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MEMBRANE CONTACTORS: MEMBRANE SEPARATIONS

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Membrane-based processes are receiving recognition for their flexibility and efficiency. Processes like reverse osmosis, ultrafiltration and dialysis are already well developed and recently, membrane application to other separation processes, such as absorption and liquid–liquid extraction, have been gaining considerable attention.

In these latter processes, the porous membrane acts as contacting media for gas–liquid or liquid–liquid phases with comparable advantages to the traditional continuous contact equipment. While in conventional two-phase processes, dispersion of one phase into another immiscible phase is used in order to promote an efficient contact and increase the transport rate, membrane extraction is accomplished without dispersion of the two phases.

Consider a liquid–liquid extraction process and a microporous hydrophobic membrane with the aqueous–organic interface stabilized inside the membrane pores (**Figure 1**). Since the membrane is hydrophobic, the organic phase spontaneously wets the membrane and may permeate through the pores to the aqueous phase. This breakthrough problem can be controlled by applying a higher pressure on the phase that does not wet the pores. This higher pressure must not exceed a critical value, Δp_{cr}, otherwise the nonwetting fluid will penetrate the pores and contaminate the other fluid phase.

If a hydrophilic membrane is used, the procedure is analogous, but in this case it is necessary to impose an organic phase pressure which is higher than that of the aqueous phase.

Although extraction can be conducted using a number of different membrane configurations, including flat-sheet, spiral-wound, rotating annular and hollow fibres, hollow fibres have received the most attention due to their high packing density: typical interfacial areas of contact per unit volume range from 1500 to 7000 $m^2\ m^{-3}$.

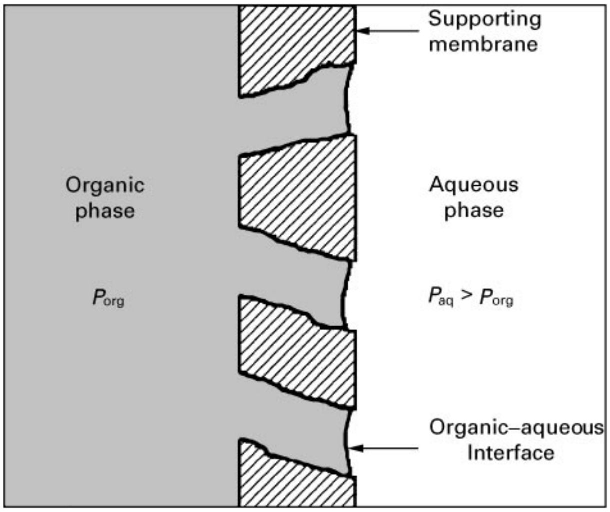

Figure 1 Organic–aqueous interface immobilized in a microporous hydrophobic membrane. P_{aq}, aqueous-phase pressure; P_{org}, organic-phase pressure.

The associated advantages of this configuration, which will be discussed in detail in the next section, have led to the development of an enormous range of processes, either with liquid–liquid phases or with gas–liquid phases.

Comparison between Membrane Contactors and Conventional Equipment

Advantages of Membrane Contactors

High contact area per unit volume Using a suitable module configuration such as a hollow fibre, membrane contactors can provide a contact area per unit volume which is 20–100 times higher than conventional equipment. The higher the interfacial area provided, the more efficient the contactor becomes and the smaller its size required for a given separation.

No loading and flooding constraints As the fluids to be contacted flow on the opposite sides of the membrane, both flow rates can be set independently. The available contact area remains constant even at very low or very high flow rates. This feature is particularly useful in applications where the required solvent/feed ratio is very low or very high, in contrast to conventional equipment, which is subjected to flooding at high flow rates and unloading at low ones.

Reduction of phase back-mixing When using membrane contactors, the mass transfer between the two phases occurs at the fluid–fluid interface immobilized at the mouth of the pores. This nondispersive contact minimizes emulsion formation and the occurrence of back-mixing is also reduced. By reducing back-mixing, a higher number of transfer units (NTU) can be achieved.

No need for density between the phases Unlike conventional dispersed-phase contactors, no density difference is required between fluids in liquid–liquid extraction because coalescence and separation of the dispersed phase are not necessary when using membrane contactors.

Reduced solvent hold-up Solvent hold-up is rather low when using membrane contactors; this may be important when using expensive solvents.

