

초청강연

MEMBRANE PROCESSES IN ENVIRONMENTAL TECHNOLOGY

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Classical membrane processes like microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO) are being applied in the last years more frequently in environmental and effluent process problems. Newer technologies and developments like pervaporation (PV) and gas separation (GS) recently found commercial applications in the treatment of waste waters and gas streams. The incentive here is either the clean-up from organic components to comply with federal emission regulations or the recovery of the organics for economical reasons. Processes still in their development stage are combinations of chemical reactions with membrane processes to separate and treat SO_x and NO_x laden waste gas streams in the clean-up of stack-gases.

In this paper we will first give a short overview of the more recent developments in MF, UF and RO. This is followed by a closer look on newer technologies applied in environmental problems. The applications looked at are the recovery of organic components from solvent laden gas streams and the separation of organic volatiles from aqueous waste waters via pervaporation. Technical solutions, the advantages and disadvantages of the processes and, where possible, cost estimations will be presented.

Introduction

Most of the pollution problems, which concern mostly aqueous systems, are tackled by the established membrane processes like microfiltration, ultrafiltration, electro dialysis and reverse osmosis. Their influence and industrial acceptance is growing steadily. Besides in the chemical industry, waste water effluent streams from other areas are also being looked at. Sewage treatment or water treatment in the nuclear industry are but two of them. In the membrane literature of recent years, various perspectives of the application of membrane processes in environmental problems were given (1-3). Some of the cases cited there, which use membrane processes of the newer generation like gas separation, pervaporation or pertraction, are now being commercialized. Gas separation and pervaporation become more and more applied in various applications to separate

and recover organic components from solvent laden gas streams or waters (4-8). Especially vapour recovery received a large push forward in the last couple of years. Systems are now commercially available in the USA, Europe and Japan.

Overview of membrane processes

To tackle the problem of a comprehensive overview of the applications of membrane technology is a rather strenuous if not insurmountable task. A review like this can never be complete. Any attempt to offer some kind of completeness would result in a booklet several volumes thick, which is by far outside the scope of this paper. In the following chapters, thus, only a few areas and points, certainly with the subjective view of the authors, are touched and described to give the reader an idea of the recent developments. As possible, it was tried to include representative references to give the interested reader a basis for further in-depth study.

Separation technology is a large field, with membrane technology being only a very small part. Slowly, membranes seem to get their feet on the ground in a few niches. In some areas, however, as in sea or brackish water desalination or in the dairy industry, membrane technology has taken a leading role as a separation or concentration process. Similar developments are foreseen for the application of membranes in environmental problems. However, one should not overlook the established and proven technologies like distillation, ad- and absorption or extraction, which have considerable potential in treating environmental effluent gas or water streams (9,10). Often, if not always, the most economical and attractive solution for a problem is a combination of several processes.

Membrane processes offer a few advantages over other separation techniques. Firstly they are flexible in their design due to their modular way of construction (this advantage converts to a disadvantage compared to conventional techniques with very large scale designs). A second advantage is their inherent possibility of product recovery, which often can be quite valuable. Membranes can be simplistically looked at as filters with a stream splitting capacity. A third point in favor for membranes is their generally low energy need. Table 1 gives a short overview of the various kinds of membrane processes available and some applications in environmental technology (11-13).

Membranes certainly not only have advantages, they also have their negative sides. With environmental problems in mind, i.e., the treatment of waste water or solvent containing gas streams, chemical and pH stability is one of the largest drawbacks. A second point is concentration polarization and fouling of the membranes that diminishes productivity. Thirdly, one might mention that often a lack of long-term experience, and thus the factor of reliability, affects the question of the implementation of a membrane process. A fourth point that could be mentioned is that a perfectly semipermeable membrane does not exist; a complete separation cannot be

achieved.

The two processes mostly used today are RO and UF. Both are pressure driven processes, and the separation is due to a difference of the size of the particles to be separated. Table 2 lists the major applications of RO and UF in waste water treatment, which are both economically attractive and useful (14-18). Both processes are often used in combination, where UF builds the first cleaning step to remove larger particles and RO is used as a sort of after-cleaning or polishing step.

Table 1. Membrane processes and their applications in environmental problems.

Membrane process	Phases* (feed/permeate)	Driving force	Separating mechanism	Environmental applications
Microfiltration (industrial scale)	L+S/L G+S/G	pressure (0.1-500 kPa)	difference in size	precipitated metals oil/water emulsions
Ultrafiltration (industrial scale)	L/L	pressure (0.1-1 MPa)	difference in size	oil/water emulsions
Reverse Osmosis (industrial scale)	L/L	pressure (1-10 MPa)	solution/ diffusion	ions, heavy metals, salts nitrates from groundwater percolation water
Electrodialysis (pilot plant)	L/L	electric potential	difference in charge	ions from water
Gas separation (industrial scale)	G/G	pressure (0.1-10 MPa)	solution/ diffusion	SO ₂ from off-gases vapors from air acid comp. from natural gas
Pervaporation (pilot plant)	L/G	activity	solution/ diffusion	volatile organic components from water
Membrane distillation (pilot plant)	L/G L/L	temperature	partial vapor pressure	ions from water
Pertraction (laboratory)	L/L	concentration	solubility	metals from water
Liquid membranes (laboratory)	L/L G/L G/G L/G	chemical potential difference	solubility	metal ions from water acid gases from air

* L = liquid, G = gaseous, S = solid

Table 2. Major applications of RO and UF in environmental problems (11,12).

