



Recent advances in VOCs removal from water by pervaporation

Ming Peng^a, Leland M. Vane^b, Sean X. Liu^{a,*}

^a *Department of Food Science, Cook College, Rutgers University, 65 Dudley Road, New Brunswick, NJ 08901, USA*

^b *National Risk Management Research Laboratory, United States Environmental Protection Agency, Cincinnati, OH 45268, USA*

Received 21 June 2002; received in revised form 23 August 2002; accepted 25 September 2002

Abstract

Pervaporation (PV) is a separation process in which minor components of a liquid mixture are preferentially transported by partial vaporization through a non-porous permselective (selectively permeable) membrane. PV is an emerging technology in environment cleanup operations, especially in the removal of volatile organic compounds (VOCs) from industrial wastewaters or contaminated groundwaters. Current state of PV membrane development in VOC removal and improvement in process engineering, and better understanding of the interactions between VOCs and membrane materials are reviewed. Among PV process parameters documented here are process temperature, permeate pressure, feed concentration, and feed flow rate. The effects of these parameters on PV selectivity and permeation flux have been studied extensively and these studies have borne fruit in a better understanding of many aspects of PV processes. The challenge in implementing PV in practical operations lies in the further enhancement of membrane quality for specific VOCs as well as improved management and control of possible adverse hurdles coming from real systems.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Volatile organic compounds (VOCs); Contaminated soil remediation; Membrane; Pervaporation; Industrial wastewater treatment

1. Introduction

Membrane technology is a separation process that utilizes differences in size, shape, electrical charge, concentration, partial pressure or solubility in membrane materials between components in mixtures. Substantial progress in membrane research and industrial

* Corresponding author. Tel.: +1-732-932-9611x240; fax: +1-732-932-6776.

E-mail address: liu@aesop.rutgers.edu (S.X. Liu).

applications has been observed since the 1970s after the impact of the energy crisis took hold. As compared with reverse osmosis (RO) or ultra-filtration (UF), pervaporation (PV) did not attract much attention from researchers until the early 1980s [1,2]. In the last two decades, there have been more than 700 publications on PV research and applications. Early PV research on issues such as membrane development, effects of operating variables, and process synthesis has shed some light on the mechanism and potential application of this technology [3–7]. Several reviews are available in such areas as modeling and aroma extraction [8–10], benzene/cyclohexane separation [11], and acetone separation from water [12]. In this paper the progress in research on volatile organic compound (VOC) removal from water by PV is reviewed. The focus is on membrane and module applicability for VOC removal, mass transfer and experimental data of permeation flux for the most commonly studied VOCs, as well as effects of operating parameters on process efficiency.

Man-made VOCs came from several sources such as municipal waste, traffic and industrial and agricultural operations. VOCs emitted from industrial effluent as well as from landfill leachate leakage into ground water have received increasing attention from the government. VOCs of particular interest include petroleum-based solvents, such as benzene, toluene, ethyl benzene, and xylenes (BTEX) and chlorinated solvents, such as trichloroethylene (TCE) and tetrachloroethylene (PCE). The water solubilities of these compounds are low, therefore, the amount of VOCs dissolved in water is too small to be economically removed from water by conventional chemical process separation technologies such as distillation. In the not-so-distant past, air stripping and/or activated carbon treatments were deployed for the task, however, the former is susceptible to fouling and merely turns a water pollution problem into an air pollution issue while the latter needs costly regeneration steps and may not be suitable for VOCs that are easily displaced by other organic compounds. Over the last decade, a growing effort has been devoted to applications of PV to VOC removal from water in order to determine if this technology is technically and economically feasible for this application.

PV is believed to be a promising technology in treating dilute VOCs in either ground water or aqueous effluents. Today, many of those efforts have borne fruit: new membrane materials developed for targeted VOC removal, pilot-scale PV trials, and successful field trials/demonstrations. In comparison with conventional methods, PV does not have emission problems or requires expensive regeneration steps, and costs less to operate for some applications. Additional advantages are compact/modular designs and possible recycling/re-use of recovered VOC solvents.

2. Overview

2.1. General theory

Pervaporation, whose term derives from the two major integral operations involved in the separation process, namely, *permeation* and *evaporation*, is defined as a separation process in which a liquid feed mixture is separated by means of selective diffusion–vaporization through a non-porous membrane. Basically, the PV system consists of a non-porous membrane in a particular module (arrangement, or configuration), a feed pretreatment and

delivery system, and a permeate condensation/recovery system. PV is usually carried out by placing a liquid stream containing two or more species in contact with one side of the membrane while a vacuum or sweep gas is applied to the other side. The species, with various affinities for the membrane material, sorb into the membrane, permeate through it, and evaporate into the vapor phase. The vapor is then condensed. The driving force for PV is the difference in chemical potential (or partial vapor pressure as the first approximation) of each component across the membrane and is often conveniently approximated as the concentration difference in the following permeation flux expression:

$$J_i = k_i^{ov} \rho' [(C_i)^L - (C_i)^V] \quad (1)$$

where k_i^{ov} (m/s), ρ' (moles/m³), C_i^L (dimensionless), C_i^V (dimensionless) are the overall mass transfer rate constant, total molar density of feed, bulk liquid phase concentration (mole fraction), and bulk vapor phase concentration (mole fraction, reported as an equivalent liquid phase mole fraction), respectively, for component i .