Modular design – direct scale-up The modular character of this equipment allows an easy straightforward scale-up procedure. Membrane operations usually scale linearly and thus, when an application requires several contactors in series or parallel, this modular design allows a given process to be easily tested on a reduced scale.

Easy process integration As membrane contactors do not involve the dispersion of the two fluid streams, it is easy to combine them with other operation units. These hybrid processes can be highly advantageous from a technical and economic point of view. For example, a combined extraction/stripping process can be designed by coupling two membrane contactors in series, without the need for an intermediate coalescence step.

Limitations of Membrane Contactors

Additional membrane resistance Besides the mass transfer resistances associated with the boundary layers of the two fluid phases, the membrane provides a third resistance. While this additional resistance is often negligible it may, under some conditions, contribute significantly to the overall mass transfer resistance. It will be discussed later in this chapter a few heuristic rules to minimize this effect.

Fluid distribution in the shell side In hollow-fibre contactors the spatial distribution of the fibres is not perfectly uniform. This uneven distribution can induce fluid flow maldistribution in the shell side and, eventually, bypassing, especially when high flow rates are used. This problem may become particularly important when large scale modules are used.

Transmembrane pressure constraints The transmembrane pressure can become quite important in porous membrane contactors, because it may induce flow across the membrane (breakthrough), causing unwanted froth, foam and dispersion between the two phases. For this reason, the option between operation with co- or counter-current mode and the setting of the fluid flow velocity has to take into consideration the pressure drop profile developed along the module. This explains why laminar flow conditions are usually used.

Construction materials Membrane contactors employ polymeric membranes and potting adhesive resins to bond the fibre bundle to the module casing. These materials may have a limited compatibility with certain organic solvents, especially with aromatic compounds.

Linear up-scaling factor It was mentioned as an advantage that the scaling-up of membrane contactors is rather simple and linear. On the other hand, this linearity is a serious drawback when comparing with traditional contacting equipment where the factor for scale-up cost is typically 0.6. This means that, if we want to double the capacity of a membrane contactor, the cost will be twice the original one, while for conventional equipment the cost will be $2^{0.6}$ of the original cost.

Membranes and Modules

Membrane Selection

Unlike most membrane operations, in membrane contactors the chemistry of the membrane is relatively unimportant, as it imparts no selectivity to the separation. The goal is to choose a membrane whose effect is not negative, i.e. that has no influence on mass transfer. Thus, the success of membrane contactors greatly depends on minimizing the membrane resistance to mass transfer. As a general rule, choose the membrane that is wet by the fluid to which the solute has more affinity (higher partition): if the solute partitions favourably to the solvent (organic), a hydrophobic membrane should be used; if it partitions favourably to the aqueous phase, then a hydrophilic membrane would be the best choice.

For gas–liquid contact two modes of operation are possible: wetted mode and dry mode. The wetted mode occurs when the pores are filled with liquid and the dry is when the pores are filled with gas: a hydrophilic membrane operates in wetted mode if the liquid phase is aqueous and in dry mode if it is organic, whilst a hydrophobic fibre will operate the inverse way. The dry mode is usually preferred to take advantage of the higher diffusivity of the solute in the gas phase, except in systems with an instantaneous interfacial reaction where the gas-phase resistance controls.

Still concerning the maximization of mass transfer, microporous membranes, typically with pore sizes between 0.05 and 1.0 μm and 20–100 μm thick have been used, in order to hinder solute diffusions as little as possible.

Hydrophobic membranes present the following advantages:

1. Higher pH and chemical stability
2. Reduced fouling with whole cells
3. Easier sterilizability

On the other hand, hydrophilic membranes are advantageous in the following conditions:

1. Systems with lysed cells or proteins, as they are likely to foul the membrane's surface to a lesser extent
2. Systems with very low interfacial tension. As hydrophilic membranes are commercially available with smaller pore sizes than the hydrophobic ones it can be easier to stabilize the interface (higher Δp_{cr}).

Module and Operating Mode Selection

Due to its high packing density (providing interfacial areas of contact up to 7000 $m^2\,m^{-3}$), the hollow-fibre modules are the most attractive configuration.

Any design should be preceded by some preliminary considerations regarding the operating mode:

1. Should the feed stream flow in the tube or in the shell side of the module?
2. Should the extraction be carried out co- or counter-currently?
3. Should the operation be carried out in unsteady-state batch mode or in continuous mode?