Reverse osmosis (RO):	<ul style="list-style-type: none"> • concentration of laundry and cleaning waters • pulp and paper industry, white and black liquor • plating industry, recovery of polyvalent metal ions, purification of plating baths • sewage treatment, percolation and seepage water waste water from agricultural and industrial effluents
Ultrafiltration (UF):	<ul style="list-style-type: none"> • automotive industry, electrophoretic paint recycling • latex recovery • PVA, dyestuff and sizing agents recovery in the textile industry • oil-water separations of grinding and lubricating water

A large scale application, which has been proven in many plants, is the treatment of percolation or seepage water from landfills and dumps by RO. Capacities range from 10 000 m³ to 250 000 m³ of water treated per year. Often a two-step procedure is applied, with tubular RO-modules that operate as a sort of prefilter in the first section, followed by spiral-wound RO modules in the second step that provide the final cleaning. Typical BOD and COD rejections are in the order of 90% with one-stage plants, and > 95 % with two-stage plants (18). This allows the permeate water to be discharged into the sewer or surface/ ground water, whereas the concentrate is returned to the landfill. Some problems have been reported with the membranes due to bacterial growth and fouling due to scaling effects.

Another large scale application is the recovery of electrophoretic paint in coating lines. The ultrafiltration system recovers drip paint and conserves rinse water. The concentrated paint is recycled back into the tank. Hence, pollution problems and water costs are reduced. Due to high fouling potential, mostly tubular systems are used that are controlled by a regular cleaning schedule. A typical system with a capacity of 70 m² produces about 1.7 m³/h of permeate and operates at an energy consumption of 30 to 100 kWh per 3.8 m³ of permeate.

The third process becoming more and more of interest in waste water treatment is microfiltration (MF). This process, however, has been used in the majority of its applications as dead-end filter, e.g. as a water clarifier. It has been only recently that MF is applied in a cross-flow configuration. Hereby, cross-flow MF is again used for the production of pure water in the treatment of industrial wastes. Examples to be mentioned may be the removal of larger sized particles of insoluble oxides and precipitants. Further examples for the use of cross-flow MF, often in combination with RO or UF, are listed in table 3 (18).

Table 3. Applications for cross-flow MF in environmental problems.

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- heavy metal hydroxide clean-up of ground water (Pb, Zn, Ni, Cr,...)
 - manure clean-up in the agricultural industry (in combination with RO)
 - removal of lignine compounds in the paper and pulp industry (with RO)
 - heavy metal removal form laundry waters in the plating industry (with UF)
 - treatment of phenol containing waste water, in combination with a biomass reactor
 - oil-water separations of cutting or grinding fluids
 - offshore formation water treatment
-

In the following paragraph an example of the utilization of microfiltration in the waste water treatment is described in somewhat more detail. Capacities for MF plants are typically in the range of 5 to 20 m³/h feed stream. Figure 1 shows photographs of two typical microfiltration plants using capillary fiber modules.

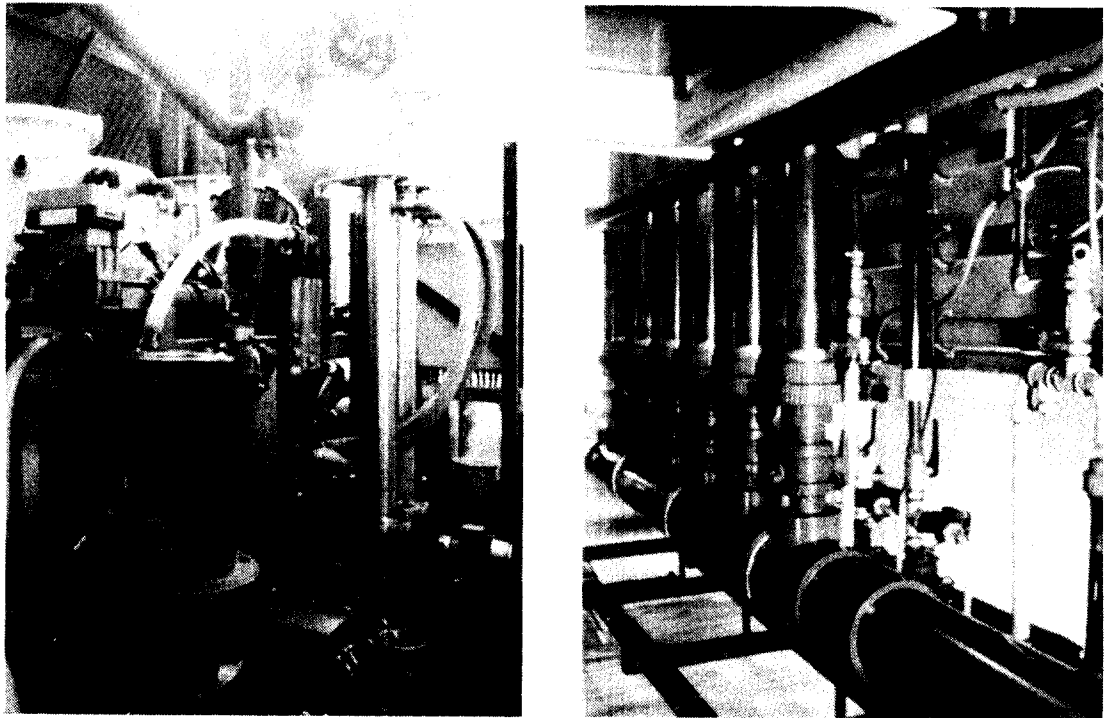


Figure 1. Photographs of MF systems using capillary fiber modules (courtesy of X-FLOW, The Netherlands).

Process water is often polluted with heavy metals and organics and the chemical manufacturer is not allowed to discharge these streams directly into the sewer systems. MF offers here an attractive solution, as seen from the flow diagram in figure 2. The incoming feed is first buffered and oil is then separated via conventional coalescence filters. Heavy metals are precipitated as hydroxides by the addition of sodium hydroxide and separated via a bank of MF capillary modules. The concentrate leaving the modules contains about 3-5 wt% dry solids and is lead to a sludge holding tank for further treatment.

