and full-scale operational experiences. If these challenges can be resolved by the research communities and organizations, MBRs will undoubtedly achieve much wider application. Several challenges [48] are shown as follows:

1. Further understanding of the mechanisms of membrane fouling and development of more effective and easier methods to control and minimize membrane fouling;
2. Increasing membrane life (increasing membrane's mechanical and chemical stability, improving cleaning strategies);
3. Reducing the cost, including membrane module cost, maintenance and cleaning cost, on cost of membrane replacement, energy requirements and labor requirements;
4. Developing full scale plants and rationalization of systems.

References

[1] Stephenson, T., Judd, S., Jefferson, B., Eds. *Membrane Bioreactors for Wastewater Treatment*; IWA Publishing: London, 2000.
[2] Judd, S. *The MBR Book: Principles and Applications of Membrane Bioreactors in Water and Wastewater Treatment*; Elsevier: Oxford, 2006.
[3] Yang, W., Nazim, C., John, I. *J. Membr. Sci.* **2006**, *270*, 201–211.
[4] Judd, S. J. *Trends Biotechnol.* **2008**, *26*, 109–116.
[5] Fane, A., Chang, S., Chardon, E. *Desalination* **2002**, *146*, 231–236.
[6] Shim, J., Yoo, I., Lee, Y. *Process Biochem.* **2002**, *38*, 279–285.
[7] Sofia, A., Ng, W., Ong, S. *Desalination* **2004**, *160*, 67–74.
[8] Wei, C., Huang, X., Zhao, S. *China Water and Wastewater (in Chinese)* **2004**, *20*, 10–13.
[9] Yu, H., Xu, Z., Yang, Q. *J. Membr. Sci.* **2006**, *281*, 658–665.
[10] Metcalf and Eddy, Inc *Wastewater Engineering: Treatment and Reuse*, 4th edn.; McGraw-Hill: New York, 2003.
[11] Yoon, S. *Water Res.* **2003**, *37*, 1921–1931.
[12] Zheng, X., Liu, J. *Water Sci. Technol.* **2005**, *52*, 409–416.
[13] Wang, Z., Wu, Z., Yu, G. *J. Membr. Sci.* **2006**, *284*, 87–94.
[14] Yu, K. C., Wen, X. H., Bu, Q. *J. Membr. Sci.* **2003**, *224*, 69–79.
[15] Ognier, S., Wisniewski, C., Grasmick, A. *J. Membr. Sci.* **2004**, *229*, 171–177.
[16] Zhang, J., Chuan, C., Zhou, J. *Sep. Sci. Technol.* **2006**, *41*, 1313–1329.
[17] Jin, Y., Lee, W., Lee, C. *Water Res.* **2006**, *40*, 2829–2836.
[18] Tay, J., Zeng, J., Sun, D. *Sep. Sci. Technol.* **2003**, *38*, 851–868.
[19] Zhang, L., Li, F., Lv, B. *J. Harbin Inst. Technol.* **2005**, *4*, 322–329.
[20] Wang, Z., Wu, S., Mai, C. *Sep. Purif. Technol.* **2008**, *62*, 249–263.
[21] Llop, A., Pocurull, E., Borrull, F. *Water Air Soil Pollut.* **2009**, *197*, 349–359.
[22] Moslehi, P., Shayegan, J., Bahrpayma, S. *Iran. J. Chem. Eng.* **2008**, *5*, 33–38 (IAChE).
[23] Clara, M., Strenn, B., Ausserleitner, M. *Water Sci. Technol.* **2004**, *50*, 29–36.
[24] Tian, J., Liang, H., Nan, J., *et al. Chem. Eng. J.* **2009**, *148*, 296–305.
[25] Li, X. Y., Chu, H. P. *Water Res.* **2003**, *37*, 4781–4791.
[26] Williams, M. D., Pirbazari, M. *Water Res.* **2007**, *41*, 3880–3893.
[27] Nerenberg, R., Rittmann, B. E. *Water Sci. Technol.* **2004**, *49*, 223–230.
[28] Meng, F., Chae, S., Drews, A. *Water Res.* **2009**, *43*, 1489–1512.
[29] Zhang, J., Chua, H. C., Zhou, J. *J. Membr. Sci.* **2006**, *284*, 54–66.
[30] Cho, B. D., Fane, A. G. *J. Membr. Sci.* **2002**, *209*, 391–403.

[31] Hwang, B. K., Lee, W. N., Yeon, K. M. *Environ. Sci. Technol.* **2008**, *42*, 3963–3968.
[32] Pang, C. M., Hong, P., Guo, H. *Environ. Sci. Technol.* **2005**, *39*, 7541–7550.
[33] Flemming, H. C., Schaule, G., Griebe, T., Schmitt, J. *Desalination* **1997**, *113*, 215–225.
[34] Jin, P., Fukushi, K., Yamamoto, K. *Sep. Sci. Technol.* **2006**, *41*, 1527–1549.
[35] Metzger, U., Le-Clech, P., Stuetz, R. M. *J. Membr. Sci.* **2007**, *301*, 180–189.
[36] Kang, I. J., Yoon, S. H., Lee, C. H. *Water Res.* **2002**, *36*, 1803–1813.
[37] Le-Clech, P., Chen, V., Fane, T. A. G. *J. Membr. Sci.* **2006**, *284*, 17–53.
[38] Huang, H., Gschwab, K., Jacanglo, J. *Environ. Sci. Technol.* **2009**, *43*, 3011–3019.
[39] Minyeon, K., Haklee, C., Kim, J. *Environ. Sci. Technol.* **2009**, *43*, 7403–7409.
[40] Kyung, M., Cheong, W., Oh, H. *Environ. Sci. Technol.* **2009**, *43*, 380–385.
[41] Wen, X., Sui, P., Huang, X. *Water Sci. Technol.* **2008**, *57*, 773–779.
[42] Chen, J.-P., Yang, C.-Z., Zhou, J.-H. *Chem. Eng. J.* **2007**, *128*, 177–180.
[43] Hong, S. P., Bae, T. H., Tak, T. M. *Desalination* **2002**, *143*, 219–228.
[44] Aileen, N. L., Ng, A. *Desalination* **2007**, *212*, 261–281.
[45] Wintgens, T., Rosen, J., Melin, T. *J. Membr. Sci.* **2003**, *216*, 55–65.
[46] Jiang, T., Myngheer, S., Dirk, J. W. *Water Res.* **2008**, *42*, 4955–4964.
[47] Meng, F., Zhang, H., Li, Y. *J. Membr. Sci.* **2005**, *262*, 107–116.
[48] Howell, J. *Desalination* **2004**, *162*, 1–11.

4.08 Membrane Technology: Latest Applications in the Refinery and Petrochemical Field

P Bernardo, Institute on Membrane Technology, ITM-CNR, at University of Calabria, Rende (CS), Italy

E Drioli, Institute of Membrane Technology, ITM-CNR, University of Calabria, Rende (CS), Italy

4.08.1 Introduction

The petrochemical industry has to meet today much more stringent environmental standards, combined with the necessity of reducing also production costs. The process-intensification strategy, which involves innovative design and process development methods aimed at decreasing equipment size, raw materials and energy utilization, and waste generation will have to be considered also in this intensive sector [1]. An effective approach to implement the process-intensification strategy is represented by the modern membrane engineering. Membrane operations and their combination in integrated systems represent already a successful strategy for solving, for example, the freshwater demand in many regions: membranes are 10 times more energetically efficient than thermal operations for water desalination [2]. Membrane processes have several advantages than many conventional separation techniques (e.g., distillation, extraction, absorption, and adsorption). No energy-intensive phase changes or potentially expensive adsorbents and/or difficult-to-handle solvents are needed for membrane separations systems, which are also compact and easy to scale up, fully automated, and with no moving parts. Moreover, modern membrane operations are of interest not only in molecular separations, but also in chemical transformations (membrane reactors) and in the optimization of mass and energy transport between different phases (membrane contactors). These innovative unit operations offer new opportunities for a novel greener engineering.

The most important membrane application in the petroleum industry, currently, is hydrogen recovery in refineries and chemical plants (process designs by Medal/Air Liquide, Air Products and UOP). Membranes are also being used for recovery of olefins such as ethylene and propylene in polyolefin production. Newer developed applications include solvent recovery in lube oil manufacturing (MaxDeWax process licensed by ExxonMobil and developed jointly by Grace Davison and ExxonMobil). A most likely area for successful application of membranes in refineries will be removal of aromatics from gasoline. However, the move of a new technology from lab scale to final industrialization is quite complicated. Implementation of large-scale membrane systems can provide significant benefits to the energy-intensive refining/petrochemical industry.

Current research trends and recent progresses in this field are addressed in this review. Membrane systems are discussed outlining their implications at different levels in the process-intensification logic.

4.08.2 Membrane Gas Separation in the Petrochemical Field

Membrane gas separation (GS) is a pressure-driven process with different industrial applications that represent only a small fraction of the potential applications in refineries and chemical industries [3]. Membrane GS is rapidly becoming a competitive separation technology since 1980, when the industrial production of polymeric membranes was implemented. Membrane GS does not require a phase change. The absence of moving parts makes GS systems particularly suited for remote locations where reliability is critical; in addition, the relatively small footprint/weight make them very attractive for offshore gas-processing platforms.

4.08.2.1 Nitrogen Production in Oil-and-Gas Industry

Nitrogen production by membrane systems has been a great success and today is the largest GS process in use. Nitrogen is used most extensively in the oil-and-gas industry to ensure fire and explosion safety during transportation, trans-shipment, and storage of hydrocarbons, as well as for testing, purging pipelines, and vessels of explosive vapors. A technological breakthrough in nitrogen production occurred in the early 1980s, when membrane systems were industrially introduced to produce nitrogen from atmospheric air. Membrane-based systems present high reliability, low dimensions and weight, and minimum pretreatment.

4.08.2.2 Hydrogen Recovery in Refineries

There are different opportunities within a refinery to recover hydrogen, since it is a valuable by-product, 3 times more valuable if recovered rather than if used as fuel [4]. Hydrogen recovery is a key strategy to meet the increased demand of hydrogen for hydrotreating (to remove sulfur) and hydrocracking (to convert heavy hydrocarbons to lighter, higher-value fuels). These processes produce a residual gas, which contains a significant amount of hydrogen at pressure and, therefore, membranes provide an economical recovery and recycling method. Membrane GS systems can be applied to treat:

- refinery fuel/flare gas;
- hydrode sulfurization/hydrocracker purges;
- catalytic reformer net gas;
- fluidized catalytically cracked (FCC) overhead gas; and
- pressure swing adsorption (PSA) tail gas.

The hydrogen concentration in refinery purges and off-gases is in the range 30–80%, mixed with light hydrocarbons (C_1–C_5); 90–95% hydrogen purity is required to recycle it to a process unit. Hydrogen selective membranes will produce a purified hydrogen stream and a hydrocarbon-enriched residue stream. This residue is recovered at the feed pressure and can be used as fuel, or treated for liquefied petroleum gas (LPG) recovery. The benefits achievable by membrane technology are reported in **Table 1** for the treatment of hydroprocessing purge gas.

Table 2 summarizes the data for H_2 recovery from refinery off-gas by means of three different separation

Table 1 Advantages of membrane GS for H_2 recovery in refinery in the process-intensification logic

More rational utilization of raw materials	Improved H_2 utilization
Improved production	Increased hydroprocessing throughput rates
Reduced costs	Prolonged catalyst life
	Reduced capacity for the H_2 production process (e.g., reduced steam amount required for reforming)
Reduced emissions/ waste	Reduced CO_2 emissions by methane steam reforming for hydrogen production

Table 2 H_2 recovery from refinery off-gas [5] – comparison among different technologies

	Membrane (80 °C)	*Membrane (120 °C)*	*PSA*	*Cryogenic*
H_2 recovery (%)	87	91	73	90
H_2 purity (%)	97	96	98	96
Product flow rate ($m^3\,h^{-1}$)	3257	3375	2643	3375
Power (kW)	220	220	370	390
Steam ($kg\,h^{-1}$)	230	400	-	60
Cooling water ($t\,h^{-1}$)	38	38	64	99
Investment ($ millions)	1.12	0.91	2.03	2.66
Installation area (m^2)	8	5	60	120
Energy intensity ($kJ\,(m^3_{H_2})^{-1}$)	251	253	403	553
Mass Intensity ($kg\,kg_{H_2}^{-1}$)	136	133	277	342
Productivity/footprint ($kg_{H_2}\,(h\,m^2)^{-1}$)	35	58	3.9	2.4

technologies (membrane, PSA, and cryogenic), as reported by Spillman [5]. A comparison among these processes is provided in terms of mass and energy intensity and of a productivity/footprint ratio. A lower investment cost than PSA or cryogenic separation was estimated for the H_2 recovery from refinery off-gas by polymeric (polyimide) membranes [5]; however, since then polymeric membrane capital prices have dropped. The membrane solution presents the lowest energy intensity (energy required for producing a fixed amount of hydrogen), and the related mass intensity, considering the required steam and cooling water, is less than 50% of that for the conventional separations. More interesting in the process-intensification logic is the productivity/footprint ratio: considering the same space occupied by the separation unit, the membrane system would provide a 10-fold higher productivity than PSA and cryogenic distillation.

MTR's hydrogen-permeable VaporSep-H_2™ membranes can provide 95–99% pure hydrogen and typically 80–98% recovery [6]. The available pressure for the purified hydrogen depends on the feed conditions, but can be as high as 100 bar. These systems handle feed pressures up to 170 bar (2500 psia), treating feed streams up to 250 000 m^3(STP) h^{-1} at 30–95 vol.% H_2. The typical size is 20 ft (L) × 8 ft (W) × 18 ft (H); 15 000 lb. Medal™ membranes can operate at as high as 120 bar at flow rates up to 350 000 m^3(STP) h^{-1}; typical hydrogen recovery can reach 98% in volume; hydrogen purity can be as high as 99.9% [7]. Other commercial systems are supplied by Ube, Japan (**Figure 1**).

The processes that use syngas to produce different chemicals (e.g., methanol, oxo-alcohols, and gas to liquids (GTL)) require a specific hydrogen-to-carbon monoxide ratio. Again, GS membrane systems can be considered to achieve this goal.

4.08.2.3 Natural Gas Sweetening

Carbon dioxide removal from natural gas is mandatory to meet pipeline specifications (down to 2 vol.% in the United States). CO_2 not only reduces the heating value of natural gas, but is corrosive and freezes at a relatively high temperature, clogging equipment lines and damaging pumps. Membrane technology is attractive for acid gases (CO_2 and H_2S) separation, since many polymeric membranes are very permeable to these species, thus avoiding significant loss of pressure for the methane product gas. The separation can be accomplished using the high wellhead gas pressure. A high natural gas recovery (>95%) requires multistage systems. Membrane GS is an environmentally friendly alternative to traditional amine absorption with significant advantages for the offshore industry, owing to the smaller footprint. Membrane systems for CO_2 separation are typically installed for small-sized applications (less than 6000 $N\,m^3\,h^{-1}$) and remote locations, since amine processes are too complicated for small productions. Membrane and amine systems become competitive at a capacity of 6000–50 000 $N\,m^3\,h^{-1}$, while bigger plants are installed for offshore platforms or for enhanced oil recovery.

Cynara-NATCO produces hollow fiber modules in cellulose triacetate [9], which can handle condensing hydrocarbons in the gas stream and has recently provided a membrane system (16-in modules) for the natural gas sweetening in an offshore platform located in the Thailand gulf (830 000 $N\,m^3\,h^{-1}$) [10]. This is the biggest membrane system for CO_2 removal, reducing the CO_2 concentration from 36%

Figure 1 UBE H_2 separation system in operation at an oil refinery. Reproduced with permission from UBE America Inc., New York, NY, USA.

down to 16% (in Southeast Asia, a CO_2 concentration of 23% is acceptable for using the gas in power stations). The 16-in module has a 17.5 times higher feed capacity than the 5-in module, while the 30-in module (the most recent development) allows a feed capacity 62.5 times higher than the smallest one, reducing weight and footprint of more than 90%. The offshore CPOC platform, in the Malaysia–Thailand Joint Development Area, has in 2009 processed 760 000 m^3(STP) h^{-1} inlet gas by using eighty 16-in Cynara-NATCO membrane modules in order to reduce the CO_2 concentration from 43% to 23% sales gas content [11].

4.08.2.4 Natural Gas Treatment – N_2 Removal

The use of membranes in the natural gas industry is expanding beyond CO_2 removal [12], primarily for removing nitrogen from natural gas and for the recovery of natural gas liquids (**Figure 2**). Composite membranes are being developed and commercialized for these applications (e.g., by MTR), offering improved resistance to aromatics and other contaminants, good separation performance, competitive capital, and operating costs [13]. Commercially proven membrane systems are beginning to be used to separate nitrogen from natural gas: the NitroSep™ system (MTR) [13] uses a selective membrane that retains nitrogen; an unit of this type has been operating continuously since September 2008 in Wyoming (USA) [6]. Two streams are obtained: a low-nitrogen (<4% N_2) stream and a high-nitrogen (30–50% N_2) residue that contains some methane and can be used as a fuel for compressors powering the membrane process. Unlike cryogenic process, membrane systems are simple and easy to operate and are suited for nitrogen removal at small- to medium-scale. The NitroSep™ process, treating gas flows down to as low as 600 m^3(STP) h^{-1}, allows to meet pipeline nitrogen specification and achieve good hydrocarbon recovery (e.g., 80–90% methane recovery). Treatment of gas streams with low levels of nitrogen may require a single membrane stage; two or more membrane stages may be required for more concentrated streams. These systems allow production from high-nitrogen natural gas reserves, complying with pipeline requirements, thus reducing transportation costs and increasing the gas heating value.

4.08.2.5 Enhanced Oil Recovery by Means of CO_2

The injection of gases miscible with oil (e.g., CO_2 and/or N_2) increases the recovery rates of oil and/or gas from a petroleum reservoir. Membranes are useful for recovering CO_2 from natural gas in enhanced oil recovery applications owing to the high CO_2 concentration (>50%) and pressure (up to 140 bar)

Figure 2 FuelSep® (MTR) unit operating in Texas (USA) for the recovery of natural gas liquids: (a) one-stage and (b) two-stage. Reproduced from 'Fuel gas conditioning: FuelSep™ (REMOVE H_2S, C_{3+}, CO_2, N_2, H_2O)', MTR – Membrane Technology & Research, http://www.mtrinc.com/fuel_gas_conditioning.html (accessed April 2010), with permission.

involved in these processes. The CO_2-enriched stream obtained as permeate is recompressed and injected in the wells. Cynara, in 1983, installed the first membrane plant of this type in Texas (USA). The system, originally designed to reduce CO_2 from 45% to 28% at a capacity of 60 000 N $m^3 h^{-1}$, is still working at a capacity of 120 000 N $m^3 h^{-1}$, reducing the CO_2 content from 80% to less than 10% [14].

4.08.2.6 Materials for CO_2 Membrane GS

Cellulose acetate is the most widely used and tested material for natural gas sweetening, as in UOP's membrane systems [15]. Typical permeation data for cellulose acetate commercial membranes are: CO_2 permeability of 9 Barrer (1 Barrer $= 7.6 \times 10^{-18}$ m^3 (STP) $m\,m^{-2}\,s^{-1}\,Pa^{-1}$) and CO_2/CH_4 separation factor of 20. The high solubility of CO_2 and H_2S in cellulose acetate induces plasticization: the polymer swells with disruption of the polymeric matrix, with an increase in the mobility of the polymer chains, thus negatively affecting the membrane performance. In order to overcome plasticization, polyimides (PIs), in particular, have attracted considerable attention due to their relatively high thermal, chemical, and mechanical stability combined with high selectivity and permeability for CO_2 [16]. PI membranes are typically used for hydrogen recovery, but are currently modified for CO_2 removal. Crosslinking of PIs was investigated for reducing the incidence of swelling and plasticization resulting from the exposure to CO_2; this approach has led to significant improvement without reducing CO_2 permeability [17, 18]. Ube industries (Japan) commercialize aromatic PI membrane modules also for CO_2 separation (**Figure 3**), suggesting as maximum operating conditions a temperature of 100 °C and a pressure of 150 bar [19]. The two-stage system shows that innovative engineering can be applied to improve the purity of the produced streams. Other membrane systems for CO_2 separation based on PI are those from MEDAL [20].

Despite the increasing number of installed membrane systems for CO_2 separation in the applications cited above, more challenging cases as the CO_2 separation from flue gas for a post-combustion capture strategy require better (more selective) materials.

New materials are under study for CO_2 membrane separation. Park *et al.* [21] obtained thermally rearranged polymers by the thermal decarboxylation of precursor PIs between 350 and 450 °C, which induces a change in the chain conformations and spatial location of rigid moieties. The size of free-volume elements can be rationally tailored by controlling the degree of the rearrangement and the flexibility of the original chain. Thermally rearranged polymers work much better than conventional membranes at separating out CO_2 from methane, since they are very permeable (CO_2 permeability of 1600 Barrer) and, unlike cellulose acetate and PIs, maintain high CO_2/CH_4 selectivity (in excess of 40) even with large CO_2 partial

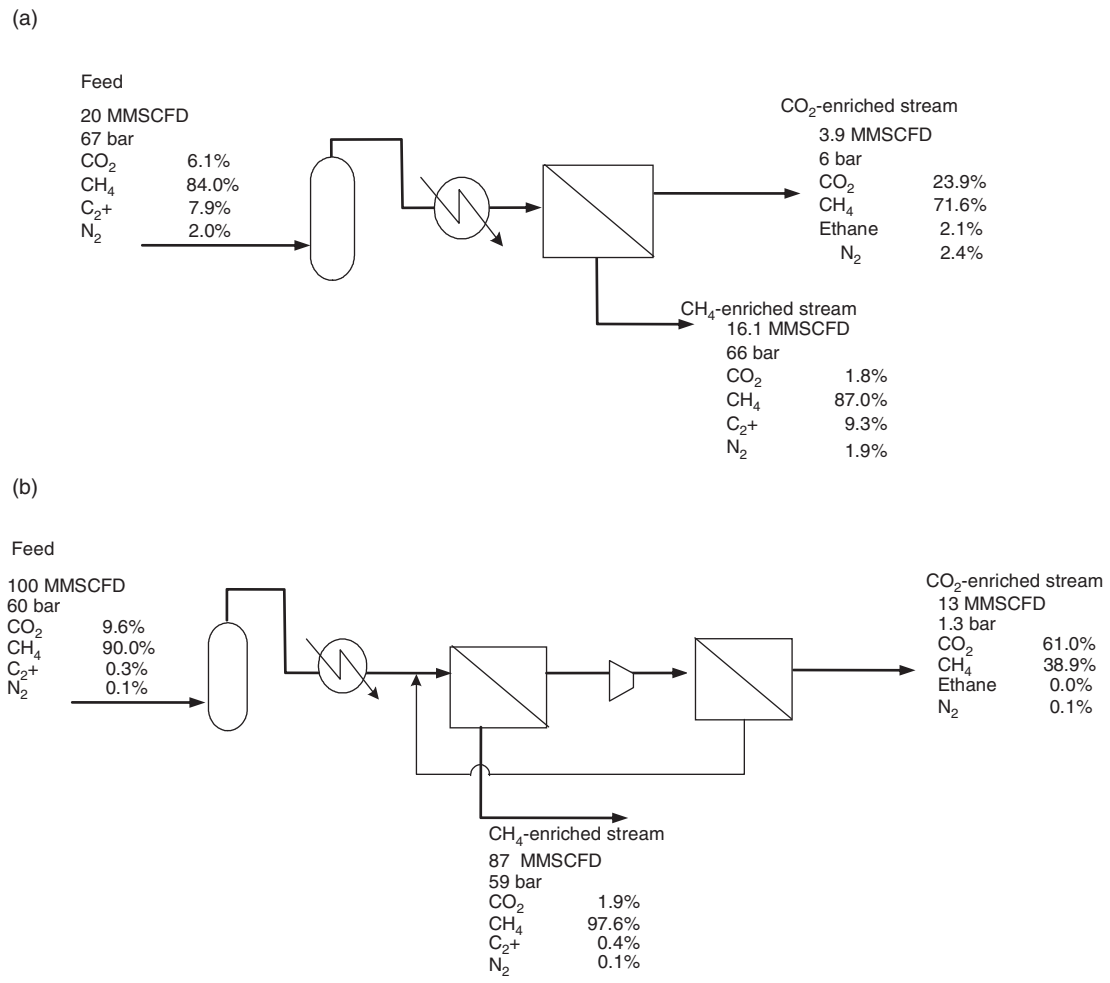


Figure 3 Natural gas treatment by membrane GS: (a) one stage; (b) two stage [19].

pressures. If this material is used to natural gas process plants instead of conventional cellulose acetate membranes, it would require 500 times less space, and would lose less natural gas [22]. Other interesting materials recently developed are polymers of intrinsic microporosity (PIM) [23], which present permeation data for the CO_2/CH_4 separation located in between the 1991 [24] and the 2008 [25] Robeson's upper bounds (e.g., CO_2 permeability of 2300 Barrer and CO_2/CH_4 selectivity 18.4). The use of plasticization-resistant perfluorinated membranes represents an alternative strategy for natural gas treatment [26]. These materials are particularly interesting for GS applications in the petrochemical/refinery processing due to their chemical resistance [27, 28]. Perfluoropolymers (e.g., Cytop) present higher CO_2 fluxes than PIs or cellulose acetate and equivalent CO_2/CH_4 selectivities, while cross-linking strategy typically results in reduced permeabilities.