The chemical potential difference is generally maintained either by reducing total pressure on the permeate-side of the membrane (vacuum) or depressing the partial pressure of the component in the vapor phase below its vapor pressure in the feed by introducing a sweep gas. The net result is the same: the partial pressure in the vapor phase is kept below the equilibrium vapor pressure (the partial pressure which would be in equilibrium with the feed liquid composition).

In addition to permeation flux, the other important experimentally determined parameter in evaluating process performance of a PV unit is the selectivity. One common representation of selectivity, the separation factor, α , is analogous to the relative volatility of the components (i and j) of a binary liquid mixture:

$$\alpha_{ij} = \frac{(C_i/C_j)^V}{(C_i/C_j)^L} \quad (2)$$

Sometimes, however, the enrichment factor, β_i , is used as an indication of the separation selectivity for component i :

$$\beta_i = \frac{(C_i)^V}{(C_i)^L} \quad (3)$$

In a very dilute system, the concentration of the component j (solvent) in Eqs. (2) and (3) will approach 1 in both the feed and the permeate. The separation factor will therefore be close to the value of the enrichment factor, β_i :

$$\alpha_{ij} \approx \beta_i \quad (4)$$

Based upon basic transport functions, the physicochemical aspects of a PV process can be properly described with a solution-diffusion model [13], which consists of the following steps (this model is widely used in analyzing experimental data and modeling a mass transfer process [10,14]):

- (1) Diffusion through the liquid boundary-layer next to the feed side of the membrane.
- (2) Selective partitioning of molecules into the membrane.
- (3) Selective transport (diffusion) through the membrane matrix.

- (4) Desorption into vapor phase on the permeate-side.
- (5) Diffusion away from the membrane through the vapor boundary-layer on permeate-side of the membrane.

2.2. Research on VOCs removal by PV

The efficiency of PV separation is determined by properties of the target substance and of the membrane as well as by operation variables like feed temperature, permeate pressure, feed concentration, and feed liquid velocity. Studies of PV performance and related issues on VOCs can be grouped into three categories:

- *PV membrane*: Membranes used for VOC separation from water are mostly non-porous hydrophobic ones in a layered composite or dense form. The aim is to test, evaluate, and/or improve the performance of the PV membrane in terms of selectivity, flux, mechanical strength, and optimization of casting techniques and ingredients.
- *Specific VOCs*: Closely related with research on membranes is the study of behavior of different VOCs and interaction between the individual organic compounds as well as between the VOCs and the membranes. For example, industrial wastewaters are multi-component systems, and often behave differently during PV as compared to a similar simple binary system.
- *Operating variables*: The PV process for separating VOCs from water is influenced by process variables. The evaluation and understanding of these variables such as feed temperature, feed concentration, vacuum, and feed velocity are always important in achieving effective separation. Generally, water and solute flux both increase with an increase in either feed temperature or feed concentration for a fixed permeate pressure. However, the extent of water and solute flux variation under these circumstances, as well as the corresponding separation factor will depend on properties of the organic compound and its interaction with the membrane and therefore need to be examined individually.

3. PV membranes

3.1. Membrane varieties

The membrane is the heart of PV. The first criteria for judging a membrane is whether it separates the target solute from water. The PV membrane can be considered as a dense homogenous medium in which diffusion of species takes place in the free volume that is present between the macromolecular chains of the polymeric membrane material. VOCs encountered in an environmental remediation operation usually have concentrations in the range of 1–500 ppm (mg/l). As a general rule, the membranes used for separating VOCs from dilute solutions are mostly hydrophobic materials. Although the partitioning behavior of the VOCs into the membrane will vary, the partitioning behavior still favors VOC sorption into the membrane. Hydrophobic materials are preferred in this application because separating a small amount of organic compounds from the mixture is easier and consumes much less energy than separating water from aqueous solutions. PV membranes used for VOC

removal from water can be either symmetric or composite with a selective layer of 1–200 μm mounted on one or two layers of porous supporting material.

The most commonly used hydrophobic membrane for VOC removal consists of a selective layer of polydimethylsiloxane (PDMS), also known as silicone rubber, which has an alternating $-\text{O}-\text{Si}-\text{O}-$ unit structure and has very good stability in operation. This membrane has very good processing properties and is suitable for manufacturing ultrathin composite membranes. The selectivity of PDMS for VOCs relative to water is high. Even in cases where PDMS exhibits moderate selectivity, this material can still meet the requirements of most applications [8,9,15]. As can be seen from Table 1, PDMS has been used to remove a wide variety of VOCs from aqueous solutions.