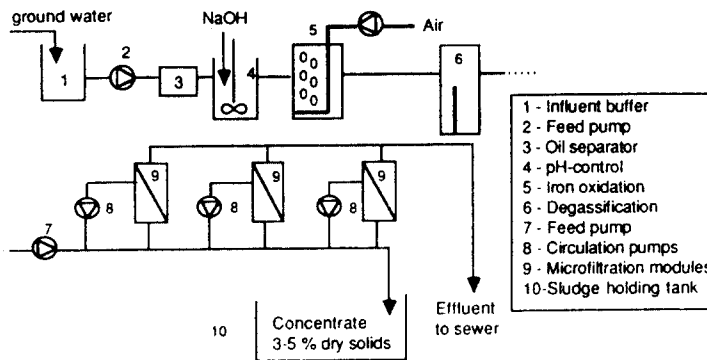


Figure 2. MF cross-flow system for the removal of heavy metals from ground water (18).

Another problem solution for similar types of waste or process waters, e.g., the removal, of metals from spent plating baths or rinsing waters is via the combination of a pelletreactor for the precipitation of the metals as carbonates followed by a cleaning step either via UF/MF or via RO. Which combination is finally chosen depends mainly on the water quality requirements for the retentate stream leaving the system. Recoveries of larger than 90% for the heavy metals are easily achieved, with effluent concentrations of less than 0.1 mg/l of metal. In combination with RO, 80% of the feed stream may be recycled as water having drinking water quality.

Using RO, UF and MF alone or in system combinations, one can summarize the main objectives of these systems with regard to environmental problems as:

- the reduction of effluent emissions,
- the volume reduction of waste water streams,
- the recovery of valuable components like paint or metals, and
- the production of clean water that complies with discharge regulations.

Recovery of organic vapors from solvent laden gas streams

Waste air streams containing low or medium concentrations of organic solvents become more and more an environmental problem. Aside from this, these solvents constitute a huge amount of both lost energy and valuable resources. The total numbers of solvent emissions are huge. For the USA, the biggest industrial nation in the world, more than 22 million tons of annually emitted solvents have been estimated. In West-Germany, an amount of approximately 2 million tons has been reported, while for the Netherlands, 200,000 to 300,000 tons per year might be a reasonable estimate. Organic solvents occur in almost every branch and part of the industry, and as can be seen from table 4, also every class of chemical solvent is represented.

Table 4. *Classes of solvents and industries where they are used.*

Major processes using solvents:	Which solvents are used?
<ul style="list-style-type: none"> • Petroleum Refining, Storage, Transport • Crude Oil Transportation • Storage and Transfer • Painting and Coating of all sorts • Adhesive and Glue Production • Explosives and Propellants • Extraction Processes • Plastic and Rubber Manufacturing • Dry Cleaning Shops • Industrial Degreasing , Cleaning • Textile Industry 	<ul style="list-style-type: none"> • Aromatic Hydrocarbons: Naphthas, Toluene, Xylene, Others • Aliphatic Hydrocarbons Hexane, C2 - C10 Mixtures, Gasoline • Chlorinated Hydrocarbons Methylene Chloride, CFK, Tri, Perc • Alcohols Methyl, Ethyl, Propyl Alcohol • Esters Ethyl Acetate, Butyl Acetate • Ketones Acetone, MEK, MIBK

Treatment of the contaminated air streams and the subsequent solvent recovery have been a constant issue in the industry during the last decades. In chemical engineering, many processes in the big field of separation technology are applicable. Improvement of the well-known conventional processes has been an ongoing task in research and industry. Even marginal process improvements, sometimes only in the low percentage range, will yield substantial economical savings, considering the huge process streams occurring in the chemical industry. Figure 3 gives an overview of the techniques available for the recovery and separation of organic effluents from gas streams (19,21). The processes can be divided in the ones without and the ones with solvent recovery; where the latter should be used as much as possible. Often combinations of the processes above are used to arrive at process designs that suffice with the economical or ecological demands. For further details on these processes, see for example references (9,10,20,21).

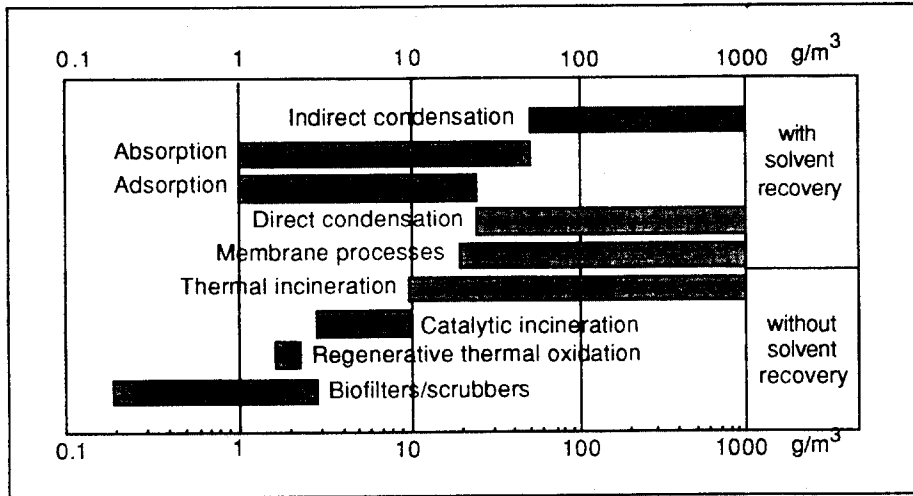


Figure 3. Solvent laden air treatment processes (19).