4.08.2.7 Monomer Recovery in Polyolefin Production

Rubbery polymers find application as hydrocarbon-selective membranes for monomer recovery in polyolefin production. This is the largest application of vapor-separation membranes. The production of polyethylene and polypropylene involves losses of monomers and other hydrocarbon feedstock (typically \$1–3 million per year in one plant). In polypropylene production, propylene is lost mostly in resin degassing vents. In the case of polyethylene, losses occur also at distillation column overhead vents in the ethylene recovery and purification step and at reactor purge

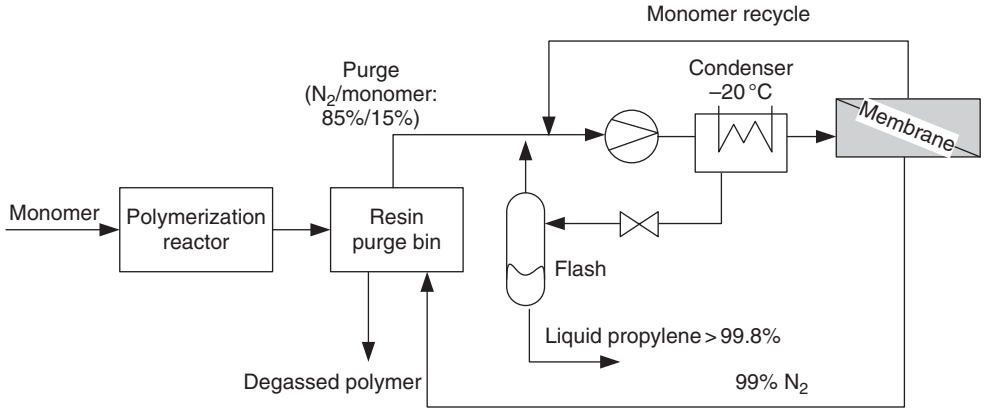


Figure 4 Scheme of monomer recovery and nitrogen recycle from polyolefin plant resin degassing by a hybrid membrane vapor–gas separation system [29].

vents. Usually, the purge-bin vent gas, containing approximately 15% hydrocarbon in nitrogen, is flared, while by using a membrane vapor–gas separation system, valuable feedstocks can be recovered and recycled to the polymerization section [29]. In this case, the vent stream is compressed and cooled to condense hydrocarbons; the gas from the condenser, still containing a significant amount of hydrocarbons, is sent to a membrane system producing a hydrocarbon-enriched permeate stream and a purified nitrogen residue stream. The permeate is recycled to the compressor and then to the condenser where the hydrocarbon is recovered; the nitrogen stream is recycled to the degassing bin. This hybrid membrane system is depicted in **Figure 4**.

The same hydrocarbon-selective membranes can be used for the stream leaving the distillation column or reactor which contains monomer contaminated with light gases (e.g., N_2 and H_2). The hydrocarbon-enriched stream is returned to the distillation column or reactor, while the light-gas-enriched stream is vented or flared. VaporSep membrane systems (MTR [6]) are currently used by major polyethylene producers (e.g., ExxonMobil, Formosa Plastics, Sabic, and Sinopec) [6]. A propylene recovery unit, delivered by MTR to GS Engineering's polypropylene plant in Sohar (Oman), is operational since February 2007; it is expected to save more than $2MM per year in operating costs through the recovery of propylene and nitrogen [6].

4.08.3 Pervaporation Processes

Different liquid organic–organic mixtures were separated successfully by means of pervaporation (PV) [30–32]. Two commercial PV processes, S-Brane™ and Tran-Sep™, have been developed for large-scale gasoline desulfurization [33, 34]; the progress in this field was recently reviewed by Lin *et al.* [35]. The production of low-sulfur fuels is of high priority in the petroleum refineries [36], owing to stricter environmental rules introduced in many countries. In Europe, Germany introduced 10 ppm sulfur limit for diesel from January 2003; other European countries and Japan introduced diesel fuel with 10 ppm to the market in 2008. The most important sulfur contributor in gasoline is the fraction obtained by fluid catalytic cracking (FCC, 30–40% of the total gasoline pool), containing mercaptans, sulfides, disulfides, thiophene, and its derivatives [37]. Sulfur removal from FCC gasoline streams is typically achieved by catalytic hydrodesulfurization (HDS) which, however, reduces octane number owing to the saturation of olefins [38]. Depending on the olefins content of the naphtha streams, most hydrotreating processes lose about 3–4 octane numbers. The mercaptane oxidation (Merox, UOP) technology converts most of mercaptans into different sulfur compounds, which can be removed easily [39]. Thiophenic compounds, being heterocyclic and thus less reactive and more difficult to remove, represent a large fraction of the sulfur compounds (>80%) in the FCC gasoline after alkali cleaning process [40].

In the membrane PV process, sulfur components are selectively removed from the feed stream owing to a higher affinity with and/or faster diffusivity in the membrane, according to the solution-diffusion transport mechanism in dense polymeric membranes [41]. These molecules permeate, evaporate, and then are condensed. The liquid feed is in contact with one side of the membrane, while vacuum or a sweep gas is

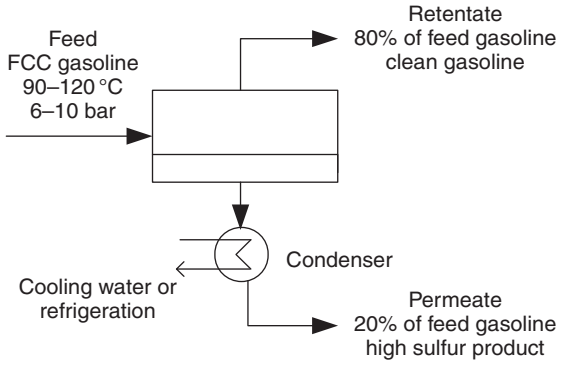


Figure 5 Scheme of the S-Brane PV process.

applied at the other membrane side. Considering the chemical complexity of gasoline, solvent-resistant membranes are required for this PV application [42].

In 2002, Grace Davison reported the S-Brane process (**Figure 5**) to selectively remove sulfur hydrocarbons from FCC and other naphtha streams [43, 44]. An S-Brane pilot plant with a capacity of 1 bpd has been operating since October 2001, treating different FCC gasoline streams to sulfur levels below 30 ppm. A demonstration plant (300 bpd, 2 $m^3 h^{-1}$ capacity) installed at the ConocoPhillips, Bayway Refinery (USA) started up in mid-2003 and operated successfully until the end of December 2003 [45, 46]. This plant (single-stage design) processed both light and intermediate naphtha streams, demonstrating over 90% sulfur reduction, with 20 ppm or lower sulfur for light naphtha. During normal operation, the vacuum was maintained by permeate condensation. A chiller-based refrigeration system was used to condense the permeate vapors.

On the basis of the successful scale-up from lab to pilot to demonstration scale, similar performance should be expected for commercial installations, with additional cost savings from economy of scale. Major process benefits of S-Brane are reported in **Table 3**; they are coupled with ease of operation and modular design, allowing for simple unit expansions and revamps [47].

Commercial systems are available from 5000 to 40 000 bpd (35–265 $m^3 h^{-1}$); these large-scale systems could require 10 000 m^2 of membrane. Membrane area depends on feed stream composition and flow rate, target purities, and capacity of available splitters and hydrogenation units. The capital requirements of S-Brane was \$100–500 per bpd capacity installed and the operating cost was 0.5–1.5 cent per gallon of product (including service fee for lease of membranes/modules and maintenance) [47]. Concerning the effect on the octane number, Kong *et al.* [48] found on the lab scale that the octane number of feed and permeation sample of FCC gasoline changed little during PV treatment with PEG membrane. In the S-Brane process, the high sulfur permeate stream (20–30 vol.% of the feed) is sent to the hydrotreater for desulfurization, while the low-sulfur-level retentate stream can be diverted away from the hydrotreater, thus preserving the octane in this stream. The total octane loss (retentate and treated permeate) is 0.5–1 octane number, depending on the hydrotreating severity [49]. S-Brane produces a gasoline stream capable of complying with low sulfur specifications, unloads existing hydrotreating facilities, and results in an overall increase in the gasoline blending pool octane value, preserving octane value in hydrotreating-based technology.

Table 3 Advantages of membrane PV for gasoline desulfurization (S-Brane) in the process-intensification logic [47]

More rational utilization of raw materials	Reduced H_2 request for the subsequent HDS process (only 20% of the original stream has to be further treated).
Reduced footprint	Substantial reduction (up to 95%) in the flow rate of high olefin gasoline that requires capital-intensive HDS (typically, only 20% of the original feed stream is sent to the HDS process).
Improved production	Compared against most hydrotreating processes, S-Brane provides a better preservation of 1.5–2 numbers of octane numbers, which represents as much as \$5 million for a unit of *c.* 30 000 bpd (200 $m^3 h^{-1}$) gasoline [35].
Reduced emissions Reduced utilities request Low operating costs	Process runs at low temperatures and pressures relative to other gasoline desulfurization processes. The operating cost of the S-Brane scenario is about \$ 1.5 MM per year less than the scenario without S-Brane [50].
Reduced capital costs	About 20% the cost/capacity bbl of other gasoline desulfurization technologies. The S-Brane unit cost of \$6 MM (about \$200 bbl^{-1}) is *c.* \$23 MM less than the total capital cost of the scenario without S-Brane [51].

S-Brane fits well with some other gasoline desulfurization processes and represents an excellent low-capital option for debottlenecking less flexible FCC feed/gasoline desulfurization units. These units can be modularized and installed with minimal impact to existing refinery infrastructure and minimal operations downtime. This is an important example where a membrane separation is integrated with other process units to improve the performance of the whole unit.

Trans Ionics Corporation has also developed a membrane PV process (TranSep^{TM}) for removal of sulfur from gasoline streams [50]. Most of the olefins remain in gasoline streams, allowing the high-sulfur product to be nonselectively hydrotreated without significant loss in octane number. In this case, permeate is recovered from a Venturi nozzle and special working fluid at atmospheric pressure, thus eliminating expensive refrigeration systems required to condense light hydrocarbons at high vacuum. This reduces the capital and operating costs for using vacuum pumps (or steam ejectors) and refrigeration units in conventional PV systems.

Although the integration of S-Brane with the conventional gasoline desulfurization process was successful, there are numerous problems to be further investigated: economic assessment, coupling optimization, total octane number loss, etc. [35]. Other refining applications could benefit by operating in PV operations, such as the separation of benzene from cyclohexane [51]. Exxon Research and Engineering has investigated PV to separate aromatics from nonaromatics in heavy cat naphtha [52] and to reduce the aromatics content of distillate [53].

MTR's BioSep™ group has worked on PV applications with USA-based EPA Cincinnati Laboratory developing novel membrane-distillation hybrid processes for bioethanol production [6]. The membrane units use either vapor permeation or PV. These processes are simple in design, offer significant separation process energy savings (more than 50%), and are cost competitive with conventional distillation-molecular sieve technology. BioSep™ processes are attractive when the ethanol concentration in the fermentation step is low, such as cellulose-to-ethanol and algae-to-ethanol. A demonstration plant is being constructed in collaboration with a cellulose-toethanol producer. In a new project funded by DOE, MTR is addressing separation issues in bio-butanol production by developing a low-cost/low-energy hybrid membrane-distillation separation process [6]. Biobutanol production is not economical, owing to the low concentration of butanol in the fermentation broth and the complexity of the conventional separation process to separate the three components – acetone, butanol, and ethanol (ABE) – from the fermentation broth. PV/vapor permeation systems developed by MTR use membranes to concentrate and dehydrate the ABE mixture. The proposed process could save up to 87% of the energy required to recover biobutanol by conventional separation techniques.

Commercial zeolite membranes (a hydrophilic LTA zeolite layer supported on a ceramic tube), produced by the Japanese companies Mitsui Engineering & Shipbuilding Co. and the Nano-Research Institute Inc. (XNRI) and most recently by the alliance between Smart (UK) and Inocermic (Germany), can be applied in the separation of water from organic solutions by steam permeation and PV. The first large-scale plant using these membranes has been applied to the dehydration of organic solvents in Japan [54], producing $13\,m^3\,d^{-1}$ of solvents (methanol, ethanol, isopropyl alcohol, etc.). XNRI has installed vapor permeation units in Brazil ($3\,m^3\,d^{-1}$) and India ($30\,m^3\,d^{-1}$) for the dewatering of bio-ethanol [55]. In lab tests at 75 °C for an ethanol/water (90/10 wt.%) mixture, the LTA membrane gave a flux of $8\,kgH_2O\,m^{-2}\,h^{-1}$ with a separation factor H_2O/ethanol $\approx$ 10 000. In the vapor permeation unit, the ethanol concentration in the feed is 93%, the permeate was not pure water but it contained 0.5–1.0% ethanol; in the retentate, it is 99.7% at 600 kPa and 130 °C [55]. XNRI developed tubular-supported FAU membranes, which are chemically more stable than LTA membranes. For a mixture of ethanol/water (90/10 wt.%) at 75 °C, fluxes of 6–9 $kg\,m^{-2}\,h^{-1}$ with a separation factor of 100–400 can be achieved for the X type and about $4\,kg\,m^{-2}\,h^{-1}$ with a separation factor of about 150 for the Y type. The LTA membranes produced by Smart Chemicals Development and Inocermic GmbH can dry organic solutions down to 0.1% of water by PV [55]. Hydrophobic zeolite membranes, such as Silicalite-1 (MFI) membranes, are under development to remove ethanol from the fermentation mixture where ethanol concentrations are of approximately 15%. These membranes (MFI type), having a pore size close to the kinetic diameter of *para*-xylene, are also promising for the separation of *para*-xylene from its isomers [56–58], particularly after the finding of a heat treatment to eliminate grain boundaries in these polycrystalline layers [58]. This application is one of the most difficult separations in the petrochemical industry. The separation and purification of *para*-

xylene from mixed xylenes is an energy and capital intensive process, typically achieved by energy-intensive cryogenic separations or capital-intensive absorbent technology. In fact, next to feed-stock costs, the purification section is the most expensive part of the *para*-xylene production.

4.08.4 Organic Solvent Nanofiltration

Organic solvent nanofiltration (OSN) is a recent area of membrane technology of great interest to industry [59–61]. In fact, the energy requirement for OSN is estimated to be 10% of comparable distillation separations [60]. Unlike nanofiltration (NF), which is used in water-treatment systems to separate ions and other compounds in aqueous phase, OSN separates organic–organic mixtures. Composite membranes used at industrial level for aqueous NF typically present polysulfone substrates, which have limited solvent resistance. OSN applications require solvent-resistant membranes. Polymers with good chemical stability (low swelling in organic solvents) include polyimides, polyamide-imides, polyacrylonitriles (copolymer, cross-linking), silicones, polyphosphazenes, polyphenylene sulfide, polyetheretherketone, and polybenzimidazol [62, 63]. The research efforts for developing new materials resulted in the production of commercial organophilic NF membranes. Starmem™ OSN membranes from Grace Davison (USA.), based on PIs and resistant to aromatic and aliphatic hydrocarbons, alcohols, ketones and esters, gained considerable success in refining, chemical, and pharmaceutical industries [64]. Other commercial membranes for these applications are produced by GMT Membrantechnik GmbH (Germany) [62].

The first large-scale application of OSN was in solvent recovery from the dewaxing operation in lubes processing (refining of lubricants) [46, 65, 66]. The process, developed by Grace Davison with Exxon Mobil Corporation, is called Max-Dewax™. Lubricant production is one of the most energy intensive processes in the refining industry. In conventional lube solvent dewaxing, waxy feed is mixed with a mixture of volatile organic solvents (typically, methyl ethyl ketone and toluene), then chilled by successive cooling and refrigeration in order to precipitate paraffin wax crystals. The wax is removed in a set of rotating drum filters, producing a filtrate which consists of lube oil and most of the solvent. This dewaxed solvent mixture is separated by a combination of multi-stage flash and distillation to recover both solvent-free lubricating oil and solvent. However, the solvent must be cooled prior to its recycle to the process. Refrigeration and recovery of the solvent consumes a lot of energy and becomes the bottleneck, which restricts the production of the unit. The dewaxing process is particularly energy intensive due to the relatively large amounts of solvent needed to refine the lube oil: typically, 4–5 barrels of solvent are recirculated to produce 1 barrel of lube. A scheme of the dewaxing process with membrane solvent recovery is shown in **Figure 6**. The retentate goes to the conventional recovery section of the plant, while the purified cold permeate is recycled as dilution solvent in the dewaxing

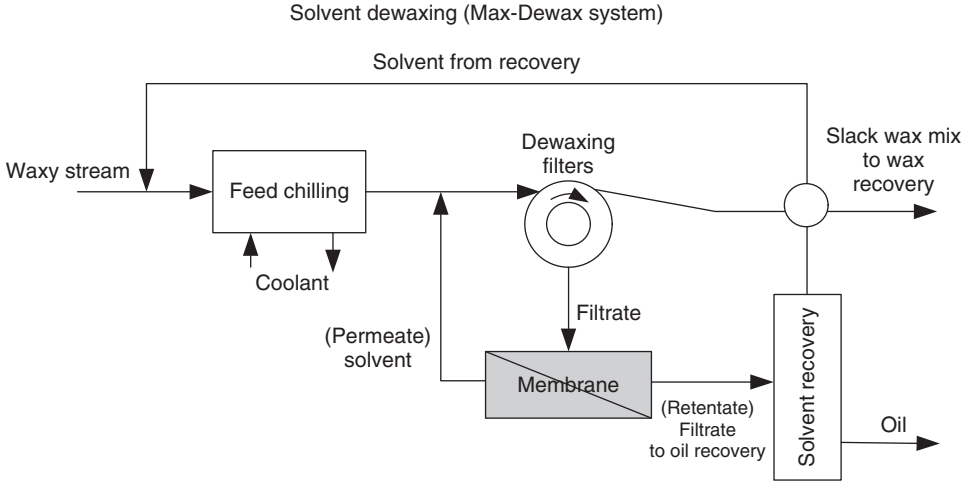


Figure 6 Scheme of the membrane solvent dewaxing process (Max-Dewax™). Reproduced with permission from Gould, R. M., White, L. S., Wildemuth, C. R. *Environ. Prog*. **2001**, *20*(1), 12–16.

chilling train. Up to 50% of the solvent is recovered by at or near the filtration temperature and can be recycled to the dewaxing process without the need for adjusting the temperature in the oil-recovery section. Consequently, energy consumption is significantly reduced by minimizing the need for energy-intensive distillation, cooling, and refrigeration.

A commercial membrane plant (**Figure 7**), designed to treat a maximum feed of 11 500 $m^3 d^{-1}$ (72 000 bpd), is in operation since 1998 complementing the existing distillation plant in the recycling of solvents in lube oil dewaxing at an ExxonMobil's refinery in Texas (USA). The key to successful operation of this membrane system was the integration with the existing process units and long-term durability of membranes even under harsh conditions. These solvent-resistant membranes (PI in spiral-wound modules) have to meet conflicting demands: high differential pressure (400–800 psi) and chilled conditions (−18–0 °C), which will depress diffusion.

The membrane operation takes 36 000 bpd of lube oil filtrate and returns 6000–9600 bpd of purified chilled solvent (>95% rejection of lube oil by the membrane). Despite the changing operating conditions caused by different blocks of lube oil feedstock processed, it is possible to maintain a constant level of cold solvent production, which is also of high quality (less than 1% oil content). The use of membranes allows more solvent to be recycled in the dewaxing operation, thus resulting in higher lubricant yields and in a reduced amount of undesirable slack wax by-products. Therefore, membranes reduce the amount of crude oil required to produce a given volume of lube base stock and the upstream processing of crude oil. The improved process lubricant selectivity also reduces operating costs. This technology can easily be retrofitted to an existing plant, requiring approximately one-third of the capital needed to accomplish the same objectives using conventional technologies. At a capital cost of $5.5 million, payback for the Max-Dewax™ unit was less than 1 year. Integration into an existing commercial installation or incorporation into a grass-roots plant design is low risk due to its modular nature. It can also be used to minimize the capital investment for new dewaxing facilities. The membranes recover and recycle the dewaxing solvents bypassing the more energy-intensive parts of the plant; this also implies a reduction in greenhouse gas emissions. Since the solvent recovered by the membranes does not need to be cooled, cooling water requirements are reduced, as well as the thermal pollution associated with cooling water utilization. Finally, the loss of dewaxing solvents, which are volatile organic chemicals (VOCs), into the environment could be decreased. Since installing the membranes requires less capital than replacing dewaxing filters, the new technology gives the refiner an economic incentive to reduce VOC emissions. These cost-competitiveness features increase the likelihood of the process being implemented, but the process is attractive also from an environmental perspective by minimizing waste generation, as shown in **Table 4**.