As a general rule, the feed stream should circulate in the tube side whilst the extract should flow in the shell side. This observation stems from the fact that commercially available hollow-fibre modules still present deficient mass transfer in the shell side due to uneven distribution of the fibres, that can produce effects of channelling, bypassing and back-mixing on the shell side. With the aim of minimizing these problems, new modules have recently been marketed with baffles and better distribution of the fibres.

However, exception may be considered when dealing with feeds containing solids or a high degree of particles. Although cost considerations should be taken into consideration, a prior filtration is suggested.

Regarding co- or counter-current operation mode, although an attractive higher driving force could be attained with the latter, the stability of interface must be taken into consideration: when operating counter-currently, the transmembrane pressure difference along the module presents a higher variation which can interfere with the interface stability and even lead to breakthrough. The breakthrough pressure, Δp_{cr}, is determined by the pore size of the membrane, the interfacial tension between the two fluids and the contact angle, according to the Laplace equation:

$$\Delta p_{cr} = \frac{2\gamma \cos\theta}{r_p} \qquad [1]$$

As to operating in batch recirculation or continuous contact mode, attention must be paid mainly towards the degree of extraction needed: the batch mode cannot achieve an extraction beyond the final equilibrium concentrations of both phases, while the single-pass continuous counter-current operation can reach further extraction, depending on the fibre length and flow rates. For not such a high degree of extraction, the design equations must be looked at so as to choose the mode that minimizes the costs inherent in the desired extraction.

Commercially Available Membrane Contactors

The best known module is the Liqui-Cel® Extra-Flow, marketed by Celgard LLC (**Figure 2**). This module uses Celgard microporous polypropylene fibres, up to 22 500, that are woven into a fabric and wrapped around a central tube feeder that supplies the shell side fluid. It also contains a central shell side baffle that improves efficiency by minimizing shell side bypassing and provides a component of normal velocity to the membrane surface, which results in higher mass transfer coefficients than those achieved with strictly parallel flow. The larger modules can operate with liquid flow rates up to several thousand litres per minute.

Also, commercial hollow-fibre microfiltration and ultrafiltration modules with hydrophilic membranes, generally with parallel flow, can also be used as membrane contactors.

For bubble-free gas–liquid mass transfer applications, Membrane Corporation and W.L. Gore market modules with different nonporous membrane arrangements: the first with the fibres potted at one end only and individually sealed at the other end, so that all entering gas permeates the membrane; the second has the fibres arranged as a helix, offering higher shell side mass transfer coefficients than the parallel configuration.

Equipment Design

A hollow-fibre membrane contactor is a continuous contact equipment and so the well-known concept of mass transfer unit is also applied here:

$$L = HTU^{*}NTU \qquad [2]$$

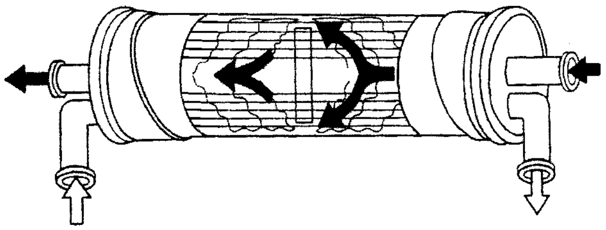

Figure 2 Schematic representation of a Liqui-Cel Extra-Flow membrane contactor.

where *HTU* is the height of the transfer unit and *NTU* is the number of transfer units necessary for a given separation. This equation allows the evaluation of the height or length of the contactor necessary to obtain the required extent of mass transfer.

The mathematical description of this design equation can be illustrated for an extraction process where the aqueous phase circulates in the tube side. In this case, a differential mass balance to the hollow-fibre module can be used to determine the change in solute concentration during a single pass:

$$-Q_{aq} \cdot dC_t = K_t \cdot dA_m \cdot (C_t - C_t^*) \qquad [3]$$

where K_t is the overall mass transfer coefficient, Q_{aq} represents the aqueous-phase flow rate, A_m the membrane transfer area, equal to $\pi.d_i.L.n_f$, where n_f is the number of fibres, and C_t is the solute concentration in the tube side phase. The superscript * refers to the solute concentration in the tube side (aqueous phase) in equilibrium with the solute concentration in the shell side (organic phase).