During the last years, another promising technique –membrane technology– with its processes based on the permeation through thin organic or inorganic films has emerged. Membrane vapor separation is a process that has been developed during the last decade. In this process, organic vapors are being separated from air or other gas streams with mostly elastomeric polymer membranes. A solvent laden airstream is fed over the modules, splitting up into a solvent depleted residue or retentate and a vapor enriched in the solvent on the permeate side. The permeate vapor must usually be condensed before it can be removed and recovered as liquid. Driving force for the transport is a reduction in partial pressure via a vacuum on the permeate side. The membranes, which are manufactured as thin-film-composite types in spiral-wound, plate-and-frame or capillary modules, achieve enrichment factors typically in the range of 20 to 100. These enrichments depend on the relative permeation rates or permeabilities of the solvent and the air and on the vacuum applied. Details of the transport and mechanism of permeation of gases and vapors can be found in a large number of literature articles, among which are several excellent reviews (11,13).

Membranes and modules

Most membranes used in vapor separation for organic solvents consist of thin-film-composite structures of a microporous support made from engineering polymers like polysulfone, polyetherimide or polyacrylonitrile to give mechanical strength. On top of these supports a thin, dense, permselective layer of an elastomeric polymer is coated. Mostly used today is the elastomer polydimethylsiloxane (PDMS) or as it is commonly called silicone rubber. PDMS has extremely high permeabilities toward the organic compounds, which are up to three orders of magnitude higher than nitrogen or oxygen.

These composite structures are manufactured either in flat or capillary form, from which spiral-wound, plate-and-frame or capillary modules are produced. Table 5 gives an overview of the membranes and modules employed by the different suppliers of vapor separation systems.

Table 5. Membrane materials and modules used for vapor separation systems.

Company	Support	Toplayer	Module	Ref.
MTR	polysulfone	PDMS	S/W	22
GKSS	polyetherimide	PDMS	P/F	23
Sempas	polyethersulfone	PDMS	C	24
Nitto	polysulfone	PDMS	S/W	25

PDMS—polydimethylsiloxane; S/W—spiral wound; P/F—plate-and-frame; C—capillary

System design

To achieve any suitable separation the membrane modules have to be incorporated into a system designed for the application desired. Figure 4 shows two possible designs taken from the literature (22). Which system to choose depends on a variety of factors, the most important one being the desired recovery of the solvent. A single stage system is often already capable to achieve 80-90% removal. Sometimes it is necessary to use a two-stage system to achieve higher permeate concentrations, which makes condensation more efficient, see figure 4a. At even higher solvent removal or recovery, a different design is necessary, the two-step process, see figure 4b. Here the retentate of the first step is fed to a second unit for further solvent reduction. Recoveries at the 95 to 99% level are easily achieved, however, at the expense of large capital costs. This is because a unit to reduce the solvent concentration from 10 to 1% of the initial value is as large as a unit to reduce the solvent level from 100 to 10% of the initial value. This makes the two-step design only feasible for more expensive solvents, such as amines or CFC's.

Commercial systems

During the last couple of years a number of systems have appeared on the market, see table 6. Driving force for the development of these systems has been the implementation of lower allowable emission limits via the TA-Luft in Germany or the Clean Air Act in the United States. Large activities can be found particularly in the field of the recovery and reduction of gasoline vapors at tank storage farms and filling facilities. Already several different systems are available. Typical sizes of these first plants were of the order of 50-500 m³/h of feed volume flow.

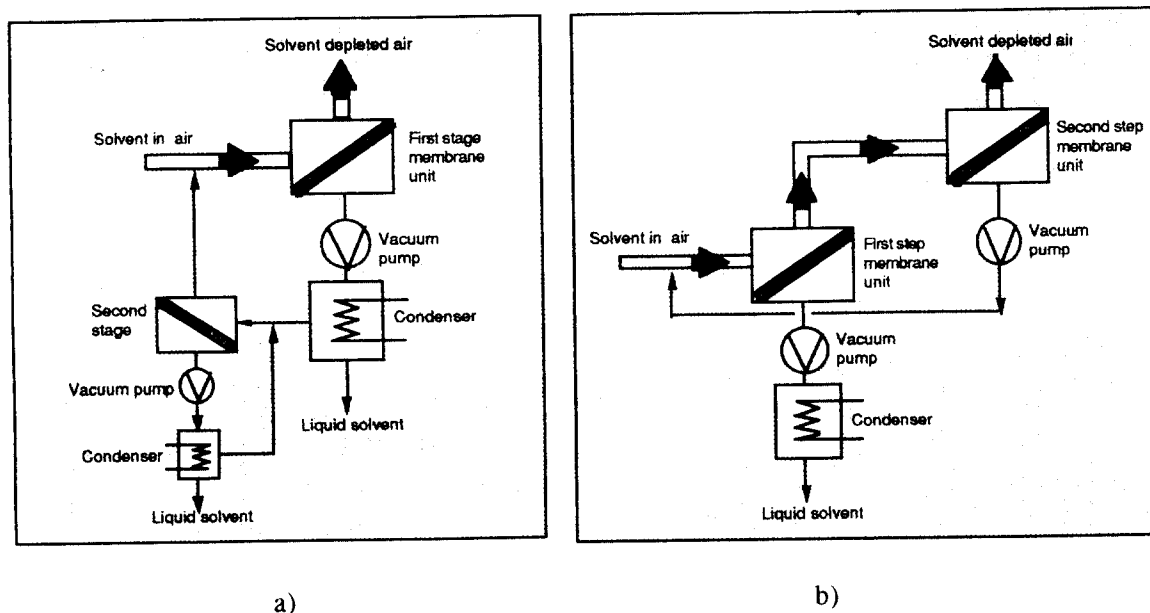


Figure 4. Simplified design scheme for a two-stage (a) and a two-step (b) vapor separation system (22).