Figure 7 View of membrane modules in Max-Dewax™ industrial plant [66].

Table 4 Advantages of membrane solvent recovery in dewaxing processes in the process-intensification logic (Max-Dewax unit, 11 500 $m^3 d^{-1}$ of solvent [66])

More rational utilization of raw materials	3–5% lube oil consumption
	2 million bbl yr^{-1} crude oil processing
	36 000 bbl yr^{-1} fuel oil
Reduced utilities request	20% energy consumption per unit volume of product [60]
	Only 25% heat
	Only 10% refrigeration capacity
	Cooling water (– 4 million gal d^{-1})
Improved production	+3–5% yield of lube and wax
	+35% lube oil production
Reduced waste/emissions	Greenhouse gas (–20,000 ton yr^{-1})
	Solvent (VOCs) loss (−50–200 ton yr^{-1})
	Thermal pollution (less cooling water demand)
	The improved process selectivity also reduces the undesirable slack wax by-products
Reduced footprint	Only 20% in size
	The additional cold solvent, made available by the membrane technology, increases the filtration rate and reduces the number of filters required to process a given amount of lube oil (in many plants, these filters are relatively old and prone to leakage)
Reduced costs	Only 1/3 of the capital expenses
	The improved process selectivity reduces operating costs

Other applications for OSN have been under pilot plant test or demonstrated at the lab-scale, as in homogeneous catalyst recovery [67], separation of phase-transfer catalysts [68] and solvent exchange [69]. Exxon Research and Engineering own different patents on organic–organic membrane separations, including reverse osmosis (RO) to recover extraction solvents [70] and separation of alkylaromatics from aromatics in an alkylation process [71]. New applications include: toluene recovery from a toluene disproportionation unit, lowering benzene levels in gasoline feedstock to <1% and integration of membrane separation with aromatics reformer or distillation operations [59]. Other refinery applications potentially benefiting from OSN implementation are gasoline desulfurization and crude oil deacidification [61, 72].

A review of the development of OSN and PV systems for large-scale refining applications [59] provides also rules-of-thumb for selecting the operation mode. Both high-pressure NF and low-pressure PV follow solution-diffusion models for mass transport and improved process economics in selected large-scale refining applications. The choice between OSN and PV depends on the specific economics and is often based on the trade-off between selectivity and operating costs. Choice of membrane depends on the composition of the feed stream and the requirements for the product stream. In some cases, the high throughput of OSN outweighs the higher selectivities achieved in PV. Concerning aromatics separation, OSN should be considered when the aromatics content is high (>80%), owing to its lower capital and operation costs. When concentrations of aromatics are lower, PV allows for better aromatics enrichment; PV is also the preferred mode for reduction to very low levels of aromatics (e.g., reducing benzene to less than 1% in gasoline) [59].

4.08.5 Membrane Contactors

Membrane contactors (MCs) are devices where a diffusive mass transfer between phases is promoted by a microporous membrane. The membranes, generally hydrophobic (e.g., polypropylene), are not selective, but allow contact between two phases. With respect to conventional absorption/stripping systems, MCs present higher interfacial area per volume (more compact devices), do not present problems of dispersion between phases, loading or flooding limitations, and can offer a constant interfacial area between phases.

Perfluoropolymers (e.g., Hyflon) [73, 74] are strongly hydrophobic; therefore, they are promising materials for MCs. Furthermore, perfluoropolymers are very resistant to a huge variety of chemicals, such as acids and alkalis, fuels and oils, low-molecular-weight esters, ethers and ketones, aliphatic and aromatic amines, and strong oxidizing substances.

Industrial applications of MCs are in the removal of VOCs from air and in CO_2 removal (e.g., from flue gases) [75, 76]. Kvaerner tested a large MC pilot plant to the north of Aberdeen (Scotland) for natural gas treatment [76]. In this process, the MC is fed with a lean amine stream (pressure 88 bar, gas flow rate 5000 N $m^3 h^{-1}$, and liquid flow rate 5 $m^3 h^{-1}$). The CO_2 concentration is reduced from an average of approximately 6–3.5%. Another pilot unit by Kvaerner is treating flue gas from a gas engine at the Statoil Gas Terminal at Kårstø (Norway) [76]. The flue gas flow rate is 2610 kg h^{-1} and 85% of the CO_2 is separated from the gas stream. TNO developed an MC pilot plant for post-combustion CO_2 capture that uses dedicated absorption liquids (CORAL) with cheap polypropylene membranes (gas flow rate 0.5–4 $m^3 h^{-1}$, liquid flow rate 0.5–20 l h^{-1} and CO_2 concentration 0.05–10% in the gas stream) [76]. Much research and development efforts are needed to commercialize the technology [76].

4.08.6 Membrane Reactors

Intense research work has been dedicated to the membrane reactors (MRs): the possibility of arranging the reaction and separation steps in a single equipment offers interesting opportunities in order to improve the efficiency of a great number of chemical and biochemical processes. The recent specialist literature presents many papers that emphasize the innovative potentialities and the emerging role of the MRs for reactions that are equilibrium limited: one of the main characteristics of the MRs is the possibility to remove selectively one of the products improving the conversion (e.g., in the processes of hydrogenation and dehydrogenation). Moreover, these devices have been used for the controlled feeding of reagents in order to reduce hot spots in the catalyst bed or to avoid parallel undesired reactions.

A recent call of European Union on large-scale integrating collaborative projects (FP7 Cooperation Work Programme 2010) is related to catalytic membranes for MRs to selectively convert nonreactive raw materials such as short-chain (C_1–C_4) alkanes [77]. MRs with Pd-based membranes, pioneered by Prof. Gryaznov [78], have been developed by Tokyo Gas Co., Ltd. for hydrogen production by methane steam reforming since 1992 [79]. Their latest development is a membrane reformer with nominal hydrogen production capacity of 40 N $m^3 h^{-1}$, which has demonstrated the possibility of an intensified process owing to single-step production of high-purity hydrogen (99.999% level) in very compact and high-energy efficient (70–76%) devices [80]. The MR applied to the production of hydrogen by methane steam reforming allows [81]:

1. the shift of the chemical equilibrium (higher CO conversion values);
2. a positive effect on kinetics (reduced reverse reaction rate); and
3. a minimization of the steam requirement.

Apart from the MR superior CH_4 conversion, the reduction in steam requirements would allow a drastic size decrease in key plant units, as well as intensification in piping. Moreover, energy savings coming from the use of waste heat contained in the retentate stream further contribute to an intensified process. A recent analysis indicates potentially viable MR using steam as sweep and retentate stream used as heating utility, addressing the challenge of developing advanced reforming technologies in the logic of process intensification [81]. This paper shows the importance of such an analysis that will enable a process philosophy compatible with energy saving and clean technologies.

The study and development of catalytic MRs for reactions at high temperature (partial oxidations, controlled combustions, and conversion of the syngas) appears of particular interest to the petrochemical industry. The development of such technology is closely connected to that of inorganic membranes (metallic and ceramic), able to operate at high temperatures and in chemically harsh atmospheres.

4.08.7 Pressure-Driven and Integrated Membrane Processes for Wastewater Treatment

4.08.7.1 Pressure-Driven Membrane Operations

Pressure-driven membrane separation processes are typically used to separate different sized materials from liquid streams. Suspended matter is retained in microfiltration (MF) operations, ultrafiltration (UF) refers to the separation of macromolecules, NF is applied in water treatment to separate multivalent ions, while RO membranes are designed to reject all species other than water.

An interesting application of MF and UF in petroleum refineries is associated to the deasphalting process. Typically, asphaltic and resinous materials are removed from reduced crude oils, lubricating oil stocks, gas oils, or middle distillates through the extractive or precipitant action of solvents. UF systems can be applied to separate and recycle the solvent from the deasphalted oil [82], otherwise asphaltenes could be removed by ceramic MF or UF membranes at approximately 450°C [83]. In a recent invention (Exxon), UF of a vacuum resid stream is proposed to produce an improved feed stream for the deasphalting unit [84]. The UF integration results in improved deasphalted oil production rates and/or quality. It can be particularly beneficial to improve existing deasphalting units without significant equipment modifications. The interest of industry toward membrane filtration technology for petrochemical/refinery applications can be recognized by some other recent patents [85–87]. The first patent (Exxon) describes a process in which a UF system is used for upgrading visbreaking (thermal cracking of large hydrocarbon molecules in the oil by heating in a furnace to reduce its viscosity and to produce small quantities of light hydrocarbons, such as LPG and gasoline) product streams to produce a feed stream with improved properties for refinery and petrochemical hydrocarbon conversion units [85]. The second invention (Exxon) concerns a high-pressure UF process, which treats an atmospheric and/or vacuum resid and produces an improved coker feed (for producing a substantially free-flowing coke) [86]. Polymers that may be useful in this application are polyimides, polyamides, and/or polytetrafluoroethylene, provided that the membrane material is sufficiently stable at the operating temperature of the separations process. The third patent describes an improved process for separation of liquid mixtures and involves vapor stripping followed by compression of the vapor, which is then sent to a membrane system for separation [87]. Another membrane process for refinery applications has been proposed in 2009 [88]. It considers a ceramic high-flux molecular sieving membrane (e.g., a zeolite membrane) to separate a naphtha feedstock into a retentate stream with a reduced concentration of normal paraffins for an enhanced reforming feed and a permeate stream with an increased concentration of normal paraffins for an enhanced cracking feed.

RO membranes are typically used in the seawater and brackish water desalination. Hollosep® (Toyobo, Japan) RO membrane modules are equipped with cellulose triacetate hollow fibers, which offer superior chlorine tolerance, thus enabling chlorine disinfection. These systems have been employed in a seawater desalination facility in a petrochemical plant in Rabigh (Saudi Arabia), which started operation in May 2008 and will be installed also in the seawater desalination facility currently under construction in Shuqaiq (Saudi Arabia) with the largest capacity (240 000 $m^3 d^{-1}$) in Middle East Gulf countries [89]. In addition, RO membrane systems have found applications in wastewater treatment, production of ultrapure water, and water softening. These new applications were made possible by the development of new-generation membranes that can tolerate wide pH ranges, high temperature, and harsh chemical environments and that present improved water flux and solute rejection.

4.08.7.2 Integrated Membrane Systems for Wastewater Treatment

In integrated/hybrid systems, different physical, chemical, and biological methods are used in combination with membrane operations, creating synergistic effects. Moreover, pretreatment issues, which are crucial for the operation of membrane systems, can be addressed by integrating other membrane systems. This is the case of RO, which can produce low-concentration permeates, but requires chemical and/or biological pretreatment. The benefits of using integrated systems with MF and UF as RO pretreatment are particularly evident in the treatment of a high-fouling wastewater:

- MF/UF filtrate quality is better (significantly lower silt density index (SDI) and turbidity). This pretreatment reduces colloidal fouling in RO and, thus, the cleaning frequencies are reduced;
- MF/UF filtrate quality is constant, even for feed sources with rapidly fluctuating characteristics;
- footprint and consequently floor space requirement is less (by a factor of 5 for large systems);
- MF/UF concentrated waste streams are easier to dispose of with respect to chemically enhanced conventional pretreatment processes; and
- capital and operating costs are competitive and, in some schemes, lower.

Successfully integrated UF/RO membrane systems applied in refinery plants are described below.

India's largest UF membrane plant provides reliable and uninterrupted water for refinery operations in Chennai [90]. This 4.5 million-inhabitants metropolitan city suffers from severe water shortages, but alternative water sources (surface water run-off, groundwater from aquifers surrounding the city, and water from the Krishna River) are polluted by sand mining and nearby textile and leather tanning plants. During the late 1980s, Chennai Petroleum Company Limited (CPCL) made a significant investment to treat municipal wastewater with a final step of RO to remove salts and small organic compounds. The wastewater reclamation plant met 40% of the total raw water needs of the refinery and was the first-of-its-kind solution for the Asian refinery industry. The system operated successfully for more than 10 years. In the late 1990s, UF hollow fiber membranes from Koch Membrane Systems, Inc. (KMS) were added as pretreatment (removing nearly all suspended solids, colloidal particles, and microorganisms) to the RO system. In 2004, CPCL commissioned a UF membrane system (hundred and eight 10-in-diameter TARGA™ PMC UF membrane cartridges mounted on six cartridge racks, with 18 cartridges per rack). UF membranes deliver product water with very low turbidity (less than 0.1 NTU) and an SDI less than 2, thus reducing RO cleaning cycles, as well as floor space concerns. Operating at 90% water recovery, producing $430\,m^3\,h^{-1}$ of treated water, it is the largest wastewater reclamation plant in India. The plant has also made more water available to Chennai, preventing any untreated sewage from damaging the environment. The RO plant was upgraded with 8822XR-400 RO membranes (KMS). Despite CPCL's harsh feed water conditions and temperatures, the new membranes are expected to have a life of 4–5 years, therefore much better than the previous membranes, which lasted only 16–18 months. These membranes also require fewer cleaning cycles and produce a higher quality permeate with a lower total dissolved solid (TDS). CPCL is examining other areas where UF and RO can be applied in new wastewater reclamation projects.

In Canada, a public–private partnership between the City of Edmonton, Alberta and Petro-Canada, one of Canada's largest oil and gas producers, is using GE Water & Process Technologies' UF and RO membranes to obtain high-purity water from municipal wastewater and use it in the oil producer's diesel desulfurization [91]. In 2002, Petro-Canada began modifications to its Edmonton refinery (approximately 135 000 bpd, $21\,500\,m^3\,d^{-1}$ of crude oil) for the desulfurization of diesel in order to reach sulfur concentrations below the new limit of 15 ppb. More water was required for the hydrogen and steam used in the process, but Petro-Canada could not increase its freshwater withdrawals from the North Saskatchewan River due to environmental regulations. The wastewater treatment plant treats municipal and industrial wastewater ($310\,400\,m^3\,d^{-1}$) for about 712 000 people, using pretreatment, primary treatment, activated sludge secondary treatment, a second set of bioreactors to remove remaining impurities, and UV disinfection. GE's ZeeWeed UF membranes were selected to treat the clarified secondary effluent from the $31\,800\,m^3\,d^{-1}$ biological treatment. Reinforced ZeeWeed-immersed UF membranes are insensitive to upsets caused by high turbidity or variable raw water quality and can deliver high-quality permeate to RO, also with a small footprint. Therefore, the RO membranes are protected from fouling, the life of RO membrane modules is extended, and the operating costs are reduced. Typical water quality results are SDI <3, turbidity <1 NTU, and total suspended solids (TSS) $<1\,mg\,l^{-1}$. The initial phase of the tertiary filtration system ($4900\,m^3\,d^{-1}$) was commissioned in December 2005; it was designed for a further expansion to $39\,800\,m^3\,d^{-1}$. Two $90\,m^3\,h^{-1}$ RO systems (GE PRO series) systems reduce the conductivity of the treated effluent (from approximately 1000 to 10–15 micro-mhos). Two new RO systems (GE PRO series) were scheduled to operate in 2008 bringing the plant capacity up to $8200\,m^3\,d^{-1}$. By 2008, Petro-Canada also began using the ZeeWeed-treated tertiary effluent to supply up to 30% of the make-up water for its cooling towers. This is Canada's first major industrial project using integrated hollow fiber UF and spiral-wound RO membranes for municipal wastewater recycling. This project is an example of how membranes can provide a cost-effective way to meet increased water demands, reducing the environmental impact of industrial operations and the need for fresh water.

4.08.7.3 Membrane Bioreactors for Wastewater Treatment

Membrane bioreactors (MBRs) are a particular case of integrated membrane operations. As other membrane filtration (e.g., MF and UF) technologies, MBRs are increasingly being installed in refineries and petrochemical plants. Typical applications of the MBR technology are related to recycling of

wastewater from downstream activities. Wastewater treatment is one of the most important applications of membranes in the petrochemical field. However, petroleum and petrochemical applications present challenging effluent streams. Wastewater in petrochemical industry is treated by activated sludge process (ASP) with oil/water separation as pretreatment. The MBR solution provides an intensified process by combining the traditional biological degradation by ASP with a solid–liquid separation by means of low-pressure membrane filtration (MF or UF membranes, with pore sizes in the range 0.05–0.4 μm). There is no need for sedimentation and media filtration to separate mixed liquor or suspended solids from treated effluent and the secondary clarifier can be eliminated. MBRs join aeration, clarification, and filtration into a single unit; therefore, the MBR solution results in a simplified process, with low space requirements and low visual impact.

MBRs, introduced in the late 1960s, have been used mainly in municipal applications, but owing to their small footprint and ease of operation, the number of installed plants for industrial purposes is increasing. In the past, MBR technology was not a cost-effective solution for the petroleum and petrochemical industry. Stricter effluent regulations and increasing need for reuse/recycling of treated water have generated interest in the petrochemical and refining industries toward the advanced MBR process, particularly in regions with freshwater scarcity (e.g., Middle East or USA (Southwest)). MBR capital costs are easily compensated by savings on effluent discharge and freshwater uptake. Considering operating costs from a wide perspective, the MBRs are a money-saving technology when recycled water and reduced effluent discharge are taken into account. The benefits (financial and environmental) allowed in the petroleum/petrochemical industries by MBRs [92, 93] are summarized in **Table 5**.

In refineries, the highly treated wastewater can be reused directly in the processing of crude, as cooling tower makeup, as boiler feedwater, or for other utility purposes. Recently, an increasing number of refineries in the Middle East have recognized not only the economic and environmental benefits coming from wastewater reuse, but also the possibility to sell the treated water for irrigation, as done by many refineries in Saudi Arabia. In 2007, Kubota installed an MBR plant in Oman, which produces 78 000 $m^3 d^{-1}$ of water reused for irrigation [94]. Many facilities in the United States are only now beginning to consider other raw water sources and water reuse strategies. MBR technology is typically added to a new-built plant or, during an upgrade, to an existing plant. However, even if the beginning of 2008 generated record profits in the oil and gas sector, the recent economic slowdown resulted in the suspension of many plans for added capacity. Revised policies about water use and effluent discharge are expected with the recent change in the US government, thus motivating the adoption of the MBR technology in the short term to reduce future costs [92].

Eni (Italy) contacted Ondeo IS to design and build a UF wastewater treatment unit at Porto Marghera to respect regulations for wastewater disposal in the Venetian Lagoon, which are much more stringent

Table 5 Advantages of MBRs for the petroleum/petrochemical industries in the process-intensification logic

More rational utilization of raw materials	Wastewater reuse for process water and thus reduced freshwater intake by *c*. 20–50%
Improved production	Improved water quality: • stringent effluent requirements met; • nearly all solids removed
Reduced waste/emissions	• Reduced or eliminated liquid effluent discharges (less sludge production) • Less demand of chemicals
Reduced footprint	• Reduced footprint of biological treatment equipment by *c*. 50% (reduced land acquisition costs) • Expanded capacity allowed within existing buildings
Reduced capital costs	• Clarifier is not needed • Biological step can be scaled down since bacteria concentration is higher
Low operating costs	• Compliance with discharge regulations (avoided penalties) • Possibility to sale treated water (e.g., for agricultural uses) • Reduced wastewater discharge fees and freshwater costs • Lower operating costs associated with total plant water cycle

than the rest of Italy [95]. Tertiary water ($48\,000\ m^3\ d^{-1}$) is treated prior to disposal into the natural environment; the discarded water contains less than $1\ mg\ l^{-1}$ of suspended matter. This is the largest unit in the world in terms of MBRs with a UF membrane technology. The upgrading of the wastewater treatment plant of the petrochemical site of Porto Marghera was completed on December 2005 and tested on September 2006 [96]. The existing ASP section was converted into an MBR and its main advantage was the possibility of installing the plant in an existing basin. The upgrading was aimed at increasing the removal efficiency of TSS and of 10 micropollutants. Recently, Veolia Water Solutions & Technologies Brazil has been selected by Petrobras for a new $7200\ m^3\ d^{-1}$ wastewater treatment plant, including an MBR process at its Henrique Lage refinery [97]. ExxonMobil Chemical, expanding the existing Singapore Chemical Plant with a second ethylene train [98], selected the MBR process for its new wastewater treatment facility. A pilot test on site was conducted using Siemens Water Technologies' Petro™ MBR technology in 2006. Among commercial MBRs, the Petro™ system is specifically designed for the treatment of hydrocarbons in the wastewater streams from petroleum and petrochemical facilities [99]. Typical applications are in the treatment of: wastewater from refineries and petrochemical plants, water draws and tank bottoms from bulk storage terminals, process water for cooling towers and boilers, VOC and H_2S emissions, wastewater for reuse/recovery/recycle, produced water from oil and gas wells, water for oil well injection, and ballast water from oil tankers.

The use of a crossflow MBR in treating refinery wastewater was investigated in a lab-scale plant using tubular ceramic membranes: a chemical oxygen demand (COD) removal efficiency of more than 93% was obtained at two mixed liquor suspended solid (MLSS) concentrations (5000 and $3000\ mg\ l^{-1}$) [100]. Qin *et al.* [101] used a bench-scale submerged MBR with an anoxic/aerobic concept and flat sheet MF membranes (chlorinated polyethylene with pore size of $0.4\ \mu m$) to study the treatment and reuse of a petrochemical wastewater; the MBR effluent met the requirement for discharge. An MBR pilot plant (equipped with submerged A4 Kubota membranes) was used to treat olefin process wastewater and total petrochemical wastewater [102]. The MBR treatment of olefin process wastewater reduced COD and total organic carbon (TOC) by approximately 90% in both cases, and removed more than 90% of the suspended solids (SS). The reduction in COD and TOC was also high for the total petrochemical wastewater, but, for some reuse purposes, a subsequent RO step would be needed.

4.08.7.4 Membrane Treatment of Produced Water from Oil and Gas Wells

The need for improved oil recovery methods is continually increasing, owing to the diminishing oil supplies and the increase of viscous oil recovery. One of the main enhanced recovery methods involves the injection of steam into the oil well [103]; therefore, massive amounts of fresh water are required. The exploitation of reserves of heavy oil (very viscous) located in Canada and Kuwait will involve much more water for these operations and will produce increasingly wastewater to be treated. In fact, injected water produced with the oil is contaminated and has to be purified to be reused and to protect the environment. Typically, the water is removed from the oil and the produced water is lightly treated and sent back into the formation as poor quality steam. This could result in an increase of the injection pressures over time as the recycled water builds up in the formation and eventually blocks oil reserves. The produced water eventually has to be disposed of to decrease the volume of water in the formation and in turn improve production. Currently, disposal of produced water represents approximately 10% of the costs of crude oil production [92]. However, disposal of produced water is problematic due to the presence of a large number of solutes, including minerals and organic compounds, varying with location and lifetime of the field; average values are reported in **Table 6**. Therefore, the standardization of water-treatment facilities is very difficult.