Eqn [3] can be integrated for the fibre length. For the module inlet ($z = 0$) $C_t = C_t^{in}$ and for the outlet ($z = L$) $C_t = C_t^{out}$, where C_t^{in} and C_t^{out} are the solute concentrations entering and exiting the module, respectively:

$$L = HTU^{*}NTU = \frac{v_{aq}}{K_t a_i} \int_{C_t^{in}}^{C_t^{out}} \frac{dC_t}{C_t^* - C_t} \qquad [4]$$

where v_{aq} is the fluid velocity circulating in the tube side, K_t is the module-averaged overall mass transfer coefficient and a_i is the interfacial area per unit module volume.

If a constant partition coefficient, P, can be assumed during the extraction process, integration of eqn [4] using $C_t^* = C_s/P$ where C_s, the solute concentration in the shell side phase, is obtained by mass balance, yields an analytical expression for the contactor length. The *NTU* expressions for a hydrophobic membrane with aqueous phase in fibre lumen and organic phase in the shell side, respectively for co-current flow and counter-current flow are the following:

$$NTU = \frac{1}{1 + \dfrac{Q_{aq}}{Q_{org}P}} \ln \frac{C_t^{out} - C_s^{out}/P}{C_t^{in} - C_s^{in}/P} \qquad [5]$$

$$NTU = \frac{1}{1 - \dfrac{Q_{aq}}{Q_{org}P}} \ln \frac{C_t^{in} - C_s^{out}/P}{C_t^{out} - C_s^{in}/P} \qquad [6]$$

For gas–liquid separations the partition coefficient may be replaced by *H*, Henry's law constant, and the aqueous and organic flow rates replaced by liquid and gas flow rates.

For systems with a variable partition coefficient it is necessary to introduce the equilibrium relation between C_t^* and C_s and a numerical integration is required.

Evaluation of Mass Transfer Coefficients

Three individual mass transfer resistances may be considered in membrane contactor extraction processes:

1. the inside tube boundary layer resistance
2. the membrane resistance to the solute diffusion through the pores
3. the shell side boundary layer resistance

The resistances are inversely proportional to the local mass transfer coefficients and a function of the system's geometry. Thus, for a hollow-fibre system when the membrane is wetted by the shell side phase, we obtain:

$$\frac{1}{K_t \cdot A_i} = \frac{1}{k_t \cdot A_i} + \frac{1}{P \cdot k_m \cdot A_{lm}} + \frac{1}{P \cdot k_s \cdot A_o} \qquad [7]$$

where K_t represents the overall mass transfer coefficient (based on the tube side phase), k_t, k_m and k_s are the local mass transfer coefficients on the tube side, membrane and shell side, respectively, and A_i, A_o and A_{lm} are the fibres' internal, external and logarithmic mean areas, respectively.

As the membrane may be hydrophobic or hydrophilic and the aqueous phase may circulate either in the fibre lumen or in the shell side, four different expressions for the overall mass transfer resistance for liquid–liquid extraction can be determined. **Figure 3** shows the concentration profiles and the overall mass transfer resistances.

The tube side and the shell side mass transfer coefficients can be obtained experimentally and several correlations may be found in the literature.

Mass Transfer Correlations

Since laminar flux is predominant in hollow-fibre membrane contactors, a Lévèque type equation can be used to correlate both the tube side and the shell side mass transfer coefficients:

$$Sh_t = \alpha \cdot Sc_t^{bt} \cdot Re_t^{ct} \cdot \left(\frac{d_i}{1}\right)^{1/3} \qquad [8]$$

$$Sh_s = \beta \cdot Sc_s^{bs} \cdot Re_s^{cs} \cdot \left(\frac{d_h}{1}\right) \qquad [9]$$

where the subscripts *t* and *s* refer to the tube and shell sides, respectively, and α and β are constants. The