Presently, larger systems of up to 1,500 m³/h are in construction in the petrochemical industry, i.e. at MTBE/MeOH and gasoline storage facilities. Two system designs marketed in Germany include membranes combined with catalytic aftertreatment and/or absorption steps depending on legal or the user's requirements.

Table 6. Commercially available vapor separation systems and applications.

Company	System	Main applications	Ref.
MTR	VaporSep	CFC's, HCFC's, hydrocarbons	26
Alu Rheinfelden	Vaconocore	gasoline and accompanying solvents	27
Preussag	VapourRed	from tank farms and filling	28
NKK/Nitto	—	stations, petrochemical industry	25

Application examples and costs

In this paragraph, a few examples of vapor separation schemes together with their capital and operating costs are presented, as they were available in the literature (22,29). Figure 5a shows a two-stage system, which is suitable for dilute streams. In this design, a 500 scfm, 1% stream is enriched 20- to 50-fold. The organic solvent recovery is 90%, the capital cost are \$850/scfm of

feed and the operating costs are estimated at \$0.76/1,000 scf of feed or \$0.42 per kg solvent recovered. A different design is the two-step, two-stage system for 99% removal of the organic solvent, see figure 5b. In this case a 1,000 scfm, 0.5% stream is treated to yield a residue concentration of 50 ppm of organic. The capital cost of this system are \$956/scfm of feed, and operating costs are calculated to \$1.0/1,000 scf feed, equivalent to \$0.8 per kg solvent. In the case of CFC as solvents, which are valuable compounds, the recovered money value of solvent far exceeds the operating cost per kilogram. Further details on various design schemes and cost estimations can be found in the literature (22,29). Cost estimation data or costs for running plants of the other systems are scarcely disclosed in the literature (17,30,31).

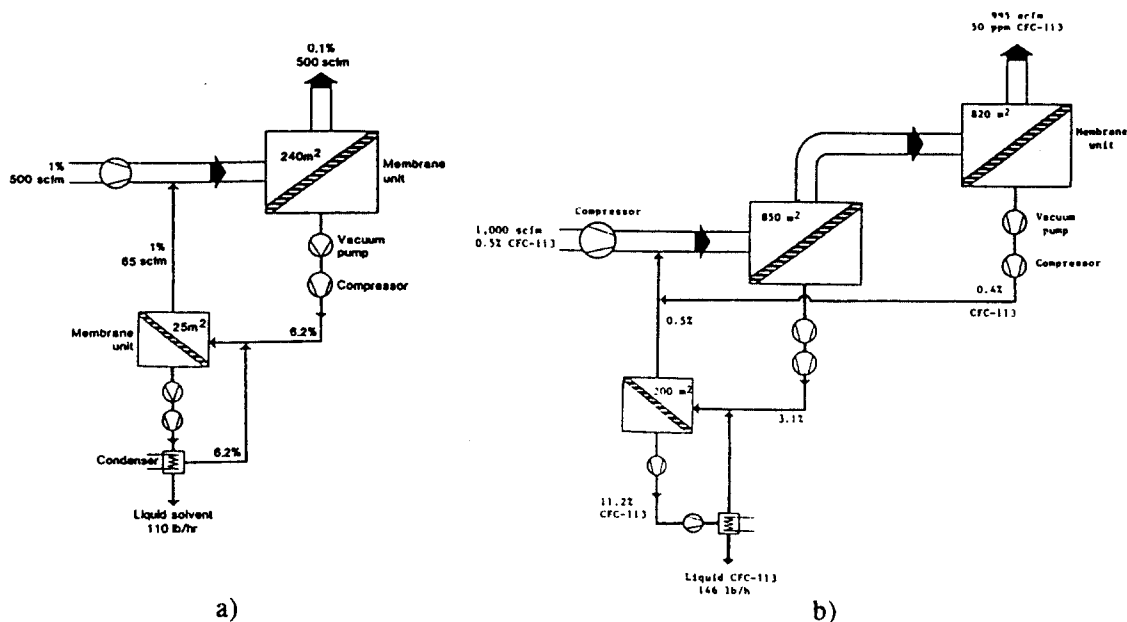


Figure 5. System configurations for a) 90% and b) 99% recovery for dilute organic solvent containing air streams (22,29).

Summarizing, one can say that organic vapor separation via membrane permeation provides an additional unit operation which is particularly useful at higher solvent concentrations at lower feed volume rates. If very low residue concentrations are required, however, additional aftertreatment is necessary. Combinations of a membrane system with adsorption, condensation, absorption or catalytic incineration have been designed to provide an optimal plant performance and operational reliability. An economical analysis has to deliver the decision which system combination or variation is to be used.

Pervaporation of organic volatiles from polluted waste water

Volatile organic components (VOC's) in ground water or surface waters create an environmental problem of increasing impact and form a threat already for the production of clean drinking water. Even small concentrations (ppm's) of toxic substances like aromatic hydrocarbons and chlorinated hydrocarbons have to be removed from waste water streams or from contaminated ground and surface water resources when explored.

Basically two techniques are commercially available nowadays which can handle this problem, viz. adsorption on activated carbon and air stripping. From an environmental point of view air stripping has to be combined with an additional process to treat the stripper off-gases. Three possibilities are available: gas phase carbon adsorption, biofilter treatment and membrane vapour separation. A third technique for direct removal of volatile organics from water is pervaporation, which is available now on a commercial scale. It is our purpose in this paragraph to explore the technical merits and limitations of pervaporation for the removal of small concentrations (10-1000 ppm) of volatile organics from water and to give a cost estimation and cost comparison with the other techniques mentioned.

Pervaporation

Pervaporation is a membrane process, in which a liquid mixture is brought in contact with a membrane at the feed side and the permeate is removed as a vapour at the permeate side. This is established by reducing the relative vapour pressure at the downstream side by either the use of an inert carrier gas or an applied vacuum. The vapour is obtained as a liquid in the condenser.