Table 6 Average composition of the produced water

	Range
BOD	$50–1400\ mg\ l^{-1}$
COD	$450–5900\ mg\ l^{-1}$
Phenols	$0.7–7.6\ mg\ l^{-1}$
Oil and grease	$15–290\ mg\ l^{-1}$
Ammonia nitrogen	$4–206\ mg\ l^{-1}$
TSS	$35–300\ mg\ l^{-1}$
Sulfides	$0.2–800\ mg\ l^{-1}$
pH	6.7–9

Produced water should be injected underground at a remote site or treated for surface discharge. Before deep-well water injection, the wastewater must also be treated to avoid damage to the injection apparatus and piping, and plugging of the formation. With increasing water quality standards and increasing volume of waste, surface discharge of the produced water has become even more problematic and has produced a need for advanced treatment methods prior to discharge. In addition, the water stress in arid regions is a strong motivation to reclaim the produced water to make it potable and usable for agriculture irrigation. If beneficial uses of produced water can justify the cost of treatment, the petroleum industry could become a net producer of freshwater instead of a net consumer. In fact, produced water is the largest waste stream generated in oil and gas industries: an average of 2–3 barrels are brought to the surface with each barrel of oil [104].

A review of the technologies for the treatment of produced water has been recently presented [105]. The required treatments are: removal of suspended solids, oil, biological growth, dissolved gases, precipitable ions, and pH control [106]. Conventional methods (gravity separation and skimming, dissolved air flotation, de-emulsification, coagulation, and flocculation) have several disadvantages such as low efficiency, high operation costs, space for installation, use of toxic chemicals, corrosion, and recontamination problems. They are not effective in removing smaller oil droplets and emulsions, leaving about 0.5–3% of residual oil in the separated water. For these reasons, major research efforts in the future should focus on advanced technologies and on combined physical–chemical and/or biological treatment of produced water. As in the case of CO_2-enhanced oil recovery, also in water-flooding operations, membrane technology can play an important role. Since produced water is typically saline (sodium = 12 000–150 000 mg l^{-1}; chloride = 20 000–250 000 mg l^{-1}), its treatment involves some pretreatment stages followed by MBR treatment and RO. Some governments and oil producers are now considering to profit from produced water by treating and providing it for industrial, agricultural, and municipal uses [92]. Membrane systems can compete with more complex technologies for treating water with high oil content, low mean particle size and flow rates greater than 3600 m^3 d^{-1}, and are suitable for medium and large offshore platforms [107].

4.08.7.4.1 Membrane filtration for treating produced water

MF (membrane pore size between 0.1 and 5 μm) or UF (membrane pore size less than 0.1 μm) or a combination of MF/UF polymeric or ceramic membranes are suitable for removing oil from oilfield-produced water. UF is one of the most effective methods for oily wastewater treatment, since, in comparison with conventional separation methods, UF offers high oil-removal efficiency, no necessity for chemical additives, low energy costs, and small space requirements [108]. MF and UF treatment have been compared in a pilot trial to treat the North Sea oilfield-produced water [109]: UF, but not MF, could meet effluent standards for total hydrocarbons, SS, and dissolved constituents. By UF membrane treatment (molecular weight cut-off (MWCO) between 100 000 and 200 000 Da), total hydrocarbon concentration was reduced to 2 mg l^{-1} (96% removal); benzene, toluene, and xylene were reduced by 54% and some metals such as Cu and Zn were removed by 95%. The NATCO group pilot-tested a hydrophilic UF membrane (pore size of 0.01 μm), in cross-flow mode, to treat oilfield-produced water [110]. A hydrocyclone was used as pretreatment, removing solids and oil content by 73% and 54%, respectively. Oil and gas concentration after UF were reduced to less than 2 mg l^{-1}. This test showed that the preferred feed-water specification for ideal performance of UF was oil and solids less than 50 and 15 ppm, respectively.

In order to address membrane fouling, novel UF membranes incorporating the amphiphilic comb copolymer additive polyacrylonitrile-*graft*-poly(ethylene oxide) (PAN-*g*-PEO) were developed and exhibit complete resistance to irreversible fouling by different organics [111]. These membranes were applied to the UF treatment of three industrial samples of oilfield-produced water and refinery wastewater [112]. The novel membranes achieved removals of dispersed and free oils of over 96% based on COD for produced water samples, comparable to a PAN commercial UF membrane. For refinery wastewater treatment, the COD removal values were substantially lower (41–44%), due to higher contents of dissolved organics. Comb copolymer-modified membranes showed significantly better fouling resistance than commercial membranes and recovered their initial fluxes after physical methods alone (backwash), thus extending membrane lifetime and improving the process economics for the treatment of oil-contaminated waters.

Addition of nano-sized alumina particles to polyvinylidene fluoride (PVDF) membranes was effective in reducing fouling, as shown in tubular UF module (cross-flow mode) treating produced water from Daqing oilfield (China) [113]. COD and TOC removal efficiencies of the system were 90% and 98%, respectively; oil and SS were below $1\,mg\,l^{-1}$.

4.08.7.4.2 Inorganic membranes for treating produced water

Ceramic membranes present better thermal and chemical resistance than conventional polymeric membranes. Ceramic UF and NF membranes are a relatively new class of materials for the treatment of produced water [114]. One of the first studies on this topic was that of Chen *et al.* [115], using ceramic cross-flow MFs to separate oil, grease, and SS from produced water: permeate quality of dispersed oil and gas was $5\,mg\,l^{-1}$ and of SS was less than $1\,mg\,l^{-1}$. A bench-scale system with bentonite clay membranes was used to purify produced water from oilfields; however, these clay membranes were not suitable for treating produced water with high TDS [116]. Zeolite membranes, having a stable crystalline structures with chemical, mechanical, and thermal resistance, are suitable for treating oilfield-produced water in RO operations in order to separate different ions (e.g., Na^+, K^+, Ca^{2+}, and Mg^{2+}) as demonstrated by Li *et al.* [117] studying desalination of oilfield brine by RO with a silicalite (MFI) zeolite membrane. They found that ion flux was independent of the operating pressure and it increased as feed concentration was raised from 0.001 to 0.3 M. The same authors carried out separation of organics from produced water by RO using an alumina-supported MFI-type zeolite membrane [118]. The organic rejection is strongly dependent on the ionic species and size of dissolved organics. An organic rejection of 96.5% with a water flux of $0.33\,kg\,m^{-2}\,h^{-1}$ was obtained for 100 ppm pentanoic acid solution at 2.76 MPa. For nonelectrolyte organics, the organics with larger molecular size show higher separation efficiency. The zeolite membrane gives an organic rejection of 99.5% and 17% for 100 ppm toluene and 100 ppm ethanol, respectively, with a water flux of 0.03 and $0.31\,kg\,m^{-2}\,h^{-1}$ at 2.76 MPa. As pentanoic acid concentration increased from 100 to 500 ppm, both organic rejection and water flux decreased slightly.

4.08.7.4.3 Integrated membrane systems for treating produced water

Membrane pretreatment and RO technology are effective methods also for produced water treatment. Doran *et al.* [119] presented a pilot process to treat produced water in California (USA). The process included precipitative softening at pH 9.5–10.0; cooling and pH reduction; fixed-film biological oxidation of organics and ammonia removal in a trickling filter; filtration; and ion-exchange softening to remove residual hardness, and, finally, RO. The treated water could meet industrial and irrigation requirements. In a pilot study to reuse oilfield-produced water for irrigation and potable water, a series of processes were proposed: the warm softening process removed 95% of the initial hardness ($1000\,mg\,l^{-1}$) and RO removed 95% of TDS [120]. Tsang and Martin [121] investigated dissolved gas floatation, walnut shell filtration, warm softening before an MBR, and RO to treat produced water. Their economical analysis showed as the treatment cost of produced water is reduced by 30–60%, passing from $\$0.15\,bbl^{-1}$ to $\$0.05–\$0.10\,bbl^{-1}$ when the treated water is sold as drinking water. Different physical, and chemical pretreatments (air floatation, clarification, softening, and filtration) for RO were proposed for a process to meet drinking water quality standards from oilfield-produced water [122]. A method comprising water softening to remove divalent cations combined with RO membrane to treat oilfield-produced waters containing boron and solubilized hydrocarbons was patented by these authors [123]. Barrufet *et al.* [124], to convert oilfield brine to irrigation-quality water, proposed adsorption on modified clay material as pretreatment to MF and RO. They showed that modified clay could remove oil better than activated carbon and RO could remove more than 95% of TDS. Another process for treating oilfield-produced water containing dissolved minerals and hydrocarbons utilizes a warm lime softening system, wherein sludge from the warm lime softening system is recycled to improve lime utilization and enhance silica and boron removal without an external source of magnesium; an MF system and/or an air stripper system may be used with an RO system to produce water that meets guidelines for surface discharge [125]. More recently, Cakmakce *et al.* [126] investigated different pretreatment alternatives to membrane RO to reduce salt content of produced water. They proposed an integrated system (primary sedimentation, oil/water separator, dissolved air floatation, 1-μm ceramic or metallic cartridge filter,

0.2-μm ceramic or metallic MF as pretreatment before RO) which could reduce COD to less than 250 mg l^{-1} (discharge standard for the petroleum industry in Turkey). In addition, BP uses RO and membrane pretreatment to generate low salinity water (500 ppm or lower) for enhanced oil recovery operations [127].

Xu *et al.* [128] investigated a two-stage lab-scale membrane system to treat gasfield produced water generated from sandstone aquifers. They studied ultra-low-pressure RO and NF membranes to meet quality standards for potable and irrigation water, and iodide concentration in brine. The ULPRO membrane operation resulted in lower treatment cost than RO and NF for meeting irrigation water standards, especially at high energy cost.

A hybrid RO-constructed wetland to treat produced water for use in irrigation was also proposed [129]. The process consisted of different size of filters, a cation exchanger, and an RO. The first stage could remove 95% and 94% of conductivity and TDS, respectively. The RO permeate is sent to a pilot-scale constructed wetland (four cells in series with vegetation collected from the oilfield site).

OPUS technology (Veolia Water Solutions & Technologies), by combining a high-rate chemical softening process (Multiflo™) with filtration, ion exchange, and RO, generates high-quality water with low waste volume. At the San Ardo Chevron's site (California, USA.), the OPUS system treats 50 000 bpd of produced water obtaining softened water suitable for producing steam for oil extraction [130].

Because of the need for frequent regeneration of physical adsorbers and high running cost and sludge production from chemical treatments, some researchers have proposed biological pretreatment before membrane treatment. The optimal treatment of highly saline wastewater involves a biological treatment of wastewater with acclimated microorganisms in a saline environment prior to membrane systems, especially with RO [131].

The goal of produced water treatment is to remove dissolved components and use the desalted water for beneficial uses, thus effectively reducing environmental impact and water shortage. Many efforts have been focused on membrane technologies including RO and electrodialysis, but no large scale produced water desalination by membranes has been reported [132]. The main obstacle is represented by the complicated chemical composition of these feed streams and associated high operating cost. Membrane technologies are energy efficient owing to single-phase operation comparing to thermal-based desalination processes. However, the presence of dissolved organics and scale deposition on membrane surfaces requires sophisticated pretreatment and frequent membrane replacement, adding to the water treatment costs. Kwon *et al.* [133] reported the results of a pilot plant where produced water was treated in surfactant-modified zeolite (SMZ) adsorbent units to remove volatile organic compounds (BTEX and acetone) and semivolatile organic compounds (e.g., solubilized), an MBR with submerged membranes for removal of the organic acid component of TOC and finally sent to RO. Removal efficiency of SMZ was 40% of the influent TOC (600 mg l^{-1}); BTEX concentrations were reduced to approximately 2 mg l^{-1} after the MBR. An economic evaluation showed as-produced water treatment by the SMZ/MBR/RO system would cost \$0.13–\$0.20 bbl^{-} at up to 40 gal min^{-1} (218 m^3 d^{-1}), while estimated disposal costs for produced water are \$1.75–\$4.91 bbl^{-} (transportation costs included), with even higher rates in some regions [133]. Polymeric membranes and molecular sieve zeolite membranes have been investigated for ion removal from produced water from oilfield and coalbed methane site by a cross-flow RO process [132]. Pretreatments, including NF and adsorption by active carbon, were studied for their influence on the RO performance and impact on the overall desalination cost. The study has revealed that most of permeation tests lasted less than 3 months due to serious fouling and drastic flux decline (>30%), scale precipitation and organic sorption are the major fouling mechanisms of membranes, multi-stage pretreatment is crucial to extend membrane lifetime, and NF is the only effective process tested that can extend the life of a RO membrane to over 6 months. Periodic chemical cleaning, typically twice a week, is necessary to maintain the desired water flux. Considering small- to mid-sized water treatment capacity (50 m^3 d^{-1}), the cost of produced water desalination by RO membranes is around \$3.7 m^{-3} including NF pretreatment [132], which compares well with disposal costs cited in [133]. Pretreatment and membrane replacement are the major factors that increase the operation cost and limits the economic efficiency of membrane technology for produced water desalination [132].

4.08.8 Technical Issues to Be Addressed

Current and proposed refinery and petrochemical applications for membranes typically involve polymeric membranes (**Table 7**), which present low cost and high packing density. However, they cannot withstand high temperatures and chemically aggressive environments; moreover, when applied in petrochemical plants, refineries, and natural gas treatment, heavy hydrocarbons in feed streams can be a problem, particularly in hollow fiber modules.

Refinery gas streams contain contaminants such as water vapor, acid gases, olefins, aromatics, and other organics. At relatively low concentrations, these impurities cause membrane plasticization and loss of selectivity, while at higher concentrations, they can condense on the membrane surface, which could be irreversibly damaged. Many polymers can be swollen or plasticized when exposed to hydrocarbons or CO_2 at high partial pressure; their separation capabilities can be dramatically reduced, or, the membranes irreparably damaged. Therefore, pretreatment selection and condensate handling are key factors for a proper operation of polymeric GS modules. Long-term combined effects of pressure and temperature, while in a solvent system on a polymer matrix, are difficult to estimate. Moreover, polymeric membrane structures are not well defined on the small molecular scale, and small structural changes can have large impact on performance. A related issue is physical aging (gradual relaxation of nonequilibrium excess free-volume in amorphous glassy polymers) [134], which should be addressed and better understood. Since refining applications require year-round operations, physical testing in practical conditions of membrane systems for any new proposed large-scale application is required. This testing should not be limited to the membrane, but include the module design, and how these modules are arranged in an engineered system [135]. In order to enhance the properties of the polymeric membranes, new mixed matrix membranes consisting in nano- or micro- particles of inorganic material (metal, zeolite, carbon nanotubes, etc.) incorporated in the polymeric matrix, have been recently studied [3, 136]. These membranes offer very interesting properties; however, their cost, difficulty of commercial scale manufacture, and brittleness remain important challenges.

Key technical obstacles to cost-effective application of membranes in produced water treatment include low average flux rate, flux reduction, and uncertain membrane life [137].

Research institutions and membrane system suppliers spent considerable efforts over the past decade to address fouling and permeability reducing factors, which negatively affect membrane technology for treatment of industrial wastewaters or other aqueous streams. Wastewater coming from petrochemical or refinery sites is particularly challenging. New membrane materials with antifouling features have been developed [111–113, 138–140]. Other research projects are focused on new materials (sulfonated copolymers) with improved resistance to chlorine [141], thus possibly eliminating any dechlorination stage in membrane water treatment. Commercial fouling-resistant UF modules are also available:

Table 7 Main materials industrially used for membrane unit operations

Gas and vapor separation	Cellulose acetate, polyimides, polysulfone are commonly used for gas separation
	Rubbery polymers (e.g., poly(dimethyl siloxane)) are used for the separation of vapors
MF/UF	Poly(vinylidene fluoride), polysulfone, poly(acrylonitrile), and poly(acrylonitrile)-poly(vinyl chloride) copolymers
	Cellulose acetate–cellulose nitrate blends, nylons, and poly(tetrafluoroethylene) are also used for MF membranes
	Poly(ether sulfone) is also used for UF membranes
NF	Cellulose acetate blends or polyamide composites (like the RO membranes), modified forms of UF membranes such as sulfonated polysulfone
RO	Cellulose acetate or polysulfone coated with aromatic polyamides
OSN	Polyimides
PV	Hydrophilic membranes (e.g., polyvinyl alcohol) are used to remove water from organic solutions
	Organophilic membranes (made of elastomer materials as nitrile, butadiene rubber, and styrene butadiene rubber) are used to recover organics
MCs	Hydrophobic polymers (e.g., polypropylene)

EXTRAN™ modules are equipped with hollow fibers based on natural cellulose, which is resistant to hydrocarbons and organic solvents, and is not fouled by oil molecules and calcium scaling [142]. Due to the hydrophilic nature of cellulose, water passes through these membranes, while hydrophobic hydrocarbons are rejected. Alternative filtration modes to limit fouling in MBRs are also under study [143]. In fact, filtration modes (e.g., continuous, relaxation or backwash) directly affect the formation and nature of the fouling layer on the membrane surface [144]. New Logic Research, Inc. [145] patented a vibration shear enhanced process (VSEP) membrane filtration system: the feed remains nearly stationary, moving in slow flow between parallel membrane leaf elements. Shear cleaning action is created by vibrating vigorously the module in a direction tangential to the faces of the membranes, thus reducing colloidal fouling and concentration polarization. Produced water was treated by VSEP in a crude oil production facility in Santa Maria, California (USA) [146].

4.08.9 Membrane Integrated Systems in Refineries

The present analysis shows that as of today, there are different successful membrane operations for refinery applications, not only from an academic point of view, but with industrial references. All three dimensions of sustainability (economic, ecological, or societal) could benefit from the integration of membrane processes in the process-intensification logic, as shown for some selected cases. The final goal for the intensification of petrochemical/refining processes, as well of the production of biofuels, is in the redesign of these processing operations by integrating different membrane systems in the separation/purification section, as well as in the chemical conversion phase [147, 148], exploiting new opportunities and synergistic effects. The integration of different membrane systems (MF, GS, MCs) for separation purposes was already proposed by our group in the case of ethylene production by steam cracking (the primary volume-base-petrochemical). A cracking plant installed in Europe, producing $800\,000\,\text{ton}\,\text{yr}^{-1}$ of ethylene and consuming approximately $30\,\text{GJ}\,\text{ton}^{-1}$ of ethylene, has been used as reference and the membrane systems considered showed exergy reduction with respect to the conventional separation methods [147]. The same strategy would allow to upgrade refineries for clean-fuels production, improving the materials utilization by a separation/recycle approach, reducing at the same time chemicals, energy/utilities consumption, and waste streams production.

Figure 8 presents a simplified scheme of a typical refinery today. Each section of this complex and energy-intensive processing could benefit from the implementation of different membrane systems. The main membrane processes, which can be adopted within a refining plant, are summarized in **Table 8**. Many of them have been examined previously, discussing their reduced impact as a result of a reduced extraction of resources and emission of wastes, and also in the installed footprint.

On the basis of the previous overview, the scheme of a typical refinery has been redesigned as proposed in **Figure 9**. In particular, very compact membrane GS systems can be helpful for H_2S separation instead or in combination with the conventional amine absorption, thus reducing input chemicals in the gas-processing section and the required space for this operation. Membrane GS systems allow the H_2 recovery from hydrotreater or hydrocracking purge gas, from FCC overhead gas, before flares and from PSA tail gas in the hydrogen production section. The same technology, but with different membrane types can also be used for the recovery of LPG from fuel gas. A PV (e.g., S-Brane) system for gasoline desulfurization could reduce the total required HDS capacity, while membrane solvent recovery, instead of the intensive vacuum distillation, is possible in the solvent dewaxing process (by OSN, e.g., Max-Dewax) and in deasphalting (by UF/MF). Concerning wastewater treatment, combined UF/RO systems for treating produced water from the wells, MCs for stripping sour water and MBRs with other membrane filtration as pretreatment for the management of wastewater are other compact and environmentally attractive options. Many other membrane systems can find application in such schemes, as MF and GS to control the emissions (particulates and VOCs) from asphalt blowing operations.

Membrane modules for the applications described above (gas and vapor separation, PV, OSN, MF, UF, NF, RO, MCs, and MBRs) are already engineered and available on the market. Innovative and under development systems as MRs should be introduced in the conversion section for H_2 synthesis on-purpose.

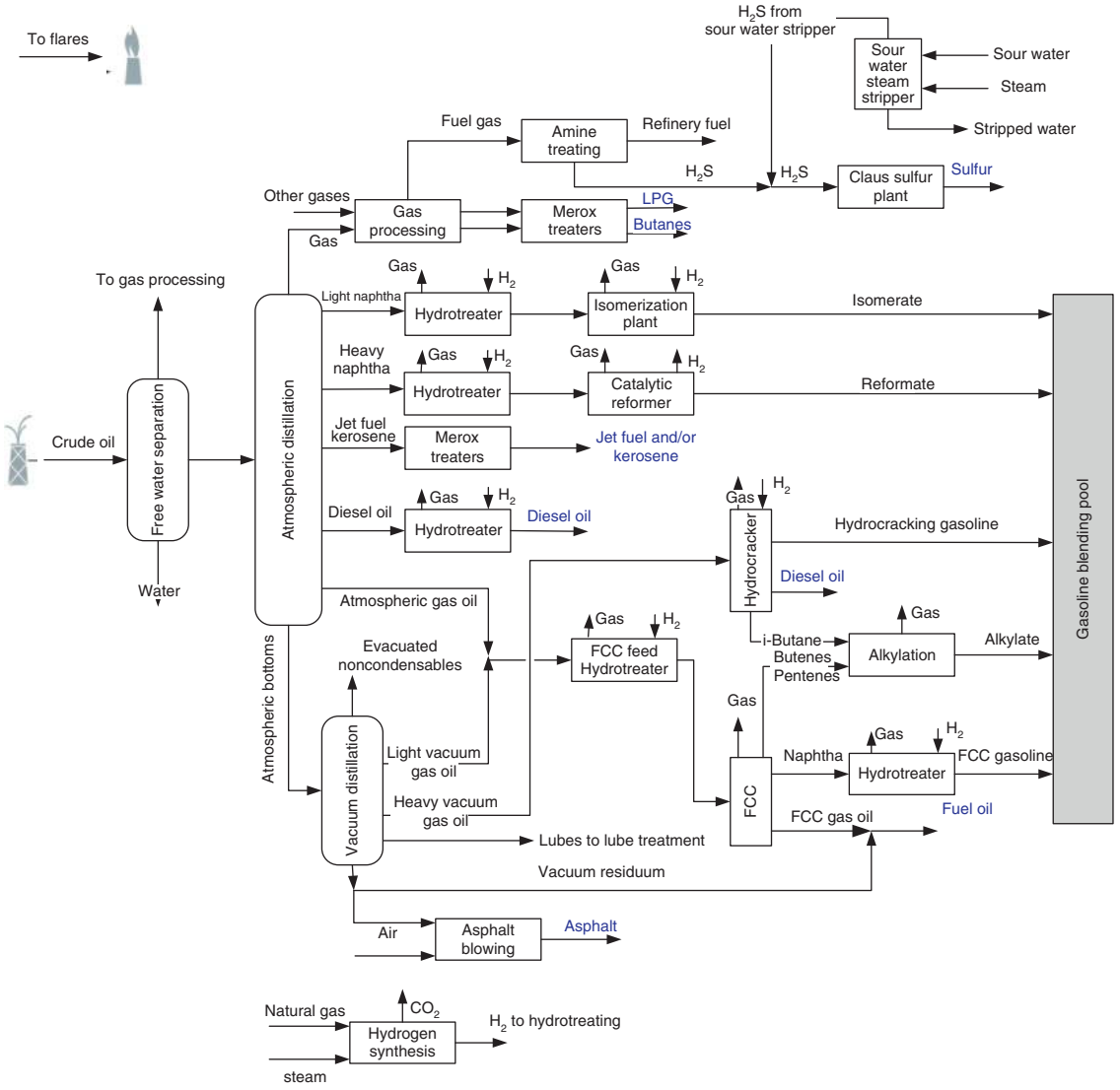


Figure 8 Scheme of a refinery today.