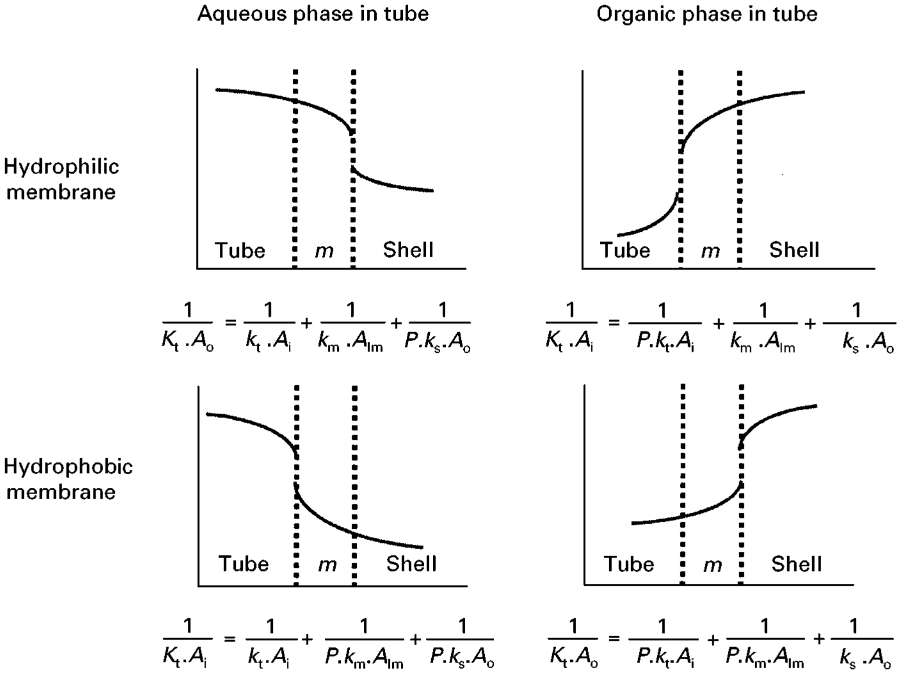

Figure 3 Concentration profiles and overall mass transfer resistance expressions for a chemical system with a solute partition coefficient favourable to the aqueous phase ($P < 1$).

Table 1 Mass transfer correlations for the tube side

Equation	*Characteristics*	*Reference*
$Sh = 1.62\ Gz^{0.33}\ Gz > 25$	Theoretical; laminar flux	Lévèque MC (1928) Les lois de transmission de chaleur par convection. *Annal. Mines* 13: 201
$Sh = 1.86\ Gz^{0.33}\ Gz > 100$	Empirical; laminar flux, heat transfer	Sieder EN and Tate GE (1936) Heat transfer and pressure drop of liquids in tubes. *Ind. Eng. Chem.* 28: 1429
$Sh = 1.64\ Gz^{0.33}\ 30 < Gz < 2000$	Hollow-fibre module; gas–liquid extraction	Yang MC and Cussler EL (1986) Designing hollow-fiber contactors. *AIChE J.* 32: 1910
$Sh = 1.5\ Gz^{0.33}$	Hollow-fibre module; liquid–liquid extraction	Dahuron L and Cussler EL (1988) Protein extraction with hollow fibers. *AIChE J.* 34: 130
$Sh = 1.4\ Gz^{0.33}\ 50 < Gz < 1000$	Hydrophobic fibre; liquid–liquid extraction	Takeuchi H, Tahamashi K and Nakano EM (1990) Mass transfer in single oil containing microporous hollow fiber contactors. *Ind. Eng. Chem. Res.* 29: 1471
$Sh = 0.2\ Re\ Sc^{0.33}(d_i/L)^{0.33} Gz < 65$	Hollow-fibre module; liquid–liquid extraction	Viegas RMC, Rodríguez M, Luque S, Alvarez JR, Coelhoso IM and Crespo JPSG (1998) Mass transfer correlations in membrane extraction: analysis of Wilson–Plot methodology. *J. Memb. Sci.* 145: 129

Gz: Graetz number $= Re\ Sc(d_i/L)$.

exponents of the Schmidt numbers (Sc), b_t and b_s, are usually 0.33; however, the exponents of the Reynolds numbers (Re), c_t and c_s, may be different from that value.

Tables 1 and **2** show some correlations collected from the literature for both tube side and shell side mass transfer coefficients in hollow-fibre membrane contactors.