In pervaporation a phase transition takes place from liquid in the feed to vapour in the permeate. This implies that at least the heat of evaporation has to be supplied. Pervaporation is therefore especially suitable for removing small quantities of a component from a bulk liquid. An important condition is that the membrane should be very selective towards the component(s) to be removed. For the separation of halogenated and aromatic hydrocarbons from water suitable membranes do exist.

In several studies (7,32-35) it has been shown that using relatively thick, dense elastomeric membrane (mostly PDMS is used), extremely high selectivities are obtained. The concentration of these pollutants in the permeate are high enough to obtain phase separation after condensation, so that these compounds are collected as almost water-free liquids, ready to be re-used or incinerated. A decrease in membrane thicknesses could further improve the fluxes. Several authors (7,34-36) pointed at the important role of a hydrodynamic boundary layer resistance at the feed side of the membrane, causing a strong decrease in selectivity, due to strongly decreased organic component fluxes upon using thinner membranes. A resistance-in-series model, combining a liquid boundary layer resistance with a membrane resistance, was first introduced by Coté and Lipski (7) and studied further in our group (37).

Resistance-in-series model

Figure 6 gives a schematic representation of the concentration profile of the preferentially permeating component in the pervaporation process.

Volume flows J^c (convection), J^d (diffusion) and J^p (permeation) are indicated as well as volume fractions ϕ_1 in the bulk, at the wall, in the membrane and in the permeate. Of course, despite possibly large ϕ_1^p values, the partial vapour pressure at the permeate side is small, due to the applied vacuum. Now the fluxes of the components are effectively described in terms of mass transfer coefficients for the liquid boundary layer k_L and the membrane k_m , respectively.

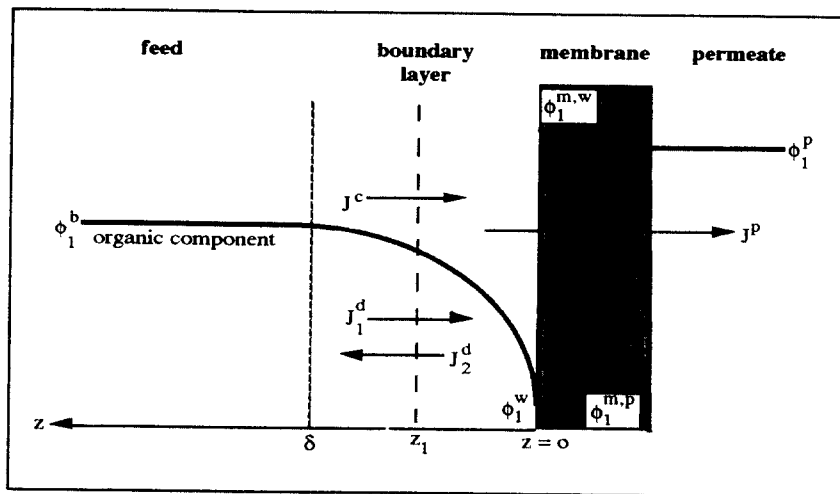


Figure 6. Concentration profile (in terms of volume fractions, ϕ) for the preferentially permeating component 1.

The expression for the component flux J_1^p reads

$$J_1^p = k_{ov} \cdot \phi_1^b$$

The overall mass transfer coefficient k_{ov} can simply be determined from measurements of the bulk feed concentration ϕ_1^b and the steady state permeate flux for component 1, both obtained in the actual pervaporation experiments. The reciprocal value of the overall mass transfer coefficient ($1/k_{ov}$) can be considered as the sum of a liquid boundary layer resistance ($1/k_L$) and a membrane resistance ($1/k_m = \ell/P_1$)

$$\frac{1}{k_{ov}} = \frac{1}{k_L} + \frac{\ell}{P_1}$$

The boundary layer resistance ($1/k_L$) is strongly influenced by the flow conditions at the feed side of the membrane. The membrane resistance ($1/k_m = \ell/P_1$) is inversely related to the permeability of the membrane for a component and it is directly proportional to membrane thickness. With increasing flow velocity (Reynolds number) the boundary layer resistance decreases and the membrane resistance becomes more dominating. Especially for relatively thick homogeneous membranes with a not too high organic component permeability the membrane resistance becomes rate limiting for the overall transport. Plotting the overall mass transport resistance ($1/k_{ov}$) as a function of the membrane thickness ℓ , a straight line should be obtained. From the intercept at zero thickness one can obtain $(1/k_L)$, while from the slope $1/P_1$ follows.

In our laboratory (37) homogeneous and composite membranes have been prepared with a broad range of effective thicknesses of the selective elastomeric layer. Out of a group of 12 materials the

- PDMS polydimethylsiloxane (silicon rubber GE, RTV 615)
- BR polybutadiene (Finaprene 250)
- EPDM ethene-propene terpolymer (Keltan 578)

Pervaporation experiments at different feed concentrations and at constant hydrodynamic conditions gave the following results:

- Water fluxes appeared to be independent of the concentration of organics in the aqueous solution and were inversely proportional to the effective thickness of the membrane layer. Using $J_w^D = P_w \ell$, the permeability coefficient for water in the various materials could be calculated (see table 7).
- An evaluation of organic component fluxes versus bulk concentration shows significant differences between PDMS and EPDM. Figure 7 shows this flux versus concentration dependence for composite and homogeneous PDMS membranes of different effective thicknesses, both for trichloroethylene/water and for toluene/water.