4.08.10 Conclusions

In the past years, membrane engineering experienced an explosive growth, which passed also through different successes, as in the water treatment/desalination, in the development of artificial organs and, in some cases, in the separation of gaseous mixtures. The expectations are for a continuous development of this field. Many opportunities and challenges are in the energy- and separation-intensive oil refining/petrochemical industry. There are already developed applications of membrane units in this area; others might come with the development of new membrane materials able to withstand more demanding process conditions in terms of temperature, pressure, and aggressive media. The development of new materials has allowed membrane separation processes such as OSN. OSN is a young technology and the effective number of large-scale industrial applications is still limited, but new industrial implementations can be expected in the near future.

Max-Dewax^{TM} (OSN) and S-Brane^{TM} (PV) are successful examples of processes that have moved from lab-scale to pilot plant, to a demonstration unit on-line at a refinery. These processes are large scale and have relatively low capital cost than

Table 8 Application of membrane operations in refining processes

Application	*Membrane process*
N_2 generation from air for safety purposes	GS
H_2S separation instead of amine absorption	GS
H_2 recovery from hydrotreater or hydrocracking purge gas	GS
H_2 recovery from fluidized catalytically cracked (FCC) overhead gas	GS
H_2 recovery from catalytic reformer net gas	GS
H_2 and/or LPG recovery before flares and/or from fuel gas	GS
H_2 recovery from PSA tail gas in the hydrogen production section	GS
Gasoline desulfurization	PV (e.g., S-Brane)
Solvent recovery in the deasphalting process	UF/MF
Solvent recovery in the solvent dewaxing process	OSN (e.g., Max-Dewax)
Control of the emissions (particulate and VOCs) from asphalt blowing operations	MF and GS
Treatment of produced water from the wells	Combined UF/RO systems
Wastewater treatment	MBRs with UF/MF as pretreatment
Stripping of sour water	MCs
H_2 synthesis on-purpose	MRs

conventional technologies, with significant gains in yield, quality, energy savings, and also environmental benefits. In fact, by improving the utilization of solvents used in lube refining, Max-Dewax^{TM} contributes to substantial reductions in the energy required to refine lubricating oils as well as in VOCs and greenhouse emissions.

Advanced membrane water-treatment technology can allow economical treatment of wastewater for potable or irrigation uses, avoiding discharging the water as waste. The disposal volume will not be completely eliminated but considerably reduced, making other resources available. The RO process is simple to design and operate in comparison with many traditional separation processes. Environmental benefits are possible with the integration of membrane unit operations. In a wastewater reclamation process with integrated membrane pretreatment, the benefits of significantly lower fouling rates of RO membranes, low cost of chemicals and disposal of pretreatment waste stream, outweigh the cost for membrane pretreatment equipment. This technology, when applied for produced water, will transform it from a costly waste to a valued product. If the water can be reused instead of being discharged, it would change the entire process of wastewater management offshore. In an attempt to fulfill a zero discharge process, no discharge of oily water represents a great move toward a better management approach for the operator as well as for the environment.

The permanent challenge in membrane technology is to improve the current processes, extending the range of application of this technology. Research in polymeric membrane technology in recent years has resulted in the development of systems, which offer the potential for generation or separation of gases for use in a range of applications at attractive cost. The significant positive results reached in GS membrane systems are, however, still far away to realize the potentialities of this technology. Problems related to the pretreatment of the streams, to the membrane lifetime, to their selectivity and permeability slow down the growth of large-scale industrial applications. Inorganic membranes, when industrially available, can find application at high temperatures, or in new applications involving hydrocarbon vapors, contributing to the success of this technology. However, implementation of value engineering (design of supermolecular membrane morphologies and economical modules) is equally critical to the full field development. The application of the membrane processes together with other separation techniques in hybrid processes may be advantageous, as shown for the desulfurization case. With the development of new process concepts, new membrane applications will emerge.

In an attempt to shift from a thermal age to a new nonthermal era, membrane engineering is a key solution. However, membrane engineering not only means energy savings, but more interestingly from a process-intensification point of view, reduced waste and material utilization, reduced footprint and environmental impact. A correct comparison with conventional unit operations should also take into account flexibility, possibility of automation, and ease of scale-up. By means of a redesign of the cycles involved in the refining/petrochemical area,

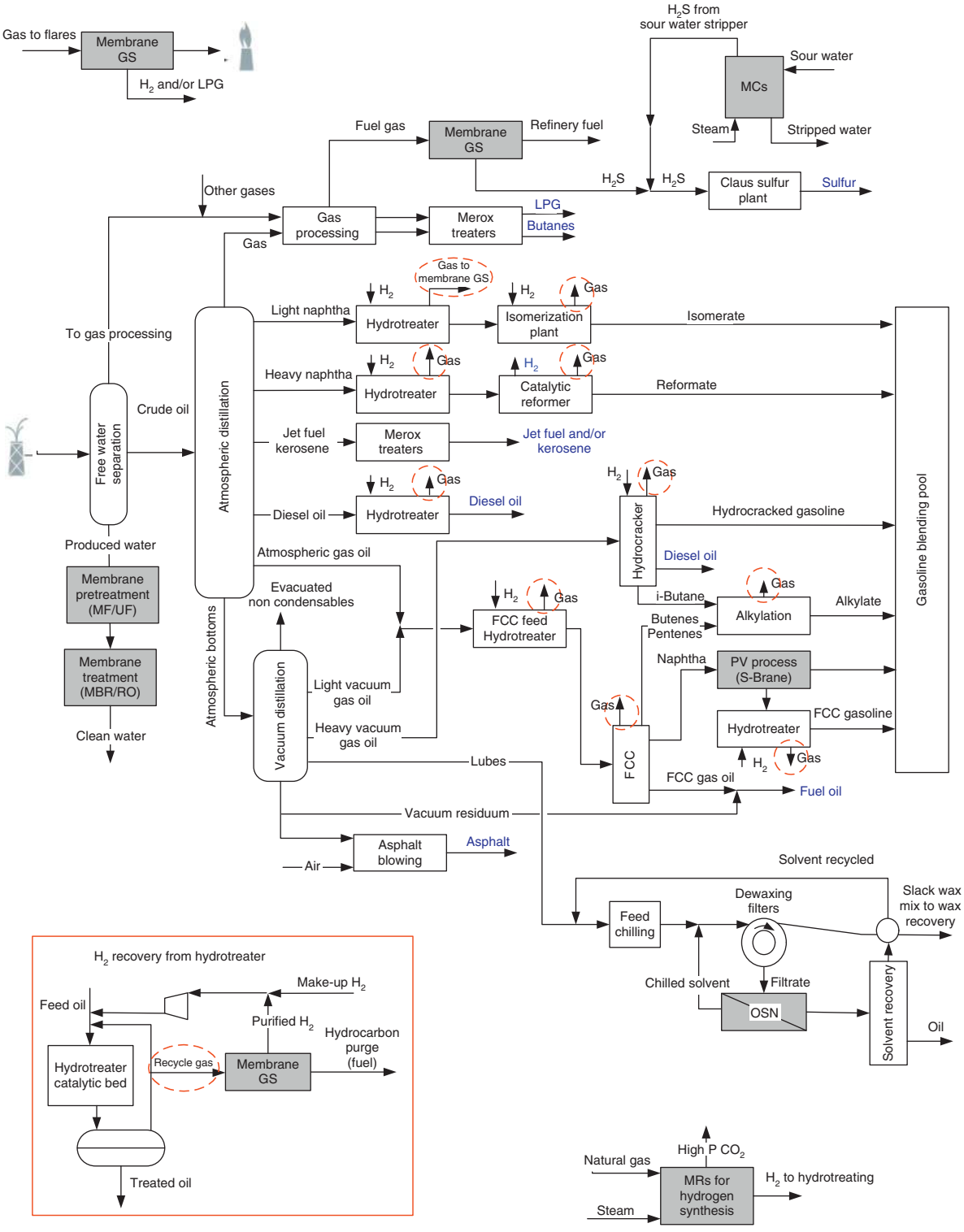


Figure 9 Scheme of a refinery with the integration of different membrane operations.

process-intensification logic can be transferred even in these energy-intensive processes through the implementation of membrane operations. However, the potential of these new design strategies in industrial scale is not fully exploited because of the lack of a general design. Not only single membrane operations should be taken into account, but an integral vision of refinery/petrochemical processes is needed. In this respect, proper research and demonstration projects are crucial.

References

[1] Dautzenberg F. M., Mukherjee, M. *Chem. Eng. Sci.* **2001**, *56*, 251–267.
[2] Koros, W. J. *J. Membr. Sci.* **2007**, *300*, 1–2.
[3] Bernardo, P., Drioli, E., Golemme, G. *Ind. Eng. Chem. Res.* **2009**, *48*(10), 4638–4663.
[4] Baker, R. W. *Ind. Eng. Chem. Res.* **2002**, *41*, 1393–1411.
[5] Spillman, R. W. *Chem. Eng. Prog.* **1989**, *85*, 41–62.
[6] Membrane Technology and Research, http://www.mtrinc.com(accessed February 2010).
[7] Membrane Systems DuPont Air Liquide (MEDAL), http://www.medal.airliquide.com (accessed February 2010).
[8] UBE America Inc., http://www.northamerica.ube.com(accessed February 2010).
[9] Kelly, R. M. (Cynara). Process for Separating CO_2 from Other Gases. US Pat. 4, 659, 343, 1987.
[10] Callison, A. Davidson, G. *Oil Gas J.* **2007**, *105*(20), 56–65.
[11] NATCO, http://www.natcogroup.com (accessed February 2010).
[12] Baker, R. W., Lokhandwala, K. *Ind. Eng. Chem. Res.* **2008**, *47*, 2109–2121.
[13] Hale, P., Lokhandwala, K. Advances in Membrane Materials Provide New Solutions in the Gas Business, http://www.mtrinc.com/publications/NG02%20GPA2004FinalPaper.pdf (accessed February 2010).
[14] NATCO, http://www.natcogroup.com(accessed February 2010).
[15] Dortmundt, D., Doshi, K. *Recent Developments in CO_2 Removal Membrane Technology*; UOP LLC: Des Plaines, IL, 1999.
[16] Matsumoto, K., Xu, P. *J. Appl. Polym. Sci.* **1993**, *47*, 1961–1972.
[17] Wind, J. D., Staudt-Bickel, C., Paul, D. R., Koros, W. J. *Ind. Eng. Chem. Res.* **2002**, *41*, 6139–6148.
[18] Staudt-Bickel, C., Koros, W. J. *J. Membr. Sci.* **1999**, *155*, 145–154.
[19] UBE America Inc., http://www.ube.com(accessed February 2010).
[20] Membrane Systems DuPont Air Liquide (MEDAL) http://www.medal.airliquide.com(accessed February 2010).
[21] Park, H. B., Jung, C. H., Lee, Y. M., *et al. Science* **2007**, *318/5848*, 254–258.
[22] New Membrane Strips Carbon Dioxide from Natural Gas Faster and Better, *Science News*, http://www.sciencedaily.com/releases/2007/10/071011142625.htm (accessed February 2010).
[23] McKeown, N. B., Budd, P. M., Msayib, K. J., *et al. Chem. Eur. J.* **2005**, *11*, 2610–2620.
[24] Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165–185.
[25] Robeson, L. M. *J. Membr. Sci.* **2008**, *320*, 390–400.
[26] Merkel, T. C., Pinnau, I., Prabhakar, R., Freeman, B. D. Gas and Vapor Transport Properties of Perfluoropolymers. In *Materials Science of Membranes for Gas and Vapor Separation*; Yampolskii, Yu., Pinnau, I., Freeman, B. D., Eds.; Wiley: Chichester, 2006; pp 251–270.
[27] Pinnau, I., He, Z., Da costa, A., Amo, K. D., Daniels, R. Gas Separation Using C^{3+} Hydrocarbon-Resistant Membranes. US Pat. 6,361,582, 2002.
[28] Pinnau, I., He, Z., Da costa, A., Amo, K. D., Daniels, R. Gas Separation Using Organic-Vapor-Resistant Membranes. US Pat. 6,361,583, 2002.
[29] Baker, R. W., Wijmans, J. G., Kaschemekat, J. H. *J. Membr. Sci.* **1998**, *151*, 55–62.
[30] Smitha, B., Suhanya, D., Sridhar, S. *J. Membr. Sci.* **2004**, *241*, 1–21.
[31] Jonquieres, A., Clement, R., Lochon, P., Neel, J., Dresch, M., Chretien, B. *J. Membr. Sci.* **2002**, *206*, 87–117.
[32] Wynn, N. *Chem. Eng. Prog.* **2001**, *97*(10), 66–72.
[33] White, L. S., Lesemann, M. *Div. Pet. Chem.* **2002**, *47*(1), 45–47.
[34] Balko, J., Bourdillon, G., Wynn, N. *Petrol. Technol. Quart.* **2003**, *1*, 18–25.
[35] Lin, L., Zhang, Y., Cong, Y. *Fuel* **2009**, *88/10*, 1799–1809.
[36] Ito, E., van Veen, J. A. R. *Catal. Today* **2006**, *116*, 446–460.
[37] Valla, J. A., Lappas, A. A., Vasalos, I. A. *Appl. Catal. A* **2004**, *276*, 75–87.
[38] Brunet, S., Mey, D., Pérot, G. *Appl. Catal. A* **2005**, *278*, 143–172.
[39] Diao, J. *Petrol. Refin. Eng.* **1999**, *29*, 24–31.
[40] Ju, S., Zeng, Y., Yao, H. *Mod. Chem. Ind.* **2004**, *24*, 56–59.
[41] Lin, L., Wang, G., Qu, H., Yang, J., Wang, Y., Shi, D., Kong, Y. *J. Membr. Sci.* **2006**, *280*, 651–658.
[42] White, L. S., Wormsbecher, R. F., Lesemann, M. (W.R. Grace & Co.) Membrane Separation for Sulfur Reduction. US Pat. 0, 211, 706 A1, 2004.
[43] Balko, J., Glaser, R., Wormsbecher, R. Reduce Your Tier 2 Gasoline Sulfur Compliance Costs with Grace Davison S-Brane Technology. In *Proceedings of the NPRA Annual Meeting*, Paper AM-02-21, San Antonio, TX, USA, 2002.
[44] Grace, http://www.grace.com(accessed February 2010).
[45] Grace, W. R. *Membrane Technology* **2004**, *5*, 1
[46] Grace, W. R. *Membr. Technol.* **2005**, *12*, 5.
[47] Balko, J., Wynn, N., Bourdillon, G. Novel S-Brane™ Technology for Improved Ultra-Low Sulphur Gasoline Economics. In *Proceedings of the ERTC 7th Annual Meeting*, Paris, France, 18–20 November 2002.
[48] Kong, Y., Lin, L., Yang, J. *J. Membr. Sci.* **2007**, *293*, 36–43.
[49] Zhao, X., Gautham, K., Todd, C. *Petrol. Technol. Quarter* **2004,** 321–27.
[50] Trans Ionics Corporation, http://www.transionics.com(accessed February 2010).
[51] Villaluenga, J. P. G., Tabe-Mohammadi, A. *J. Membr. Sci.* **2000**, *169*, 159–174.
[52] Ho, W. W., Sartori, G., Thaler, W. A., Dalrymple, D. C. Separating Aromatics from Non-Aromatics by Polyimide-Polyester Membrane. US Pat. 5,670,052, 1997.
[53] Sweet, J. S., Chen, T. J., Darnell, C. P. Membrane Process for Enhanced Distillate or Hydrotreated Distillate Aromatics Reduction. US Pat. 5,643,442, 1997.
[54] Morigami, Y., Kondo, M., Abe, J., Kita, H., Okamoto, K. I. *Sep. Purif. Technol.* **2001**, *25*, 251–260.
[55] Caro, J., Noack, M., Kolsch, P. *Adsorption* **2005**, *11*, 215–227.

[56] Xomeritakis, G., Lai, Z. P., Tsapatsis, M. *Ind. Eng. Chem. Res.* **2001** *40*, 544–552.
[57] Lai, Z. P., Bonilla, G., Diaz, I. *et al. Science* **2002**, *300*, 456–460.
[58] Choi, J., Jeong, H.-K., Snyder, M. A., Stoeger, J. A., Masel, R. I., Tsapatsis, M. *Science* **2009**, *325*, 590–593.
[59] White, L. S. *J. Membr. Sci.* **2006**, *286*, 26–35.
[60] Boam, A., Nozari, A. *Filtr. Sep.* **2006**, *43*(3), 46–48.
[61] Vandezande, P., Gevers, L. E. M., Vankelecom, I. F. J. *Chem. Soc. Rev.* **2008**, *37*, 365–405.
[62] Beeskow, T., Hoting, B. Nanofiltration Comes to Organic Solvents. *Achema Worldwide News* 2009.
[63] White, L. S., Nitsch, A. R. *J. Membr. Sci.* **2000**, *179*, 267–274.
[64] Livingston, A. Organic Solvent Nanofiltration: A New Technology for Molecular Separation. In *Proceedings of the Innovation for Sustainable Production*, Bruges, Belgium, 22–25 April 2008.
[65] Bhore, N. A., Gould, R. M., Jacob, S. M., *et al. Oil Gas J. 97* **1999**, *46*, 67–74.
[66] Gould, R. M., White, L. S., Wildemuth, C. R. *Environ. Prog.* **2001**, *20*(1), 12–16.
[67] Scarpello, J. T., Nair, D., Freitas dos Santos, L. M., White, L. S., Livingston, A. G. *J. Membr. Sci.* **2002**, *203*, 71–85.
[68] Luthra, S. S., Yang, X., Freitas dos Santos, L. M., White, L. S., Livingston, A. G. *J. Membr. Sci.* **2002**, *201*, 65–75.
[69] Livingston, A. G., Peeva, L., Han, S. *et al. Ann. N. Y. Acad. Sci.* **2003**, *984*, 123–141.
[70] Thompson, J. A. Selective Extraction Solvent Recovery Using Regenerated Cellulose Membrane under Reverse Osmosis Conditions. US Pat. 4,510,047, 1985.
[71] Black, L. E., Boucher, H. A. Process for Separating Alkylaromatics from Aromatic Solvents and the Separation of the Alkylaromatic Isomers Using Membranes. US Pat. 4,571,444, 1986.
[72] Livingston, A. G., Osborne, C. G. A Process for Deacidifying Crude Oil. WO Pat. /2002/050, 212, 2002.
[73] Arcella, V., Colaianna, P., Maccone, P. *et al. J. Membr. Sci.* **1999**, *163*, 203–209.
[74] Gordano, A., Clarizia, G., De Santo, M., Arcella, V., Drioli, E. Composite Membranes from Amorphous Perfluoropolymers for Novel Applications in Membrane Processes. In *Proceedings of the ACS Spring Meeting, ''Polymeric Materials: Science and Engineering,''* San Diego, CA, USA, 1–5 April 2001.
[75] Liu, Y., Feng, X., Lawless, D. *J. Membr. Sci.* **2006**, *271*, 114–124.
[76] Mansourizadeh, A., Ismail, A. F. *J. Hazard. Mater.* **2009**, *171* (1–3), 38–53.
[77] European Commission *Nanosciences, Nanotechnologies, Materials and New Production Technologies – NMP, Work Programme 2010*, Cooperation, Theme 4, 29 July 2009, ftp://ftp.cordis.europa.eu/pub/fp7/docs/wp/cooperation/nmp/d_wp_201001_en.pdf (accessed February 2010).
[78] Gryaznov, V. M., Orekhova, N. V. Reactors with Metal and Metal-Containing Membranes. In *Structured Catalysts and Reactors*; Cybulski, A., Moulijin, J. A., Eds.; Marcel Dekker: New York, 1998; pp 435–461.
[79] Shirasaki, Y., Yasuda, I., Kobayashi, K., Fujimoto, Y., Kuroda, K. New Concept Hydrogen Production System Based on the Membrane Reformer. In *Proceedings of the International Conference on Power Engineering*, Xi'an, China, 8–12 October 2001; p 1519.
[80] Shirasaki, Y., Tsuneki, T., Ota, Y., *et al. Int. J. Hydrogen Energy* **2009**, *34*, 4482–4487.
[81] Bernardo, P., Barbieri, G., Drioli, E. *Chem. Eng. Sci.* **2010**, *65/3*, 1159–1166.
[82] Trambouze, P., Euzen, J. P., Bergez, P., Claveau, M. (Insitut Francai du Petrol). Process for Deasphalting a Hydrocarbon Oil. US Pat. 4, 816, 140, 1989.
[83] Baker, R. W., Cussler, E. L., Eykamp, W., Koros, W. J., Riley, R. L., Strathmann, H., Eds. *Membrane Separation Systems: Recent Developments and Future Directions.* Noyes Data: Park Ridge, NJ, 1991; pp 329–359.
[84] Leta, D. P., Rogers, L. M., Miranda, M. J., *et al.* (Exxon). Deasphalter Unit Throughput Increase Via Resid Membrane Feed Preparation. WO Pat. 2009/058263, 2009.
[85] Leta, D. P., Brown, L. D., Ferrughelli, D. T., *et al.* (Exxon). Upgrade of Visbroken Residua Products by Ultrafiltration. US Pat. Appl. 20090057198, 2009.
[86] Leta, D. P., Brown, L. D., Siskin, M. (Exxon). Production of an Enhanced Resid Coker Feed Using Ultrafiltration. US Pat. Appl. 20090057198, 2009.
[87] Vane, L., Alvarez, F. R. Liquid Separation by Membrane Assisted Vapor Stripping Process. US Pat. Appl. 20090057128, 2009.
[88] Rice, L. H. Integrated Refinery with Enhanced Olefin and Reformate Production. US Pat. Appl. 20090069616, 2009.
[89] Textileinfo.com, http://www.textileinfo.com(accessed February 2010).
[90] Water Efficiency, http://www.waterefficiency.net(accessed February 2010).
[91] GE Power, and Water, Water and Process Technologies, http://www.gewater.com (accessed February 2010).
[92] Wilson, C. MBR Applications Offer Advantages to Petroleum & Petrochemical Wastewater Treatment, http://www.waterworld.com(accessed February 2010).
[93] Sundstrom, G. *Hydrocarbon Engineering, Unifying Solutions*, Farnham, Surrey, UK, January 2005; p 94.
[94] Arnot, T. Aerobic Membrane Bioreactor Technology. In *Proceedings of the Promembrane – International Conference*, Sfax, Tunisia, 5–6 May 2008.
[95] Ondeo Industrial Solutions, http://www.ondeo.nl (accessed February 2010).
[96] Cattaneo, S., Marciano, F., Masotti, L., Vecchiato, G., Verlicchi, P., Zaffaroni, C. *Water Sci. Technol.2008, 58(9),*1789–1796.
[97] Veolia Water Solutions & Technologies to Provide MBR in Refinery Wastewater Treatment Plant. *Hydrocarbon Online*, March 19, 2009.
[98] Cashion, B. S., Wenta, R. J., Migliavacca, M., *et al.* Evaluation of Treatment of an Ethylene Plant Waste Water with a Membrane Bioreactor. In *Proceedings of the AIChE Spring Conference 2008, The 20th Ethylene Producers' Conference*, New Orleans, LA, USA, 6–10 April 2008.
[99] Siemens, http://www.water.siemens.com(accessed February 2010).
[100] Rahman, M. M., Al-Malack, M. H. *Desalination* **2006**, *191*, 16–26.
[101] Qin, J.-J., Oo, M. H., Tao, G., Kekre, K. A. *J. Membr. Sci.* **2007**, *293*, 161–166.
[102] Llop, A., Pocurull, E., Borrull, F. *Water Air Soil Pollut.* **2009**, *197*, 349–359.
[103] Jones, L. G. (Mobil Oil Corporation). Method of Recovering Oil Using Continuous Steam Flood from a Single Vertical Wellbore. US Pat. 5, 080, 172, 1992.
[104] Wang, L. K., Hung, Y.-T., Lo, H. H., Yapijakis, C., Eds. *Waste Treatment in the Process Industries*; Taylor and Francis: London, 2005 ; Chapter 6, pp 235–306.
[105] Ahmadun, F.-R., Pendashteh, A., Abdullah, L. C., Awang Biak, D. R., Madaeni, S. S., Abidin, Z. Z. *J. Hazard. Mater.* **2009**, *170*, 530–551.
[106] Chilingar, G. V., Robertson, J. O., Kumar, S., Bertness, T. A. *Surface Operations in Petroleum*