Table 2 Mass transfer correlations for the shell side

Equation	*Characteristics*	*Reference*
$Sh = 1.25(Red_h/L)^{0.93} Sc^{0.33}$	Hollow-fibre module; gas–liquid extraction	Yang MC and Cussler EL (1986) Designing hollow-fiber contactors. *AIChE J.* 32: 1910
$Sh = 8.8(d_h/L) ReSc^{0.33}\ Re < 100$	Hollow-fibre module; liquid–liquid extraction	Dahuron L and Cussler EL (1988) Protein extraction with hollow fibers. *AIChE L.* 34: 130
$Sh = 5.85(1-\phi)d_h/L) Re^{0.6} Sc^{0.33}$ $\phi < 0.2\ Re < 500$	Hollow-fibre module; liquid–liquid extraction	Prasad R and Sirkar KK (1988) Dispersion-free solvent extraction with microporous hollow fiber modules. *AIChE J.* 34: 177
$Sh = 0.85(d_h/L)^{0.25}$ $(d_e/d_s)^{0.45} Re^{0.33} Sc^{0.33}\ Re < 700$	Hydrophobic fibre; liquid–liquid extraction	Takeuchi H, Tahamashi K and Nakano EM (1990) Mass transfer in single oil containing microporous hollow fiber contactors. *Ind. Eng. Chem. Res.* 29: 1471
$Sh = 0.017$ $(d_e/d_s)^{0.57} Re^{0.8} Sc^{0.33}\ 700 < Re < 2000$	Hydrophobic fibre; liquid–liquid extraction	Takeuchi *et al.* (1990)
$Sh = (0.53 - 0.58?) Re^{0.53} Sc^{0.33}$	Hollow-fibre module; gas–liquid extraction	Costello MJ, Fane AG, Hogan PA and Schofield RW (1993) The effect of shell side hydrodynamics on the performance of axial flow in hollow fibre modules. *J. Memb. Sci.* 80: 1
$Sh = 8.7\ Re^{0.74}(d_h/L)\ Sc^{0.33}\ Re < 50$	Hollow-fibre module; liquid–liquid extraction	Viegas RMC, Rodríguez M, Luque S, Alvarez JR, Coelhoso IM and Crespo JPSG (1998) Mass transfer correlations in membrane extraction: analysis of Wilson–Plot methodology. *J. Memb. Sci.* 145: 129

d_e, external fibre diameter; d_s shell diameter; d_h hydraulic diameter; ϕ packing factor $= n_f d_e^2/d_s^2$.

Concerning the tube side, in most published works an exponent of $c_t = 1/3$ is usually obtained for a higher tube side Reynolds numbers range. However, using tube side Reynolds numbers in a low range ($Re < 50$ and $Gz < 100$), values of $c_t = 1$ were reported.

For the shell side, the values of the exponent of the Reynolds number are $0.5 < c_s < 1$. Values of 0.5 for laminar flow and 0.6 for turbulent flow on the shell side of a shell and tube heat exchanger are reported. Deviation from these values may be due to the nonuniform distribution of the fibres and their deformation by action of organic solvents, both inducing an irregular flow due to the formation of stagnant zones, preferential pathways and deficient mixing.

Applications

Liquid–Liquid Extraction

Liquid–liquid extraction cover quite a broad range of applications, including metal extraction, wastewater treatment and extraction of pharmaceutical and other products of biotechnological interest, such as organic acids and proteins.

Recovery of metals from industrial process wastewater is important, not only because metals are valuable, but also because of environmental legislation restrictions. Several examples of metal extraction (Cu, Zn, Ni, Cr(VI), Cd) using membrane contactors, have been reported. Reactive extraction is usually employed and extractants such as organophosphorous compounds (TOPO, D_2EHPA), tertiary amines (tri-*n*-octylamine) and liquid ion exchangers (Aliquat 336) are used.

Extraction of pollutants from wastewater such as phenol, toluene and volatile organic compounds (VOCs) using methyl isobutyl ketone (MIBK), hexane and kerosene as solvents and also reactive extraction with several extractants were reported. A pilot-scale plant for extraction of chlorinated and aromatic compounds from industrial wastewaters in the Netherlands was in operation for periods up to 3 months, reducing contaminant levels to $10\ \mu g\ L^{-1}$.

Reactive extraction of organic acids produced by fermentation, such as acetic, citric, lactic and succinic acid, were also reported. Extraction of amino acids using reversed micelles was also studied.

Protein extraction can be accomplished either by two-phase aqueous extraction or by reversed micelles. Problems of interface stabilization caused by emulsions due to the adsorption of surfactant to the membrane surface, thus lowering the interfacial tension, were reported. Careful control of the pressure difference across the membrane was required for a stable operation.