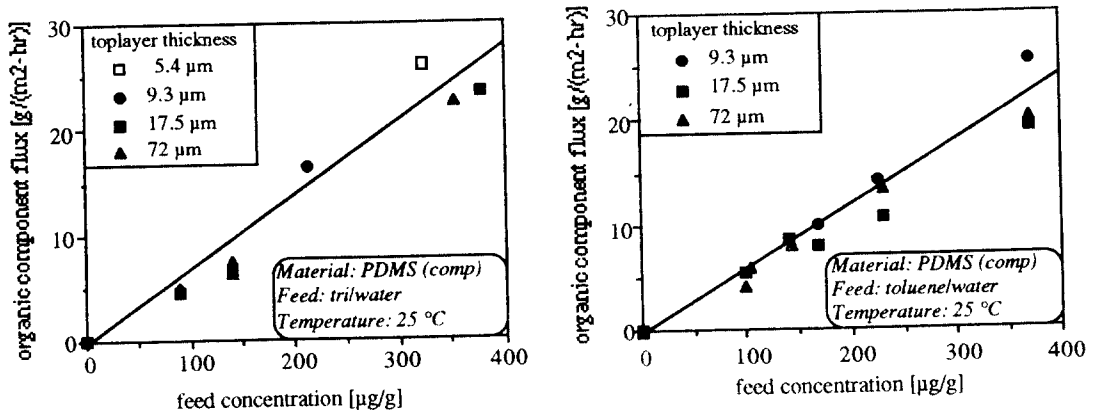


Figure 7. Trichloroethylene fluxes (left) and toluene fluxes (right) for PDMS membranes as a function of the feed concentration of the organic compound in water.

It is evident that in both cases, over a broad range of thicknesses the flux data are represented by a straight line. This means that k_{ov} is constant for each of the organic solutes used. Hence the total resistance is *not* influenced by the membrane thickness. Obviously because of large P_1 values for PDMS the term ℓ/P_1 is negligible with respect to k_L here. In figure 8 results are given for EPDM membranes of two different thicknesses. Here the membrane resistance does show up, although for a 2.8 fold increase in membrane thickness the value of k_{ov} (slope of the curve) only drops by a factor 1.4. Hence the liquid boundary layer contributes to the overall resistance, even for those relatively thick membranes. For smaller thicknesses this will become more pronounced.

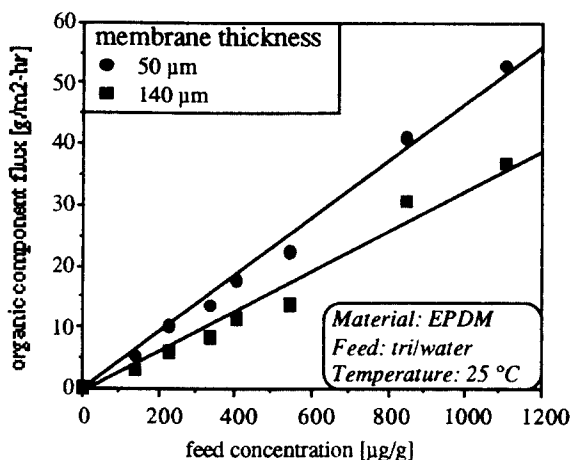


Figure 8. Trichloroethylene fluxes for two homogeneous EPDM membranes (50 and 140 μm) as a function of the feed concentration

Figure 9 gives the calculated overall resistances ($1/k_{ov}$) as a function of membrane thickness for PDMS and EPDM membranes for toluene/water and tri/water. From the intercepts in figure 9 an average liquid boundary layer mass transfer coefficient k_L of $2.0 (\pm 0.5) \cdot 10^{-5} \text{m/s}$ can be calculated, operative in the laboratory measuring cell used. In well designed modules this k_L value can easily be obtained (and surpassed).

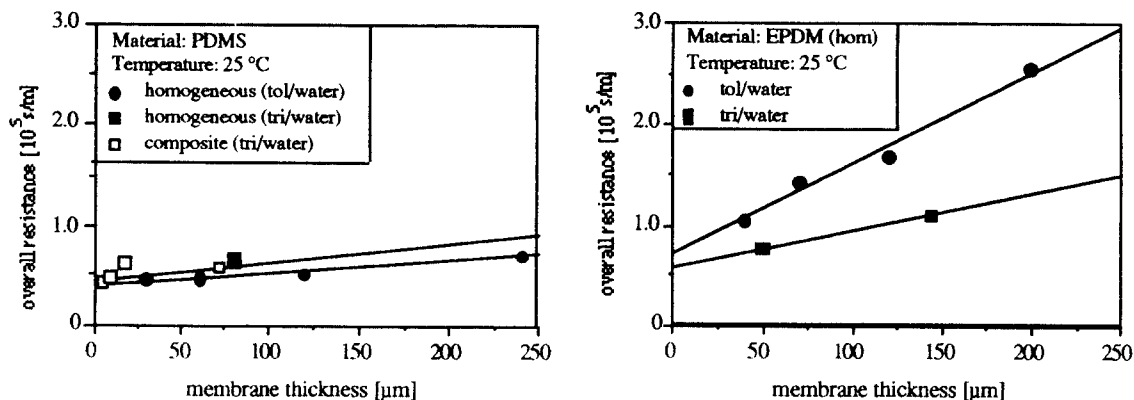


Figure 9. Overall mass transfer resistances as a function of membrane thickness for PDMS (left) and EPDM (right) membranes.

This figure also shows that membrane permeabilities (obtained from the reciprocal slopes) are higher for PDMS than for EPDM. Table 7 gives an overview of actual P values for three different elastomers. As one can see the ideal selectivities $\alpha_{id} = P_i/P_w$ (ideal here means in the absence of concentration polarization effects) are one order of magnitude higher for EPDM membranes than for the other ones. This is mainly due to the much lower water permeability for EPDM at comparable permeability values of the organic components.