Production: Technology & Engineering; Elsevier: **1989**; Vol. 2, p 424.
[107] Ciarapica, F. E., Giacchetta, G. The Treatment of ''Produced Water'' in Offshore Rig: Comparison between Traditional Installations and Innovative Systems. In *Proceeding of the Fifth International Membrane Science and Technology Conference*, Sydney, NSW, Australia, November 2003.
[108] He, Y., Jang, Z. W. *Filtr. Sep.* **2008**, *45*(5), 14–16.
[109] Bilstad, T., Espedal, E. *Water Sci. Technol.* **1996**, *34/9*, 239–246.
[110] Lee, J. M., Frankiewicz, T. Treatment of Produced Water with an Ultrafiltration (UF) Membrane – A Field Trial. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, Dallas, TX, USA, 9–12 October 2005.
[111] Asatekin, A., Kang, S., Elimelech, M., Mays, A. M. *J. Membr. Sci.* **2007**, *298*, 136–146.
[112] Asatekin, A., Mayes, A. M. *Environ. Sci. Technol.* **2009**, *43*, 4487–4492.
[113] Yan, L., Li, M. L., Hong, L. J., Li, Y. S. *Sep. Purif. Technol.* **2009**, *66*, 347–352.
[114] Ebrahimi, M., Shams Ashaghi, K., Engel, L. *et al. Desalination* **2009**, *246*, 160–167.
[115] Chen, A. S. C., Flynn, J. T., Cook, R. G., Casaday, A. L. *SPE Prod. Eng.* **1991**, *6*, 131–136.
[116] Liangxiong, L., Whitworth, T. M., Lee, R. *J. Membr. Sci.* **2003**, *217*, 215–225.
[117] Li, L., Liu, N., McPherson, B., Lee, R. *Desalination* **2008**, *228*, 217–225.
[118] Liu, N., Li, L., McPherson, B., Lee, R. *J. Membr. Sci.* **2008**, *325*, 357–361.
[119] Doran, G. F., Carini, F. H., Fruth, D. A., Drago, J. A., Leong, L. Y. C. Evaluation of Technologies to Treat Oil Field Produced Water to Drinking Water or Reuse Quality. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, San Antonio, TX, USA, 5–8 October 1997.
[120] Funston, R., Ganesh, R., Leong, L. Y. C. Evaluation of Technical and Economic Feasibility of Treating Oilfield Produced Water to Create a ''New'' Water Resource, 2002, Kennedy/Jenks Consultants: Bakersfield, CA, http://www.kennedyjenks.com (accessed February 2010).
[121] Tsang, P. B., Martin, C. J. Economic Evaluation of Treating Oilfield Produced Water for Potable Use. In *Proceedings of the SPE International Thermal Operations and Heavy Oil Symposium and Western Regional Meeting*, Bakersfield, CA, USA, 16–18 March 2004.
[122] Tao, F. T., Curtice, S., Hobbs, R. D. *et al. Oil Gas J.* **1993**, *91*, 88–96.
[123] Tao, F. T., Pilger, P., Dyke, C. (Texaco, Inc.) Reducing Aqueous Boron Concentrations with Reverse Osmosis Membranes Operating at a High pH. US Pat. 5, 250, 185, 1993.
[124] Barrufet, M., Burnett, D., Mareth, B. Modeling and Operation of Oil Removal and Desalting Oilfield Brines with Modular Units. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, Dallas, TX, USA, 9–12 October 2005.
[125] Laraway, J. W., Weber, R. E., Thomas, D. J. (Water & Power Technologies, Inc.) Water Treatment Process for Oilfield Produced Water. US Pat. 7, 520, 993, 2009.
[126] Çakmakce, M., Kayaalp, N., Koyuncu, I. *Desalination* **2008**, *222*, 176–186.
[127] BP Global, http://www.bp.com *Frontiers,* August 2009.
[128] Xu, P., Drewes, G. E., Heil, D. *Desalination* **2008**, *225*, 139–155.
[129] Murray-Gulde, C., Heatley, J. E., Karanfil, T., Rodgers, J. H., Myers, J. E. *Water Res.* **2003**, *37*, 705–713.
[130] ''Opus successfully desalinates oilfield-produced water'' *Membrane Technology* **2008**, *2008/4*, 8.
[131] Lefebvre, O., Moletta, R. *Water Res.* **2006**, *40*, 3671–3682.
[132] Muraleedaaran, S., Li, X., Li, L., Lee, R. Is Reverse Osmosis Effective for Produced Water Purification? Viability and Economic Analysis. In *Proceedings of the SPE Western Regional Meeting*, San Jose, CA, USA, 24–26 March 2009.
[133] Kwon, S., Sullivan, E. J., Katz, L., Kinney, K., Bowman, R. Pilot Scale Test of a Produced Water-Treatment System for Initial Removal of Organic Compounds. In *Proceedings of the SPE Annual Technical Conference and Exhibition*, Denver, CO, USA, 21–24 September 2008.
[134] Huang, Y., Paul, D. R. *Polymer* **2005**, *45*, 8377–8393.
[135] Razdan, U., Joshi, S. V., Shah, V. J. *Curr. Sci.* **2003**, *6*, 761–771.
[136] Merkel, T. C., Freeman, B. D., Spontak, R. J., *et al. Science* **2002**, *296*, 519–522.
[137] Zaidi, A., Simms, K., Kok, S. *Water Sci. Technol.* **1992**, *25*, 163–176.
[138] Wei, J., Helm, G. S., Corner-Walker, N., Hou, X. *Desalination* **2006**, *192*, 252–261.
[139] Akthakul, A., Salinaro, R. F., Mayes, A. M. *Macromolecules* **2004**, *37*, 7663–7668.
[140] Kang, S., Asatekin, A., Mayes, A. M., Elimelech, M. *J. Membr. Sci.* **2007**, *298*, 42–50.
[141] Park, H. B., Freeman, B. D., Zhang, Z.-B., Sankir, M., McGrath, J. E. *Angew. Chem. Int. Ed.* **2008**, *120*, 6108–6113.
[142] Separation Dynamics Inc., http://www.separationdynamics.com(accessed February 2010).
[143] Wu, J., Le-Clech, P., Stuetz, R. M., Fane, A. G., Chen, V. *Water Res.* **2008**, *42*, 3677–3684.
[144] Jiang, T., Kennedya, M. D., Van der Meerb, W. G. J., Vanrolleghem, P. A., Schippers, J. C. *Desalination* **2003**, *157*, 335–343.
[145] New Logic Research, Inc., http://www.vsep.com(accessed February 2010).
[146] Galimberti, M. VSEP Treatment of Produced Water – A Comparison of Conventional Treatment Methods and VSEP, a Vibrating Membrane Filtration System. In *Proceedings of the Water Environment Federation, Industrial Water Quality*, RI, USA, 29 July–1 August 2007; pp 515–530.
[147] Bernardo, P., Criscuoli, A., Clarizia, G., *et al. Clean Technol. Environ. Policy* **2004**, *6/2*, 78–95.
[148] Bernardo, P., Barbieri, G., Drioli, E. *Chem. Eng. Res. Des.* **2006**, *84*(A5), 405–411.

Biographical Sketches

Paola Bernardo, PhD in chemical engineering and materials, has been working since 2001 in the research group of Prof. Drioli at the Research Institute on Membrane Technology (ITM-CNR), Italy, in different national and international research projects. Her research activities include study of integrated membrane systems for the petrochemical industry; process simulation and assessment by means of green metrics, energetic and exergetic analyses; transport analysis in membranes for gas and vapor separation; development of catalytic zeolite membranes; and study of membrane reactors for high-temperature reactions (e.g., carbon monoxide selective oxidation in hydrogen-rich streams, water gas shift, methane steam reforming, and propylene epoxidation).

Enrico Drioli is full professor at the School of Engineering of the University of Calabria. He has been professor of chemistry and electrochemistry at the School of Engineering of the University of Naples, dean of the School of Engineering of the University of Calabria, director of the Institute on Membranes and Chemical Reactors of the National Research Council, and director of the Institute on Membrane Technology of Consiglio Nazionale delle Ricerche (CNR).

His main research activities focus on membrane science and engineering; membranes in artificial organs; integrated membrane processes; membrane preparation and transport phenomena in membranes; membrane distillation and membrane contactors; and catalytic membrane and catalytic membrane reactors.

He received the following awards and honors: Doctorate Honoris Causa from the University of Paul Sabatier of Toulouse; International Cooperation Honor Award given by the Membrane Industry Association of China for his special dedication to the International Cooperation between China and Europe in the field of membrane and science technology; guest professor in the Environment and Safety Engineering Department at the Jiangsu Polytechnic University, China; honorary member of the A. V. Topchiev Institute of Petrochemical Synthesis at the Russian Academy of Sciences, Moscow; Doctorate Honoris Causa in Chemistry and Chemical Technology from the Russian Academy of Science; and honorary professor at the China Northwest University in Xi'an, Shaanxi, People's Republic of China.

He is involved in many international societies and scientific committees. Currently, he is member of various editorial boards and international advisory boards as well as chairman of the Working Party on Membranes of the European Federation of Chemical Engineering.

He is author of more than 530 scientific papers and 18 patents in the field of membrane science and technology.

4.09 Membrane Systems for Seawater and Brackish Water Desalination

F Macedonio, University of Calabria, Arcavacata di Rende (CS), Italy

E Drioli, Institute of Membrane Technology, ITM-CNR, University of Calabria, Rende (CS), Italy

Abbreviations

AEM	Anion-Exchange Membrane
CEM	Cation-Exchange Membrane
ED	Electrodialysis
EDR	Electrodialysis Reversal
ERD	Energy Recovery Device
MBR	Membrane Bioreactor
MCr	Membrane Crystallization
MD	Membrane Distillation
MDBC	Murray-Darling Basin Commission
MED	Multi-Effect Distillation
MF	Microfiltration
MGD	Million of Gallons per Day
MSF	Multi-Stage Flash
NF	Nanofiltration
ppm	parts-per-million
RO	Reverse Osmosis
SWRO	Reverse Osmosis Desalination
TDS	Total Dissolved Solids
UF	Ultrafiltration
VC	Vapour Compression
WHO	World Health Organization

4.09.1 Introduction

In the past few years, increasing water scarcity and deteriorating water quality are becoming growing problems in many regions of the world, even in countries that are not typically considered to have problems with water scarcity but in which the continuous growth in population, the standard of life, tourist infrastructure, and in industrial development has increased water consumption and the stress on water supplies. Moreover, other causes of the current alarming water crisis include: (1) the unequal distribution of rainwater and occasional drought, (2) the excessive exploitation of groundwater sources and its insufficient recharge, and (3) the deterioration of water quality due to indiscriminate discharge of both domestic and industrial effluents without adequate treatments.

Our blue-green-brown oasis (the Earth), surrounded by the limitless black desert of space, has in fact a finite stock of water. Scientists sustain that humanity is facing water bankruptcy as a result of a crisis even greater than the financial meltdown now destabilizing the global economy. Moreover, what is more serious that the water crisis has already set in and it seems that there is no way of bailing the earth out of water scarcity, except for a more rational use and reuse of the existing water sources.

4.09.2 Worldwide Water Situation

According to the US Geological Survey, the world's potable water reserve, which is able to support the needs of agriculture and human consumption as well as ecosystem and industrial production, represents approximately 2.5% of the world's total water resources. When availability is considered, 68.9% of this precious limited supply is locked in the polar ice and 31.1% can be found as groundwater, lakes, natural reservoirs, and rivers. Approximately only 1% of global freshwater (≈0.01% of global waters ≈200 000 km^3) is available for people and ecosystems.

The availability of water might be sufficient for the overall world population (**Figure 1**); nevertheless, the geographic distribution of water sources is not proportional to the resident population. Therefore, nowadays, out of a worldwide population of roughly 6.8 billion, one-third is living in water stress countries (this takes place when the consumption exceeds 10% above the total supply). If this trend continues, the forecasts are that two-thirds of the world population will live in water scarcity in many regions around the globe by the year 2025.

US Filter has predicted water stress only 15 years from now in China, Southeast and Southwest Asia, India, the Middle East, North Africa, South Africa, and the western United States. Approximately half of the European countries, representing almost 70% of the population, are currently facing water stress issues [1]. **Figure 2** ranks the European countries

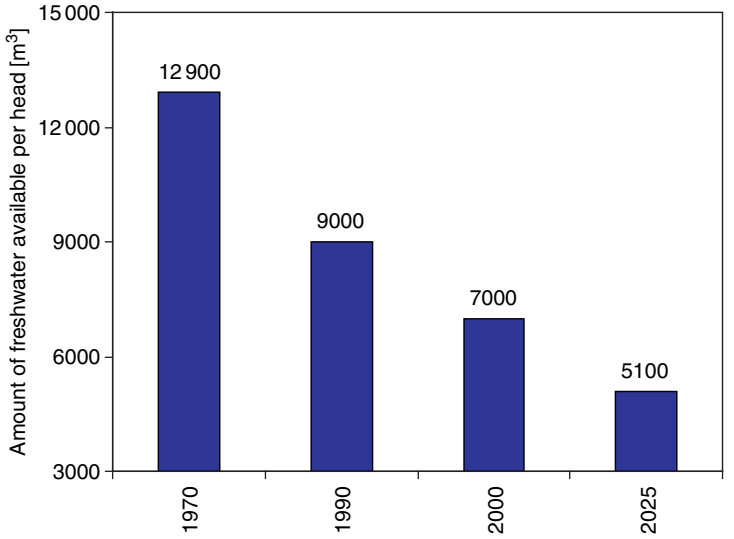


Figure 1 Trend of the estimated, but not effective, worldwide average per capita water availability with time.

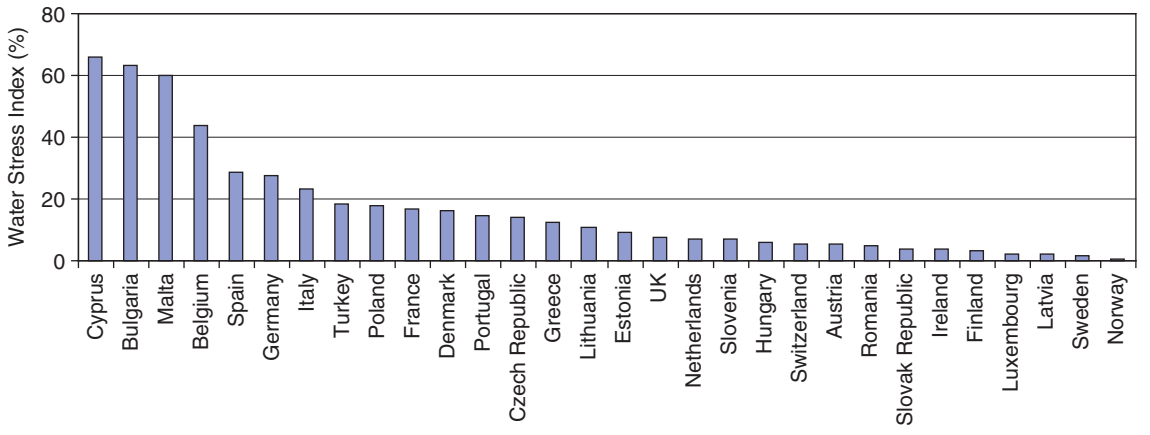


Figure 2 Water stress index for the European countries. [1].

according to their water stress index (the ratio of a country's total water withdrawal to its total renewable freshwater resources).

The water stress index serves as a rough indicator: with values less than 10%, water stress is considered low; a ratio in the range of 10–20% indicates that water availability is becoming a constraint on development and that significant investments are needed to provide adequate supplies. A water stress index above 20% is supposed to necessitate comprehensive management efforts to balance supply and demand [1].

Frank Rijsberman [2], director of the International Water Management Institute (the world's leading body on freshwater management), and Kofi Annan [3], the seventh secretary-general of the United Nations and the winner of the Nobel Peace Prize in 2001, sustain that, globally, water usage has increased by 6 times in the past 100 years. Mr. Rijsberman also declared that water use would double again by 2050, driven mainly by irrigation and demands of agriculture.

Some countries have already run out of water to produce their own food. The absence of improvements will result in an even more widespread water scarcity and rapidly increasing water prices. Mr. Rijsberman foresees the price of water to increase everywhere to meet an expected 50% increase in the amount of the world's food requirement in the next 20 years.

Moreover, it is predicted that water conflicts will become common in many countries. Several years ago, a World Bank official also suggested that water wars are not too far, particularly in countries such as Turkey, Syria, Iraq, and Egypt.

For example, the Tigris and the Euphrates rivers both originate in Turkey and uninterruptedly flow to Syria and Iraq, where they provide the irrigation water needed in the arid climate (**Figure 3**). Turkey has proposed a series of dams that would reduce river flow, which, obviously, causes alarm downstream.

Egypt, whose population of 68 million may reach 97 million by 2025, essentially receives no rainfall. It

Figure 3 Tigris and Euphrates rivers. From Ofori-Amoah, A. Water Wars and International Conflict, http://academic.evergreen.edu/g/grossmaz/OFORIAA.

imports more than half of its food because it does not have enough water to grow it domestically. All agriculture is irrigated by seasonal floods from the Nile River, and from water stored behind the Aswan High Dam. Any interference with the water flow by Sudan or Ethiopia could starve Egypt (**Figure 4**).

The situation is serious in China as well where, with 1.26 billion people, 550 of the country's 600 bigger cities are running short of water. In this country, in spite of the total volume of water resource being 2812.4 billion m^3 (occupying the sixth place in the world), the pro-capita water resource volume is only one-fourth of that of the world average, making China as one of the 13 poorest water-shortage countries in the world. Water shortage has already become a serious problem, especially in the northern coastal area and in several islands (Tianjin, Beijing, Hebei, Shandong, Henan, Shaanxi, Liaoning, Ningxia, etc.). The coastal area represents 15% of the country's total land mass. The coastline is more than 18 000 km long; the islands are more than 6500 in number; the coastal population accounts for more than 40% of the whole country; and it is also the most developed economical area of China. Marq de Villiers says that, only in the dry Northern China "the water table is dropping one meter per year due to over-pumping" [6]. The huge Yellow River is now left with only 10% of its natural flow, sometimes failing to reach the sea altogether [7]. Lloyd Timberlake, spokesperson for the World Business Council on Sustainable Development, sustains that the growing demand for water in China can potentially lead to over-exploitation and a decline in the availability of water for domestic, agricultural, industry, and energy production use. Moreover, some Chinese rivers are so polluted with heavy metals that they cannot be used for irrigation. This inevitably leads to loss of production, both industrial and agricultural; eventually, China will have to import more food, which can also affect public health – all of which in turn will ultimately lead to an economic downturn [2].

The Aral Sea in Central Asia is another example of massive diversion of water for agriculture in the Soviet regime, causing widespread water scarcity and one of the world's worst environmental disasters.

The Himalayas, which act as gigantic water banks supplying water to 2 billion people in Asia, are melting ever faster as global warming accelerates. Meanwhile, devastating droughts are crippling Australia and Texas. Australia is faced with water scarcity in the Murray–Darling Basin as a result of diverting large quantities of water for use in agriculture and in various other areas.

In India, there are areas facing perennial water shortage. A large number of villages in various parts of the country are known to be suffering from excess salinity, fluoride, nitrate, iron, arsenic, and microbial contaminations of groundwater. About 200 000 km^2 of land has a problem with inland salinity. With more than 3.5 million hand pumps and 5.6 million tube wells in operation, pumping in groundwater is now nearly double the rate of aquifer recharge from rainfall. The water demand in India will increase by 50% over the next 20 years, while the country's population is expected to touch 1650 million by 2050. This means the demand for water will rise from 800 billion m^3 now to 1500 billion m^3 [8].

Figure 4 Nile flows through Egypt, Sudan, and Ethiopia. From Nor Any Drop to Drink, http://www.flatrock.org.nz/topics/environment/effluent_for_the_affluent.htm.

Israel, with a population 6.2 million, invented many water-conserving technologies; however, water withdrawals still exceed resupply. Overpumping of aquifers along the coast is allowing seawater to pollute drinking water.

Jamie Pittock, director of WWF's freshwater program, maintains that in the United States large areas are already using substantially more water than can be naturally replenished. This situation will only be exacerbated as climate change is predicted to bring lower rainfall, increased evaporation, and changed patterns of snow melting.

Under this global situation, solutions such as water transfer or dams construction cannot be sufficient methods to satisfy the increasing water demand and decreasing supply. As countries continue to develop and cities to expand, few new water resources are available to support daily freshwater needs.

Therefore, in the past few decades, water scarcity encouraged the development of new water-saving technologies and better management of water sources. In particular, water reuse and desalination have emerged as the essentials to sustain future generations across the globe.

Some governments have already issued large-scale programs to recover and reuse treated municipal wastewaters, rehabilitate saline and contaminated wells and other sources, and desalinate brackish and marginal water sources (marginal water includes industrial, agricultural, and municipal effluents as well as contaminated surface and well waters).