Gas–Liquid Contactors

In gas–liquid extraction with membrane contactors, most efforts have been conducted in the areas of gas absorption/stripping and of wastewater treatment. Other fields like dense gas extraction and semiconductor cleaning water have been the object of study more recently.

Commercial applications include the Pepsi bottling plant in West Virginia that has been operating a bubble-free membrane-based carbonation line since 1993, showing reduced foaming, improved yield, lower CO_2 pressures and increased filling speed at high temperatures. Also, several beer production plants are using this technology for CO_2 removal to obtain a dense foam head, while others remove oxygen from beer to preserve its flavour; the stripping of oxygen from water, which is then used to dilute beer, is also being applied. Other commercial applications include the treatment of boiler feedwater, stripping of CO_2 from anion exchange feed streams and ultrapure water production for semiconductor manufacture.

In wastewater treatment, air stripping of VOC has been studied using polypropylene hollow fibres to remove chloroform, tetrachloroethylene, carbon tetrachloride, 1,1,2-trichloroethane and trichloroethylene from aqueous streams. Also, several studies have reported the use of membrane contactors for bubble-free aeration in wastewater treatment. Advantages include the absence of foaming, higher aeration rates, lower power input and ability to handle solids.

A list of applications is summarized in **Table 3**.

Membrane Distillation

In membrane distillation a nonwetted hydrophobic microporous membrane separates two phases of different water chemical potential. The difference in the water chemical potential may be induced by a temperature difference of the aqueous

Table 3 Applications of membrane contactors on gas absorption/stripping processes

Application
SO_2, CO_2, CO and NO_x removal from flue gases
CO_2 and H_2S removal from natural gas
CO_2 removal from biogas
VOC removal from offgas
NH_3 removal from air in intensive farmery
Recovery of volatile bioproducts
O_2 transfer in blood oxygenation and in aerobic fermentation
Ultrapure water production for semiconductor manufacturing
Dense gas extraction
Separation of saturated/unsaturated (ethane/ethylene)

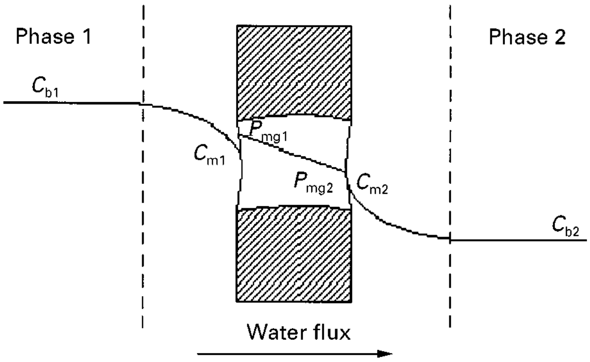

Figure 4 Schematic representation of water transport in osmotic distillation.

solutions corresponding to a difference in vapour pressure at both ends of the membrane. It may also be due to the different nature and concentration of the solute components of both phases, thus causing a different osmotic pressure of the two liquids. Since the osmotic pressure of an electrolyte solution is about 10 times higher than an equimolar solution of electrically uncharged particles, salt solutions (NaCl, $CaCl_2$, KH_2PO_4) are efficient and relatively cheap systems to create high osmotic pressure differences. In both cases, water evaporates in the solution of higher chemical potential and the water vapour formed is transported across the membrane pores before being condensed in the solution of the lower water potential (**Figure 4**).

Solutions whose vapour pressure is relatively unaffected by the presence of the solute are ideal candidates for concentration using osmotic distillation. This includes solutions consisting primarily of sugars, such as fruit juices.

Two pilot-plant facilities located in Melbourne and Mildura (Australia) are successfully operating for concentration of fruit juices. Colour, flavour and aroma retention is good due to the lower operating temperature and stresses.

Grape juice concentrates used for production of high quality wines may also be concentrated by membrane distillation. Since these concentrates are stable for long periods of storage they can be shipped over long distances and high priced wines can be produced in regions where these grapes are not available or are too expensive.

Opportunities also exist for the concentration of pharmaceutical products, which are susceptible to thermal degradation.

Biphasic Membrane Bioreactors

Multilayer membrane bioreactors can readily be constructed from several membrane films to which different biocatalysts have been attached or from combinations of permselective and catalytic membranes.