Table 7. Permeability P and ideal selectivity values $\alpha_{id} = P_i / P_w$ for three elastomeric membranes.

elastomer —> solvent	PDMS		BR		EPDM	
	P (m ² /s)	α_{id}	P (m ² /s)	α_{id}	P (m ² /s)	α_{id}
toluene	8.1·10 ⁻⁹	24,000	5.3·10 ⁻⁹	47,500	1.1·10 ⁻⁹	130,000
trichloroethylene	5.4·10 ⁻⁹	17,500	3.9·10 ⁻⁹	35,000	2.7·10 ⁻⁹	320,000
water	3.4·10 ⁻¹³	—	1.1·10 ⁻¹³	—	0.08·10 ⁻¹³	—

A conclusion from this work clearly is that for this type of application, where high membrane permeabilities and rather low bulk concentrations of organic compounds are prevailing, the improvement of liquid boundary layer mass transfer in the module is more important than lowering the active membrane layer thickness. The organic component flux can profit directly from the improved boundary layer transport, without an effect on the water flux. On the other hand the water flux is increased significantly with reduction of membrane thickness. For moderate to poor hydrodynamic conditions the flux of organics may not be improved at all by a decrease in membrane thickness.

For module design purposes this means that one should find ways to increase the boundary layer mass transfer coefficient k_L at minimum cost. Lipsky and Coté (38) give an excellent example how to proceed: They showed that energy requirements for a certain separation task by pervaporation were a factor 2 to 4 lower for a (laboratory) module with transversal flow to a bundle of hollow fibers, than for a classical flow pattern in hollow fiber or spiral-wound modules.

Cost evaluation

Surveying the available literature data on the economic factors for VOC removal from waste water, one should realise that at this moment only pilot studies on this type of separations by pervaporation are available, from which cost evaluations have been obtained by computation.

A first point to be noticed is that for the pilot studies performed, actual selectivity values, always fall short with respect to ideal selectivities by a factor of 30 to 100. This is partly caused by a trivial

factor: α being calculated on the basis of inlet feed concentration, while the actual feed concentration is decreasing steadily over the membrane surface from feed inlet to outlet. More severe limitations to reaching ideal selectivities are nonideal hydrodynamic boundary layer conditions (as discussed extensively above) and pressure drops, e.g., at the permeate side, in the connections to condenser or vacuum pump or even in the porous support of the membrane itself.

Obviously negative effects of lower selectivities are the larger membrane areas needed (higher capital costs) and the need to condense and handle larger quantities of permeating water at the same amount of organic compound removed (larger energy costs).

Table 8 reflects the cost situation for pervaporation of VOC's presented in four recent papers. As one can see the cost calculations represent comparable situations with respect to capacity of the plants installed. Except for the latest MTR data (39) the table reflects a cost level of roughly \$1.0 per m³ feed water treated, at a level of purification of 99%. One still wonders whether the feed concentration of the last two examples (10 ppm) is well chosen for the case of pervaporation at a level of component removal of 99%. Nijhuis (37) showed that at roughly the same cost as indicated in the table one could obtain a 99.9% solute removal by a hybrid process, using pervaporation to clean up the feed at a 90% level and taking an active carbon liquid phase treatment of the retentate to obtain a recovery of 99.9%.

Table 8. Cost comparison of several techniques for removal of organic compounds from aqueous streams, taken from four recent literature sources.

Reference	Amount treated (m ³ /h)	Conc. organic (ppm)	Recovery (%)	Required area (m ²)	Capital cost (\$)	Operating cost total annual (\$)	Operating cost per m ³ feed (\$)
Blume, et.al. (8)	16	1,000 organic	90	360	187,000	80,000	0.62
Wijmans, et.al. (39)	3.2	1,000 benzene	99	200	180,000	85,000	3.70
Lipski, et.al. (38)	10	10 trichloroethylene	99	77	193,000	—	1.41
				96	69,000	—	0.56
				160	140,000	—	1.10
Nijhuis, et.al. (37)	10	10 trichloroethylene	99	400	335,000	78,000	0.98

Table 9. Cost comparison of several techniques for VOC removal at a 99% level from contaminated water (one case 99.9%); feed flow rate 10 m³/h.

Technique	Costs given by Nijhuis (\$/m ³)	Costs given by Coté (\$/m ³)
liquid phase activated carbon adsorption	1.16	0.80
air stripping, incl. gas phase adsorption	1.12	0.40
air stripping, incl. biofilter treatment	1.05	—
pervaporation, stand alone	0.98	0.56-1.10
pervaporation, incl. liquid phase adsorption (99.9%)	0.85	—

Finally table 9 shows a comparison of clean-up costs for VOC contaminated waters using the various techniques mentioned in this paragraph. Data for this table have been collected from two literature sources (37,38). Although the two sets of data differ somewhat they do indicate that pervaporation alone or in combination with an active carbon aftertreatment can form a cost effective alternative for the already existing commercial methods.

Summary and outlook

Membrane processes offer interesting alternatives and possibilities for the process engineer in the treatment of effluent or waste streams. Ultrafiltration and reverse osmosis have found to be economically attractive and useful in a number of applications on an industrial scale. Waste treatment of liquid and gaseous effluent streams seems more and more necessary in view of the increasing environmental pollution problems we face today.

Recently, newer techniques incorporating membranes have emerged from the laboratory into the industrial world. Worth mentioning here are the separations of organic compounds from aqueous or gaseous streams via pervaporation and gas-vapor permeation. Still on the laboratory benches are hybrid developments that utilize membranes in a specific manner, e.g., a membrane reactor in the Claus reaction. Nevertheless, some hindrances for the progress of membrane technology should be mentioned. Chemical resistance is one of the most important factors that needs to be improved. There is also a strong need for membranes with a permeability and selectivity behaviour specifically designed and tailor-made for a certain problem or problem group.

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