Advance technologies in water purification, as molecular separations based on artificial membranes combined with water reuse systems, have taken on a key role in water desalination and reclamation schemes that are aimed at higher-water-quality reuse applications. At present, membrane operations contribute prominently in alleviating the water stress problem worldwide and, in future, they might also help to completely redesign water production, water treatments, and water distributions for a modern and advanced city planning in a cheaper and more sustainable way.

4.09.3 Sea/Brackish Water Desalination

Undoubtedly, sea/brackish water desalination has emerged in the past few decades as the most promising contributor to solve the water-shortage problem.

Generally, desalination refers to any of the several processes that remove salts and other minerals from water. Water is desalinated in order to be converted to freshwater suitable for human consumption or irrigation in regions where the availability of freshwater is limited. These processes can also produce different types of salts as by-products.

Water is defined to be fresh when it contains less than 500 ppm of total dissolved salts (TDS). However, many countries have higher upper salinity limits for freshwater (e.g., 1000 or 3000 ppm) [9]. For example, the World Health Organization (WHO) and the Gulf Drinking Water standards recommend a drinking water standard of 1000 $mg\,l^{-1}$ TDS. Australia and California [9] also have a drinking water standard of 1000 $mg\,l^{-1}$ TDS. The state of Utah has a TDS limit of 2000 $mg\,l^{-1}$, while Florida has a standard of 500 $mg\,l^{-1}$ TDS [9].

The salinity of the waters fed to the desalination facilities ranges from 1000 to 60 000 ppm TDS [9]. Waters with TDS in the range 1500–15 000 ppm are labeled as brackish waters, whereas seawater sources contain 15 000–50 000 ppm TDS [10]. Unlike governmental standards, most desalination facilities are designed to achieve a TDS of 500 $mg\,l^{-1}$ or less [11–14], while higher TDS concentrations are allowed for desalinated waters used for other purposes (such as crop irrigation).

The principal desalination technologies can be classified by their separation mechanism into thermal and membrane desalination methods. Thermal desalination separates salt from water by evaporation and condensation, whereas membrane processes use semi-permeable membranes and pressure to separate salts from water.

An overview of the available desalination techniques is given in **Table 1**.

Table 1 Membrane and thermal applied desalination technologies

Membrane desalination technologies	*Thermal desalination technologies*
Reverse osmosis (RO)	Multi-stage flash (MSF)
Nanofiltration (NF)	Multieffect distillation (MED)
Electrodialysis (ED)	Vapor compresssion (VC)

Thermal desalination has been used for hundreds of years to produce freshwater, but the first large-scale thermal desalination plants sprouted in the desert areas only in the 1960s. The Gulf Region (Middle East) pioneered the design and implementation of seawater thermal desalination processes. Today, the Middle East collectively holds approximately 50% of the world's desalination installed capacity [9, 10] and primarily uses multistage filtration (MSF) technology due to the low cost of fossil fuel in this region.

While thermal desalination has remained the most frequently applied technology in the Middle East, membrane processes have rapidly developed over the past 40 years and now surpass thermal processes in new plant installations.

As a matter of fact, statistics show that membrane and thermal processes equally share production capacity, with RO dominating the membrane processes and MSF dominating thermal processes. However, the statistics change dramatically when the number of plants is considered: among the current and future sea/brackish water desalination plants, membrane-based systems are the most widely used processes, whose installations represent 80% of the number of the desalination plants worldwide (90% of which use RO technology), with thermal processes representing just 20% [15].

Saudi Arabia is the world leader in desalination with approximately 26% of the global production capacity (86% achieved using MSF technology). United States is the second with 17% of the global production capacity (84% achieved using membrane processes (RO + nanofiltration (NF)) [9].

In Europe, desalination capacities are concentrated around the Mediterranean Sea, in particular in Spain and Italy: 69% of desalination plants in Spain use RO technology, while only 20% of plants in Italy use RO [16].

Asia is becoming a fast growing market due to its enormous population and economic growth. As a result, this is leading to a water demand that cannot be satisfied with conventional water sources. By the end of December 2008, 56 seawater desalination plants were established in China with a global production capacity up to 276 100 $m^3 d^{-1}$ (72.1% achieved using RO). Currently, 45 seawater desalination plants are under normal operation accounting for 79.4% of the total water production in China. Water production capacity will increase up to 288 000 $m^3 d^{-1}$, thanks to nine seawater desalination plants to be installed in Tianjin, Shandong, Zhejiang, Liaoning, and Hebei.

The increasing use of desalination around the world demonstrates the extent to which sea/brackish water desalination contributes to alleviate water-shortage problem: according to the 2008–09 edition of IDA's Desalination Yearbook (*The International Desalination and Water Reuse*, 2008 [17]), the amount of global contracted (planned) capacity grew in 2007 by 6.8 million $m^3 d^{-1}$, up from 4.7 million $m^3 d^{-1}$ in total contracted capacity in 2006. This means that, as of 30 June 2008, the cumulative contracted capacity of desalination plants around the world was at 62.8 million $m^3 d^{-1}$. Seawater desalination makes up 62% of that total, with brackish water desalination representing another 12.2 million $m^3 d^{-1}$. Wastewater applications of desalination technologies for water reuse are growing fast, currently representing 5% of the total capacity. By the end of 2008, the 456 000 $m^3 d^{-1}$ plant serving Fujairah in the United Arab Emirates was the largest single desalination plant in operation. However, there were five other plants with capacities in excess of 500 000 $m^3 d^{-1}$ under construction in the Middle East region. The largest of these was the 880 000 $m^3 d^{-1}$ Shoaiba 3 unit in Saudi Arabia.

Later, in 2009, the Jebel Ali Desalination Plant (phase 2), in the United Arab Emirates, became the world's largest desalination plant. It is a dual-purpose facility that uses multistage flash distillation and is capable of producing 300 million m^3 of water per year [18].

The largest desalination plant in the United States is the one at Tampa Bay, Florida, which began desalinating 95 000 m^3 of water per day in December 2007.

The largest SWRO desalination plant in the world is the one in Ashkelon (Israel). The project was developed by a consortium of three international companies: IDE Technologies (50% and lead partner), Vivendi Water (25%), and Dankner-Ellern Infrastructure (25%) [19]. In fact, the plant produces more than 100 million m^3 of desalinated water per year and it is fully operational since December 2005.

For what concerns brackish water desalination, brackish groundwater is treated at the El Paso plant since around 2004 producing 104 000 m^3 of freshwater daily by RO.

The world's largest brackish water RO desalination plant was completed in 2006 in Wadi Ma'in, Jordan, operating at 129 000 $m^3 day^{-1}$, with a maximum capacity of over 150 000 $m^3 day^{-1}$ [20]. Algeria plans to

increase its number of plants from 10 to 43 by the year 2019, with a production goal of 2 million m^3 day^{-1} [9].

The 2008–09 Desalination Yearbook [17] also reports that the number of contracted desalination plants worldwide totaled to 13 869 as of 30 June 2008, up from 13 080 the prior year, most of which use RO technology.

4.09.4 Desalination Technologies: An Overview

Although thermal and membrane desalination processes equally share current worldwide desalination production capacity, RO has emerged as the leader in future desalination installations since it typically uses less energy than thermal distillation. Desalination remains energy intensive, however, and future costs will continue to depend on the price of both energy and desalination technology.

MSF continues to be the most frequently applied thermal desalination technology in the Middle East due to the low available energy price, its suitability to combination with generation of electric energy, and its capacity to better deal with more saline water and deliver even higher permeate quality. RO is by now the most common membrane-based desalination option, particularly in the area around the Mediterranean Sea.

Table 2 illustrates key operational data for thermal and membrane-based desalination options.

In the following sections an overview of the most common membrane-based desalination technologies is presented.

4.09.4.1 Electrodialysis

Electrodialysis (ED) is a membrane operation for seawater or brackish water desalination. ED is based upon transport of the dissolved salts through a stack of cationic and anionic membranes by applying an electric potential, so that a diluted stream is obtained. It can also be used for the concentration of charged species in aqueous solutions.

ED has been used on an industrial scale since the 1960s [10] and it has been in commercial use for desalination of brackish water for the past three decades, particularly for small- and medium-scale processes [21, 22].

The general principle of ED is shown in **Figure 5**.

In an ED unit, several cation-exchange membranes (CEMs) and anion-exchange membranes (AEMs) are stacked together in an alternating sequence. Dissolved cations (e.g., K^+ and Na^+) of sea/brackish water migrate toward the negative electrode (cathode) through the CEMs, which allow only cations to pass. On the other hand, the anions (e.g., Cl^- and NO_3^-) migrate toward the anode (positive electrode) through the AEMs permeable

Table 2 Comparsion of operational data of thermal and membrane-based desalination technologies

Thermal desalination processes (MSF, MED, VC)	*Membrane desalination processes (RO)*
Typical salt content of raw water[a] = 30 000–100 000 ppm	Typical salt content of raw water[a] = 1000–45 000 ppm
Desalted water with low tatal dissolved solids concentrations (10–20 ppm)	Desalted water with total dissolved solids concentrations between 100 and 550 ppm
Thermal energy consumption = 12 k Wh m^{-3}(data for MSF)[a]	Thermal energy consumption = 0
Energy consumption (MSF)[b] = 17–18 k Wh m^{-3}	Energy consumption[c,d,e] = 2.2–6.7 k Wh m^{-3}
Recovery factor ≈ 10%	Recovery factor[f,a] ≈ 40–60%
High capital costs	Low capital costs
High operating costs	Low operating costs
Desalted water cost[f,a] ≈ 0.9÷1.4 $\$m^{-3}$ (MSF)÷2.34 $\$m^{-3}$ (MED, TVC)	Desalted water cost ≈ 0.50–0.70 $\$m^{-3}$ (in the most part of SWRO plants[d,g]) and 0.36 $\$m^{-3}$ (from brackish water sources[a,h])

[a] From Fritzmann, C., Löwenberg, J., Wintgens, T., Melin, T. *Desalination* **2007**, *216*, 1–76.
[b] From New desalination capacity up by 39% in first half of 2008. *Int. Desalin. Water Reuse*, **2008**, *18*(3).
[c] From Kores, W.J. **2004**
[d] From http://www.water.technology.net/projects/israel/specs.html
[e] From Water Desalination Reports **2008**
[f] From Ettouney *et al*. **2002**
[g] From Van der Bruggen, B., Vandecasteele, C. *Desalination* **2002**, *143*, 207–218.
[h] From http://www.epwu.org/167080115.html

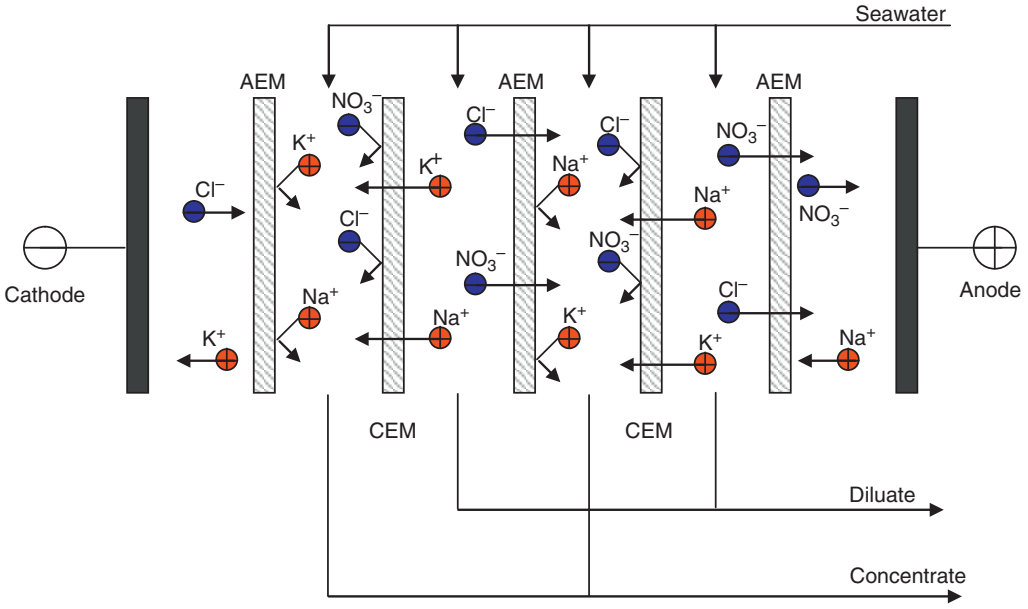


Figure 5 Principle of the electrodialysis process.

only for anions. Therefore, the CEMs/AEMs are ion-selective membranes, which control the movement of ions. Thus, the concentration of ionic species is reduced in the so-called diluate compartments and increased in the concentrate compartments.

To prevent scaling, the process utilizes inverters which reverse the polarity of the electric field about every 20 min. This process is called electrodialysis reversal (EDR) [21].

ED process is noneconomical for waters with high salt concentrations [10, 23], but is competitive for brackish waters with up to 3000 ppm salt, while it is rarely used for seawater desalination. For water with low salt concentrations, ED/EDR is considered to be the most advantageous technique.

4.09.4.2 Reverse Osmosis

RO is a membrane process capable of rejecting nearly all colloidal or dissolved matter from an aqueous solution, producing a concentrate brine and a permeate which consists of almost pure water. In this process, the solvent (pure water) is forced to pass thorough the molecular structure of a membrane by applying a pressure larger than the osmotic pressure of the seawater, while impurities and salts are trapped. Therefore, in RO process, the membrane is permeable for water, but not for the dissolved salts. In this manner, a separation between a pure water fraction (the permeate) and a concentrated fraction (the retentate or the concentrate) is obtained.

Desalination by RO entered the commercial market in the late 1960s when the membrane manufacturing process became efficient enough to produce desalted water that was competitive with thermal processes. However, though more efficient than vaporization or distillation and requiring far less physical space for the same operation, the first plants demanded a high-energy input. In the late 1970s, early SWRO plants consumed as much as 20 kW h m^{-3}. Over time, engineers developed energy recovery systems (such as Pelton turbine and pressure exchanger system) that take advantage of the high pressure of the RO waste brine streams. This led to a sheer drop in the energy consumption and, as a consequence, in the desalted water cost.

By 2000, the power consumption rate decreased to approximately 3.5 kW h m^{-3} of desalinated seawater. This was in large part due to several advances in technology that occurred during the 1990s, which include

- new low-energy RO membranes with improved salt rejection and lower price,
- high-efficiency pumps and motors, and
- more efficient energy recovery devices (ERDs).

Recent studies performed in the United States by the Affordable Desalination Collaboration demonstrated

that energy requirements for the RO desalination process alone could be lowered to 2 kW h m^{-3} through the use of low-energy RO membranes and high-efficiency ERDs. A recent request is to aim for a consumption of 1.5 kW h m^{-3} by 2030, not far from the theoretical inferior limit that remains around 0.6 kW h m^{-3} due to the osmotic pressure (**Figure 6**) (Drioli and Macedonio, submitted).

At the same time, also the cost of the RO membranes dropped by about 50%. An example can be found in some SWRO elements developed by the Dow Chemical Company in the 1980s and 1990s. In 1996, the company introduced in the market the SW30HR-380 element as the improvement of its SW30HR-8040 element (another SWRO membrane of 9 years older, with a nominal flux <25% and a salt passage <33%): the market price of an SW30HR-380 element in 1996 was about 50% that of an SW30HR-8040 in 1985 [24].

The decreasing trend of the membranes' price per unit capacity from 1980 to 2006 is shown in **Figure 7**.

The progress in SWRO desalination caused a decrease in the cost of the reclaimed water from membrane plants (**Figure 8**) and an increasing use of membrane technology for water desalination.

4.09.4.2.1 RO: Technical description

A typical RO desalination plant includes the following stages:

1. water abstraction and pretreatment,
2. pumping system,
3. RO membrane unit,
4. energy recovery system,
5. permeate posttreatment, and
6. brine disposal strategy.

Pretreatment and posttreatment steps are required to condition water before and after the RO membrane

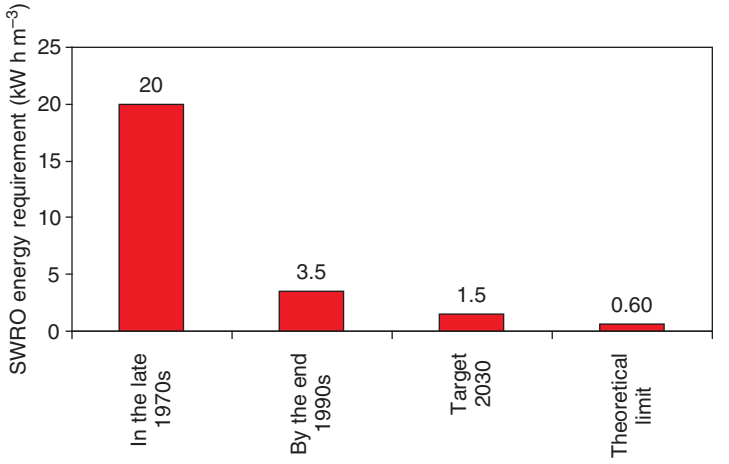


Figure 6 History of power consumption required for seawater reverse osmosis (SWRO) desalination processes. Adapted from Drioli, E., Macedonio, F. *Water Sci. Technol.* (submitted).

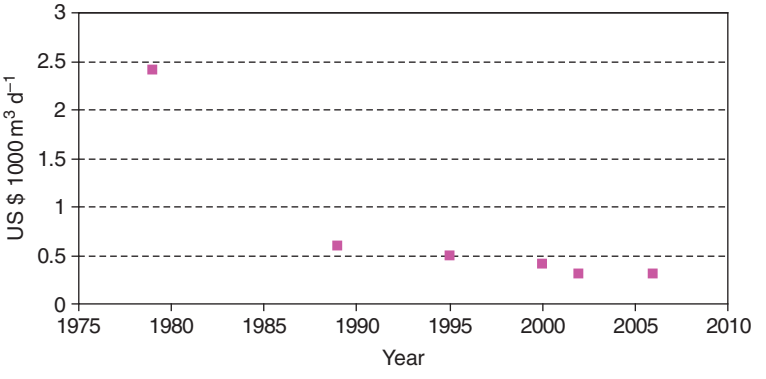


Figure 7 Price of membranes per unit capacity over the past 20 years. Adapted from Desalination **2008**, *3*(1), 12–14.

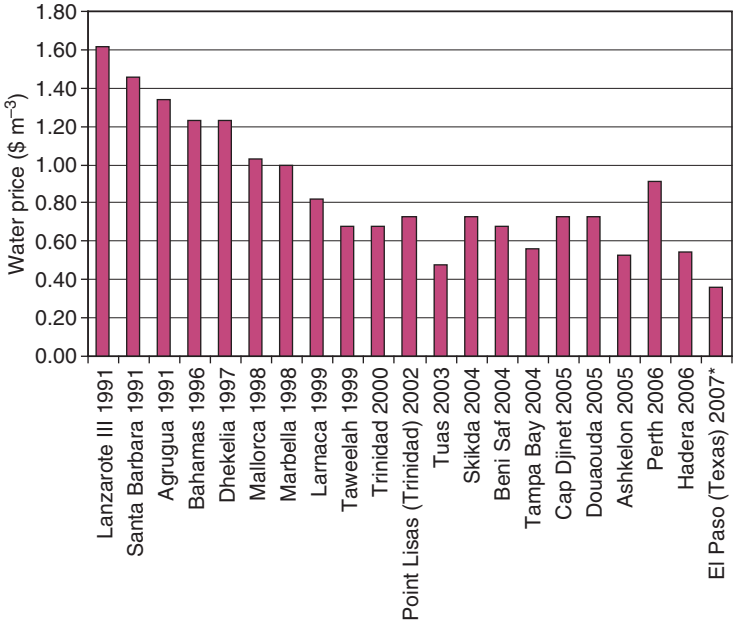


Figure 8 Water price from several selected seawater RO desalination plants (*brackish water desalination plant).

process to make it suitable to the application. Pretreatment (step 1) includes all activities to adjust intake seawater in order to reduce membrane fouling, scaling, and deterioration.

Subsequently, before entering the polymeric RO thin-film composite membranes, the clarified feedwater has to be pressurized (step 2). Pressures needed for the separation vary nowadays from 15 to 20 bar for brackish water desalination and 55 to 85 bar for seawater desalination, depending on the temperature and the salinity of the water.

In the RO membrane (step 3), salt is separated from water with a rejection of 98–99.5% depending on the membrane in use.

Generally, desalination can be carried out by a single-pass configuration or double-pass RO arrangements: in a single-pass configuration, one or more modules containing highly rejecting membranes are installed in parallel to give permeate water that can be directly utilized; in double-pass operation, each stage is fed by the reject of the previous stage (**Figure 9**).

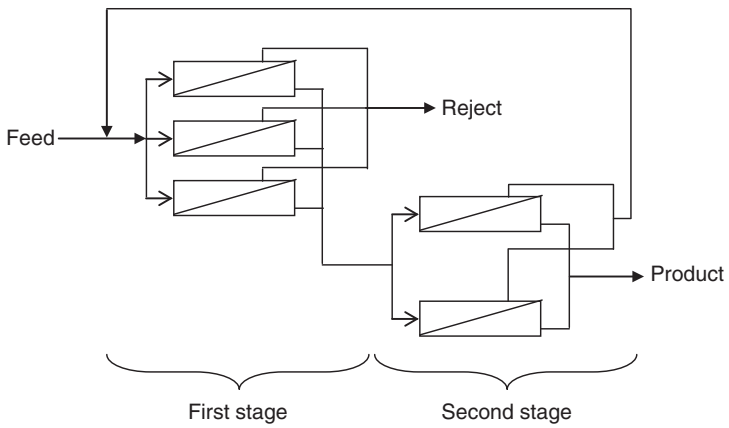


Figure 9 Twin-pass RO system.

Moreover, although the rejection values are very high, in some cases (e.g., for boron and arsenic) they are not sufficient to produce water with concentrations that satisfy the WHO drinking water quality guidelines. The recourse to several pass-stages (**Figure 9**) also helps to solve this problem. At the first pass-stage, the most part of salt in the seawater is removed. By treating the resulting product water with other RO membrane elements, the solute concentration is brought to below the regulation value.

The produced permeate, however, needs to be remineralized, re-hardened, disinfected by chlorination, and adjusted to drinking water standards (step 5).

For what concerns the RO retentate, it is highly concentrated and it is released from the membrane module at high pressure. Thanks to ERDs, such as energy recovery turbine (which mostly are either Pelton wheel or turbocharger systems) and pressure exchanger, it is possible to reuse the energy from the concentrate flow (step 4). The concentrate is directed to the ERD, where its energy is directly transferred to part of the incoming feedwater. Depending on the overall recovery and efficiencies of ERD and pumps, this can substantially reduce the energy consumption of an RO plant.

Once the energy of the RO retentate has been recovered, it needs to be disposed (step 6). Several disposal options are available for inland desalination plants; some of them are [10]

- disposal into the sea through long pipeline systems,
- disposal onto land surface,
- discharge into solar evaporation ponds,
- disposal to wastewater systems,
- land application (spray irrigation and percolation ponds), and
- injection into deep saline aquifer (nondrinking water aquifer).