The use of permselective membranes in conjunction with catalytic films (or catalytic compartments) makes possible a high degree of control over the fluxes of the reaction participants, and hence over the course of reaction, that is impossible to achieve with catalyst particles. By using an adequate permselective membrane the fluids on either side of a membrane can be segregated, thus providing an additional degree of freedom in reactor design.

Most research work has been oriented to the development of biphasic membrane bioreactors where a microporous (hydrophobic or hydrophilic) membrane is used to separate an aqueous from an organic compartment. In this way, two immiscible liquid phases can be contacted across a membrane without one of the phases having to be dispersed in the other, as is required in most conventional multiphase reaction systems. In this type of reactor the biocatalyst may be linked to the membrane (**Figure 5**) or dispersed in one of the bulk phases.

The opportunity for development of biphasic membrane bioreactors is quite clear: the demand for selective removal of defined pollutants and the need for enantioselective transport and reaction for chiral synthesis in the pharmaceutical and food industries require new approaches in this field. Special attention has been devoted to the development of biphasic membrane bioreactors for enzymatic esterification and hydrolysis reactions.

Future Developments

Membrane contactors are unique equipment for promoting mass transfer while avoiding the dispersion of the fluid phases involved. This article has briefly reviewed the potential of membrane contactors in different areas of application and the problems which are still to be solved.

The industrial future of membrane contactors for liquid–liquid extraction processes, and in some defined situations for gas absorption, will depend very strongly on the ability to synthesize specific carriers or receptors with the potential to achieve recognition of individual solutes. Therefore, the trend will be the development of very selective carriers, in some cases with the ability for chiral recognition.

Membrane stability, in the sense of avoiding contamination between the two contacting fluids, is of major importance for the penetration of membrane contactors in some industrial markets. In particular, in the food and the pharmaceutical industries, trace contamination between the two fluid phases is a sufficiently strong reason to reject this type of process.

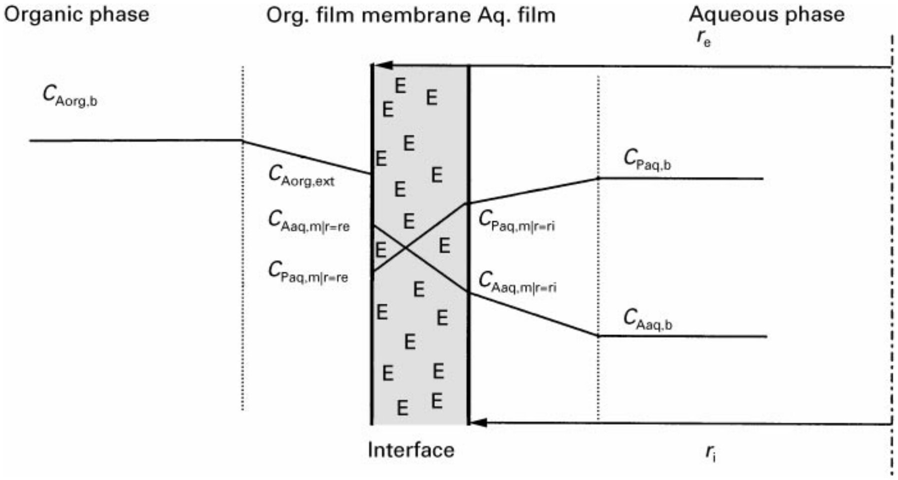

Figure 5 Representation of the enzymatic conversion of a substrate (subscript A) soluble in the organic phase to a product (subscript P) soluble in the aqueous phase. The enzyme is entrapped inside the porous structure of a hydrophilic membrane.

Development of organic solvents which are insoluble in water, nonvolatile and without the tendency to form emulsion would be highly desirable. Recently, the development of ionic liquids has been reported in the literature. These are entirely comprised of ions (complete absence of water), and are nonvolatile and insoluble in water. This type of solvent opens a world of new opportunities for liquid–liquid extraction and gas absorption using membrane contactors, without the risk of fluid cross-contamination. Also the use of dense gases and supercritical fluids has been suggested in membrane contactors. Again, the problem of contamination with the solvent phase could be eliminated.

Finally, new module design and new manufacturing materials will be welcome for certain type of applications, especially when viscous fluids and aggressive solvents are used. Further increases in membrane contactor performance are expected with the use of hollow-fibre fabrics and baffled modules.

Further Reading

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