Negative influences of the discharged brine may damage the environment and also result in financial penalties if toxicity standards are not met. Possible measures to mitigate environmental impact of the discharged brine are as follows:

- lower recovery rates and/or dilution of the brine with seawater prior to the discharge to reduce its salinity [10];
- discharge devices, such as multiple port diffusers, spreading the brine across a larger area and increasing dispersion velocity [10];
- dilution of the brine with water from other processes, for example, with cooling water from power [10];
- discharge in an area with strong currents and at depth [10]; and
- processing the concentrated waste streams in order to extract the valuable components contained.

In literature, various studies can be found for the recovery of the compounds present in the retentate steams of the desalination plants:

- The Murray–Darling Basin Commission (MDBC) converts the salts present in the water into commercial products addressed to the market: first the retentate is evaporated and then it is sent to a conventional crystallizer for the extraction of NaCl and epsomite ($MgSO_4 \cdot 7H_2O$) [26].
- M. Turek [27] suggested dual-purpose desalination-salt production systems. Precisely, he proposed (ultrafiltration (UF)–NF–MSF-crystallization) and (UF–NF–RO–MSF-crystallization) processes for the recovery of salts and water by the desalination plants.
- In various works, Drioli and co-workers [28–31] proposed the recourse to membrane distillation (MD) and membrane crystallization (MCr) techniques for the exploitation of the components present in the retentate streams of the desalination plants. MD/MCr techniques, thanks to their intrinsic characteristic of temperature driven membrane processes, allow us to produce freshwater also from highly concentrated feeds (such as the brine streams) with which NF and RO cannot operate due to the osmotic phenomena. Therefore, the introduction of an MD/MCr unit downstream RO and/or NF retentate allows us to increase the recovery factor of the desalination plant, thus reducing the volume of concentrated streams usually discharged and, in the case of MCr, recovering the dissolved salts in the form of high-quality crystals.

4.09.4.3 MF, UF, and NF: Pressure-Driven Membrane Operations for Water Desalination

Other membrane-based technologies used in water treatment are microfiltration (MF), UF, and NF.

As we go from MF through UF to NF and RO, the size of the particles or molecules separated

diminishes and, consequently, the pore size of the membrane becomes smaller. This implies that the resistance of the membranes to mass transfer increases and the applied pressure (e.g., the driving force) has to be increased to achieve the same flux.

Both in MF and UF the separation is based on sieving mechanisms. UF membranes have originally been developed and proven for many years in a wide range of much more difficult liquid environments than seawater, such as highly polluted municipal and industrial wastewaters [32]. UF membranes provide a positive barrier to particulates, pathogens, macromolecules, colloids, and small bacteria and not only toward suspended solids and large bacteria as in the case of MF membranes.

For what concerns NF, it is based on the same principle of RO, that is forcing a solvent through the molecular structure of a membrane while trapping impurities and salts. NF membranes are similar to RO membranes, with the exception that the latter have a tighter structure. This means that NF membranes are generally used in softening, disinfection, and removal of organic materials, metals, and bivalent ions, whereas monovalent species (such as Na^+ and Cl^-) are retained only by 10–50% depending on the membrane properties. NF and RO are used for a wide range of applications, such as the purification of water to produce potable water (mainly sea and brackish water desalination) and the production of ultrapure water for the semiconductor industry.

In the past few years, the growth in MF, UF, and NF installations in water purification processes has been almost explosive. In 1995, it was estimated that, in North America, the installed capacity for MF/UF was less than 25 MGD [33]. Five years later this number increased to over 400 MGD. MF systems have been installed in both the potable water markets and for water reuse applications treating municipal secondary effluents, while UF systems have been gaining wide acceptance for potable water enhancement.

NF membranes (originally called open RO) were used as early as 1976 in Florida for the treatment of drinking water sources [34]. However, NF–RO combinations were used in commercial desalination plants only in 1991. Actually, large NF plants have been put into operation, for example, in Florida for organic removal (e.g., Plantation that has an 18 MGD capacity). One of the largest NF plants is used in Méry-sur-Oise (France) with a capacity of $140\,000\ m^3\ d^{-1}$. It was designed to improve drinking water quality, removing organic pollutants, and softening water by rejecting multivalent ions [35].

In the past few years, the development of MF, UF, and NF operations has also greatly increased the reliability of RO. Some of the major problems in RO applications are, in fact, fouling and concentration polarization phenomena. While concentration polarization can be minimized by hydrodynamic means, such as an appropriate feed-flow velocity and membrane module design, the control of membrane fouling is more difficult. It can never be fully prevented but it can be reduced and controlled through the pretreatment of the feed solution. An adequate pretreatment, supplying high-quality feedwater, regardless of fluctuation of raw water quality, is essential for an efficient plant operation. Ineffective pretreatment can lead to problems with the RO system, including high rates of membrane fouling, high frequency of membrane cleanings, lower recovery rates, high operating pressure, poor product quality, and reduced membrane life – all having a direct impact on plant productivity and operational costs [32]. Accordingly, pretreatment optimization is the key factor for a successful RO desalination system. In the past, conventional RO pretreatment (which is defined as chemical and physical pretreatment without the use of membrane technologies) has been widely applied. With the cost of membranes constantly declining and the quality of feedwater continually deteriorating, an increasing number of plant owners are nowadays considering the use of membrane-based pretreatments to replace less efficient, conventional pretreatment systems, which do not represent a positive barrier to colloids and suspended solids and produce unsteady quality of RO feedwater [32].

Pressure-driven membrane operations (such as MF and UF) are the new trend in designing pretreatment systems because they are able to remove a wide range of contaminants. Moreover, membrane application in water pretreatment also provides many other advantages over conventional treatment, including capability of handling wide fluctuations in raw water quality, enabling operation with a high and stable permeate flux in long-term operation even during storm events and algae blooms [10, 32, 36]; small footprint; and low energy consumption. Therefore, the use of membrane pretreatment allows us to provide an RO feedwater of good quality which results in the reduction of membrane fouling as well as in capital and operating costs of the desalination plant.

Moreover, for the treatment of very bad water quality, it is necessary to add a coagulation and settling/flotation [37]. The coagulation and settling are considered as the pretreatment of the pretreatment, which helps in improving the quality of the water fed to the RO and, in turn, which allows higher RO flux.

Further improvements can be achieved through the introduction of NF as RO pretreatment process. Since NF retains turbidity, microorganisms, hardness, the most part of multivalent ions, and 10–50% of monovalent species, as a consequence, the osmotic pressure of the RO feed is decreased thus allowing the unit to operate at higher recovery factors. In fact, according to Drioli and co-workers [29], coupling NF and RO for seawater desalination, a global recovery factor of 52% can be obtained (higher than that of a typical RO operation which is in the range of 35–40%). Moreover, the integrated NF–RO process is more environmentally friendly, because less additives (antiscalants and acid) are needed [23].

A successful example of an integrated water treatment process is in the world's largest integrated membrane system put into operation by the PWN Water Supply Company North Holland (the Netherlands) [38]. In this plant, UF and RO are the most essential process elements, having a capacity of 18 million m^3 per year (13 mgd). Water extracted from the Ijssel Lake is processed in the membrane plant. The produced drinking water meets the most stringent water quality criteria regarding desired low salinity, minimal corrosion, and optimal low hardness and organic matter content.

4.09.4.4 Integrated Membrane-Based Desalination System

Seawater desalination through RO technology epitomizes the success of membrane technology and is probably the clearest example today of what can be achieved through the integration of different membrane operations. The key characteristics of membrane operations are, in fact, their large flexibility, operational simplicity, and mutual compatibility for integration. These distinctive features offer the possibility to combine different membrane technologies for minimizing the limits of the single membrane units and for increasing the efficiency of the overall system.

In the previous sections, it has been shown, in fact, that the widespread use of RO desalination around the world is the consequence of the development of RO membranes (with higher salt rejection, more stability and resistance to chemicals, and lower price) and ERDs. Moreover, the understanding, the control, and the minimizing of RO membrane fouling phenomena have been further causes of the success of RO desalination and a suitable pretreatment is indispensable for an efficient plant operation. MF, UF, and NF operations are increasingly applied for the pretreatment since they ensure many advantages over conventional pretreatment.

Currently, another membrane operation is studied as RO pretreatment: membrane bioreactor (MBR). Usually, MBR is employed in wastewater treatment and reuse for the separation of effluent from activated sludge, providing effluents disinfected and of high quality, especially suitable for reuse and recycling of wastewater. In the Membrane-Based Desalination: An Integrated Approach (MEDINA) project (one of the projects funded by the European Commission within the 6th Framework Program), MBR has been investigated for the removal of a variety of anthropogenic organic pollutants and fouling agents that are increasingly present in sea/brackish water. MBR is considered a high-tech process with high initial investment costs when applied to wastewater treatment. However, this should not have to be the case when MBR is used to treat seawater, with a typical total organic carbon concentration in the range of 1.0–3.0 mg l^{-1}. As a consequence, under such conditions, the use of MBR technology as RO pretreatment might be a very cost-effective process.

As previously described, one of the main problems related to seawater desalination plants is that of brine disposal and an interesting solution is one more time offered by membrane engineering and, in particular, by the novel and avant-garde membrane contactor operations (which include MD and MCr).

As single units, membrane contactors might be more efficient than corresponding traditional unit operations; however, it is their coupling with other membrane operations that is expected to improve the efficiency of the overall process.

MD and MCr are thermally driven membrane processes, all of which operate at relatively low temperature. In these processes, a hydrophobic microporous membrane separates a hot (feed or retentate) and cold (distillate or permeate) stream of water. The temperature difference produces a vapor pressure gradient, which causes water vapor

to pass through the membrane. Only volatile components of the feed may be transported from the retentate to the permeate due to the hydrophobic nature of the membrane. The result is a distillate of very high purity, which does not suffer from the entrainment of species that are nonvolatile. The water vapor condenses on the low-temperature side and pure water is formed.

MD and MCr operations have several advantages. One of the most important is that they are not limited by concentration polarization phenomena. Therefore, NF and/or RO retentate streams can be treated with MD/MCr for the recovery of water and salts contained in them.

As stated earlier, in recent years, Drioli and coworkers [28–31, 38] have been developing and applying membrane contactor technology in order to reduce pollutant emissions and to ensure a more rational use of natural resources. According to their studies, when the NF and RO retentate streams of a desalination plant are processed in a MCr unit (1) the salts present (sodium chloride, magnesium sulfate, and calcium carbonate) can be recovered in the form of crystals valuable for medical, domestic, or agricultural use; and (2) the recovery factor of the desalination plant increases so much to reach 92.8%, higher than that of an RO unit (about 40%) and much higher than that of a typical MSF (about 10%).

Moreover, since MD operates on the principles of the vapor–liquid equilibrium, it can also be used for the treatment of polluted water (if pollutants are nonvolatile) in order to convert it into pure water and in a concentrate containing the substances present in the parent solution. For example, MD can be and has been also used for boron and arsenic removal from water, in order to obtain substantial pollutant reduction in the permeate streams of the water treatment plants [39, 40].

Finally, membrane contactor technology has another application in water treatment systems. In fact, it can also be used for the reduction of the amount of oxygen or carbon dioxide dissolved in the streams. Oxygen and carbon dioxide present in seawater affect the performance and the material life of the desalination plants. Removal of these gases is usually made by stripping in a packed column and the final water pH is adjusted by means of caustic soda. This operation is difficult to fine control – due to the very low dosing rates – and is not well accepted by end users who do not prefer chemically treated waters. Membrane contactors working on RO permeate and/or feed can efficiently lead to the desired control of the oxygen and carbon dioxide content avoiding the final use of chemicals.

4.09.5 Conclusions

Reclamation and reuse of purified sea/brackish waters represent an important water supply in many areas of the world, able to solve the increasing municipal, industrial, and agricultural demands for water.

Over the past few decades, more and more membrane technology has emerged as the most promising contributor to alleviate worldwide water shortage. Numerous pilot-plant studies and commercial facilities operating all over the world have demonstrated the technical and economic feasibility to desalinate waters through pressure-driven membrane separation processes.

Actually, the challenge is to supply freshwater at lower costs and of better quality through environmentally friendly industrial processes. Membrane engineering offers the possibility to more sustainable freshwater production through those integrated membrane-based systems whose basic aspects satisfy the requirements of process intensification strategy. The latter is an innovative strategy that contributes significantly to the competitiveness of the process industries by making industrial processes more efficient and faster, by replacing large, expensive, energy-intensive, polluting equipments and/or processes, with avant-garde versions that are smaller, less costly, less polluting, and highly safe. In brief, this strategy aims “to produce much more with much less [41]”. This is particularly true when, for the human necessities and in the industrial cycles, water (and often high-purity water) is used in large amount.

Currently, nanostructured artificial membranes and, in particular, the integration of various membrane technologies are providing unprecedented opportunities to develop more cost-effective and environmentally acceptable processes, able to solve, in principle, problems from water quality, to brine disposal, to water costs, and to recovery factors. In fact, the integration of diverse but complementary membrane units in the RO pretreatment and posttreatment steps (from MF, to UF, NF, MD, and MCr) offers the possibility to minimize the problem of RO membrane fouling and to increase the recovery factor of the desalination process, thus reducing brine disposal problem and approaching the concept

of zero-liquid discharge and total raw material utilization.

In conclusion, it is expected that, in the near future, all the different available membrane operations, from the more traditional pressure-driven units (as RO, NF, UF, and MF), to the membrane reactors (MBRs), to the membrane contactors (membrane distillation and membrane crystallizer), will be considered for realizing new integrated water production, purification, and reuse systems. The integration of MCr on NF and/or RO brine might also offer the possibility of producing solid materials of high quality and controlled properties with important added values, transforming the traditional brine disposal cost into a potential new profitable market.

References

[1] Bixio, D., Thoeye, C., Koning, J., *et al. Desalination* **2006**, *187*, 89–101.
[2] Vidal, J., Ed. Cost of Water Shortage: Civil Unrest, Mass Migration and Economic Collapse, http://www.guardian.co.uk/environment/2006/aug/17/water.internationalnews (accessed February 2010).
[3] Annan, K. Terre umide e terre secche, http://www.greencrossitalia.it/ita/speciali/speciale_goldwater/kofi_annan.html (accessed February 2010).
[4] Ofori-Amoah, A.*Water Wars and International Conflict*http://academic.evergreen.edu/g/grossmaz/OFORIAA(accessed February 2010).
[5] Nor Any Drop to Drink, http://www.flatrock.org.nz/topics/environment/effluent_for_the_affluent.htm (accessed February 2010).
[6] Water Woes, http://whyfiles.org/131fresh_water/2.html (accessed February 2010).
[7] Lean, G. Water scarcity 'now bigger threat than financial crisis'. By 2030, more than half the world's population will live in high-risk areas. *The Independent* 15 March 2009,http://www.independent.co.uk/environment/climate-change/water-scarcity-now-bigger-threat-than-financial-crisis-1645358.html (accessed February 2010).
[8] Tewari, P. K. *Int. Desalin. Water Reuse* **2006**, *16*(3), 39–41.
[9] Greenlee, L. F., Lawler, D. F., Freeman, B. D., Marrot, B., Moulin, P. *Water Res.* **2009**, *43*, 2317–2348.
[10] Fritzmann, C., Löwenberg, J., Wintgens, T., Melin, T. *Desalination* **2007**, *216*, 1–76.
[11] Gaid, K., Treal, Y. *Desalination* **2007**, *203*, 1–14.
[12] Petry, M., Sanz, M. A., Langlais, C., *et al. Desalination* **2007**, *203*, 141–152.
[13] Sanz, M. A., Bonnélye, V., Cremer, G. *Desalination* **2007**, *203*, 91–99.
[14] Xu, J., Ruan, G., Chu, X., Yao, Y., Su, B., Gao, C. *Desalination* **2007**, *207*, 216–226.
[15] Frenkel, V. *Int. Desalin. Water Reuse* **2008**, *17*(4), 47–50.
[16] Miller, J. E. *Review of Water Resources and Desalination Technologies;*Sandia National Laboratories: Albuquerque, NM, 2003; http://www.prod.sandia.gov/cgi-bin/techlib/access-control.cgi/2003/030800.pdf.
[17] New desalination capacity up by 39% in first half of 2008. *Int. Desalin. Water Reuse*, **2008**, *18*(3). News Release.
[18] Desalination from Wikipedia, http://en.wikipedia.org/wiki/Desalination (accessed February 2010).
[19] Ashkelon Desalination Plant Seawater Reverse Osmosis (SWRO) Plant, Israel, Israel, http://www.water-technology.net/projects/israel/specs.html (accessed February 2010).
[20] Mohsen, M. S. *Desalination* **2007**, *203*(1–3), 27–46.
[21] Charcosset, C. *Desalination* **2009**, *245*, 214–231.
[22] AlMadani, H. M. N. *Renewable Energy* **2003**, *28*, 1915–1924.
[23] Van der Bruggen, B., Vandecasteele, C. *Desalination* **2002**, *143*, 207–218.
[24] Lomax, I. *Desalination* **2008**, *224*, 111–118.
[25] *Desalination* **2008**, *3*(1), 12–14.
[26] Borgate, T. E. *Value Adding to Salts Recovered from Saline Waters in Disposal Basins in the Murray-Darling Basin;*Murray-arling Basin Commission: Canberra City, ACT, 2004http://www2.mdbc.gov.au/__data/page/334/MDBCintroduction.pdf(accessed February 2010).
[27] Turek, M. *Desalination* **2002**, *153*, 173–177.
[28] Drioli, E., Curcio, E., Criscuoli, A., Di Profio, G. *J. Membr. Sci.* **2004**, *239*, 27–38.
[29] Macedonio, F., Curcio, E., Drioli, E. *Desalination* **2007**, *203*, 260–276.
[30] Curcio, E., Criscuoli, A., Drioli, E. *Ind. Eng. Chem. Res.* **2001**, *40*, 2679–2684.
[31] Macedonio, F., Drioli, E., Curcio, E., Di Profio, G. *Desalin. Water Treat.* **2009**, *9*, 49–53.
[32] Wolf, P. H., Siverns, S., Monti, S. *Desalination* **2005**, *182*, 293–300.
[33] Truby, R. Membrane Separation Markets in North America, *IDA News*, January–February 2001, 4.
[34] Conlon, W. J., McClellan, S. A. *J. Am. Water Works Assn.* **1989**, *81*(11), 47.
[35] Ventresque, C., Bablon, G. *Desalination* **1997**, *113*, 263–266.
[36] Lee, E. K., Chen, V., Fane, A. G. *Desalination* **2008**, *218*, 257–270.
[37] Bonnélye, V., Guey, L., Del Castillo, J. *Desalination* **2008**, *222*, 59–65.
[38] Peinemann, K.-V., Pereira Nunes, S., Eds. *Membranes for Water Treatment*: *Volume 4.* Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2010.
[39] Macedonio, F., Drioli, E. *Desalination* **2008**, *223*, 396–409.
[40] Macedonio, F., Drioli, E. *Membr. Water Treat.* **2010**, *1*(1), 75–81.
[41] Charpentier, J. C. *Ind. Eng. Chem. Res.* **2007**, *46*, 3465–3485.

Biographical Sketches

Francesca Macedonio graduated in chemical engineering at the University of Calabria (Italy) in July 2005 and obtained her doctor's degree in 2009. Her primary research interests are in the fields of membrane processes for sea-, brackish-, and wastewater treatment, integrated membrane desalination processes, membrane distillation and membrane crystallization, energetic and exergetic analyses, as well as economical evaluations of membrane systems.

She was the winner of the Premio Sapio per la Ricerca Italiana 2008 – Premio Sapio Speciale Decima Edizione, and the recipient of the international award for poster presentation at the Euromembrane conference 24–28 September 2006, Taormina, Italy for the paper 'Integrated membrane systems for seawater desalination'.

She is a member of the Section on Membrane Engineering of the European Federation of Chemical Engineering and has authored or co-authored 11 scientific papers on international journals, three chapter of books, and participated in 25 conferences in the field of Membrane Science and Technology.

Professor Enrico Drioli has been working in Membrane Science and Membrane Engineering for many years even when a student in chemistry at the University of Naples. He is a full professor at the Department of Chemical Engineering and Materials at the University of Calabria where he founded, in 1993, the Institute of Membrane Technology of the Italian Research Council. He served there as a director until December 2008. He also served as dean of the School of Engineering of the University of Calabria during the years 1982-85.

He received various award and honors: Doctorate Honoris Causa from University of Paul Sabatier of Toulouse (France) (8 July 2009); International Cooperation Honor Award on September 2005 given by the Membrane Industry Association of China (MIAC) for his special dedication to the International Cooperation between China and Europe in the field of membrane and science technology; guest professor in the Environment and Safety Engineering Department at the Jiangsu Polytechnic University, China (since June 2005); Honorary Member of the A. V. Topchiev Institute of Petrochemical Synthesis at the Russian Academy of Sciences, Moscow (since 1999); Doctorate Honoris Causa in Chemistry and Chemical Technology from Russian Academy of Science (February 1992); Honorary Professor at the China Northwest University in Xi'an, Shaanxi, People's Republic of China (September 1991); President of the European Society of Membrane

Science and Technology (known today as the European Membrane Society) (1982–98); Honorary President of the European Membrane Society (since 1999); Member of the International Scientific Advisory Committee of the Grand Water Research Institute at Technion – Israel Institute of Technology, Israel (since 2004); Member and Moderator of the Research Advisory Council of the Middle East Desalination Research Center Oman, Muscat (since May 1997); Member of the International Advisory Board of the State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences (since 2007); Founding member of the European Federation on Regenerative Medicine (since 2006); Expert in the panels of the OECD project 'Nanotechnology and clean water' (www.oecd.org/sti/nano).

His scientific activity has been mainly in: Membrane Science and Engineering; Membranes in Artificial Organs; Integrated Membrane Processes; Membrane Preparation and Transport Phenomena in Membranes; Membrane Distillation and Membrane Contactors; and Catalytic Membrane and Catalytic Membrane Reactors.

He is the author of more than 530 scientific papers, and 10 scientific books and holds 18 patents in the field of Membrane Science and Technology.

Drioli is the Member of the Advisory Boards of: *Journal of Membrane Science* - Elsevier, and *Polish Journal of Chemical Technology*. In addition, he is the member of the International Advisory Board of *Journal of Water Supply: Research and Technology* – AQUA. He is also the senior advisor to *Chinese Journal of Membrane Science and Technology* (China), and *Technology of Water Treatment Journal*.

Drioli is the member of the editorial boards for *Chemical Engineering and Processing* Elsevier: *Desalination* – Elsevier; *Chemical Engineering and Technology Journal* – Wiley-VCH; *Industrial* & *Engineering Chemistry Research* (from January 2002 to 2006) – American Chemical Society; *Separation Science and Technology* – M. Dekker; *Clean Technologies and Environmental Policy* – Springer-Verlag; *Water Treatment* – China Ocean Press (China); *Russian Journal of Physical Chemistry* – MAIK Nauka, Interperiodica Publ. (Russia); and *Journal of Separation and Purification Technology* – Childwall University Press (China).