Interaction between organic compounds and the membrane can be described by the solubility parameter theory. The solubility parameter is calculated from three force components during the solubilization process, i.e. dispersion forces δ_d , polar forces δ_p , and hydrogen bonding forces δ_h . For example, the solubility parameter of PDMS is 15–16 $\text{mPa}^{1/2}$ [15]. By comparing the solubility parameters of organic compounds to those of PDMS, an approximation of the affinity of a solute to PDMS membrane can be made. As for the sorption and diffusion behavior of organic compounds in the membrane, often experimental studies are required, though some models are available for predictions [16]. Chandak et al. [17] studied TCE and 1,1,1-trichloroethane (TCA) sorption isotherms and showed good representation of the sorption isotherms by the Flory–Huggins model. The diffusivities of TCE and TCA in PDMS were found to be 1.44×10^{-6} and 3.23×10^{-6} cm^2/s at 25 °C, respectively.

In addition to PDMS, there are several other membrane materials that can be used in VOC removal from aqueous solutions. Polyether-block-polyamide (PEBA) is a block copolymer of polyether which has a flexible backbone and low glass transition temperature separated by polyamide blocks. This polymer was used in the separation of toluene, TCA, dichloromethane, etc. from water [12,18,19]. The PEBA membrane (27 μm) exhibited a 40% lower organic flux than was observed with a PDMS membrane (135 μm) [18]. Similarly, a polyurethane (PUR) membrane was used to remove TCA, toluene and dichloromethane from aqueous solutions [18,20]. The PUR polymer has a chain structure that provides both a flexible soft segment for facilitating organic diffusion and a hard segment for mechanical strength [12]. Polyvinylidene fluoride (PVDF) is a crystalline polymer that has good mechanical properties. It was used for benzene separation from water [21]. Ethylene propylene diene monomer rubber (EPDM) has been tested for the separation of TCE and toluene from water [22,23]. Poly[bis(phenoxy)phosphazene] (PPOP) [24] was used for separating methylene chloride from a 1% water mixture at 24 °C. This membrane was reported to be resistant to organic solvent attack.

A sampling of PV membrane materials which have been used for VOC removal from water are listed in Table 2. It should be noted that the same membrane material, but from different suppliers, could show different properties owing to variations in the degree of polymerization and production parameters. This is especially true for copolymers such as PEBA.

3.2. Research on PV membranes

Modifications of membranes with filling, grafting or coating have been performed to achieve high selectivity or high flux for specific organics. For example, an hydrophobic

Table 1
PV operations and results from literature

Membrane & module	Thickness (μm)	VOCs	C_0 (ppm)	T ($^{\circ}\text{C}$)	P (Torr)	VOC flux ($\text{g}/(\text{m}^2 \text{h})$)	α	Reference
PDMS flat sheet	n.a.	Acetone	45000	50	1	750	55	[12]
SC flat sheet	n.a.	Acetone	45000	50	1	1100	50	[12]
PEBA flat sheet	n.a.	Acetone	45000	50	1	200	5	[12]
PDMS hollow fiber	80	Toluene	500	32	0.5–1.5	44	4500	[14]
PDMS flat sheet	140	Methylene chloride	230	30	0.09	15	1450	[18]
PDMS flat sheet	140	Toluene	92	30	0.09	10	2320	[18]
PDMS flat sheet	140	Trichloroethane	146	30	0.09	13	2040	[18]
PEBA	27	Methylene chloride	200	30	0.09	5.7	300	[18]
PEBA	27	Toluene	125	30	0.09	12	700	[18]
PEBA	27	Trichloroethane	300	30	0.09	11	450	[18]
PEBA	100	Phenol	10000	50	1	80	130	[19]
BA-co-AA flat sheet	40	Trichloroethylene	2000	25	10	46	610	[20]
PVDF flat module	10	Benzene	300	25	19	32	1180	[21]
PVDF flat module	10	Toluene	312	25	19	42	1700	[21]
PVDF flat module	10	Xylene	20	25	19	2	840	[21]
PDMS flat sheet	50	Trichloroethylene	250	25	2.3	18	1700	[22]
EPDM flat sheet	50	Trichloroethylene	250	25	2.3	7.0	38800	[22]
PPOP flat sheet	2–17	Dichloromethane	10000	24	200	65	10000	[24]
PPOP flat sheet	2–17	Dichloromethane/ chloroform	500	62.5	200	300	9700	[24]
PE flat sheet	12.7	Chlorobenzene	10	30	7.6	0.39	1000	[28]
PE, irradiated flat sheet	12.7	Chlorobenzene	10	30	7.6	0.35	960	[28]
HDPE-g-BA	n.a.	1,1,2-Trichloroethane	1350	25	0.2	139	1100	[30]
S-B-S flat sheet	70	Trichloroethane	100	30	1–1.4	7	3000	[33]
S-B-S flat sheet	70	Trichloroethylene	100	30	1–1.4	13	5600	[33]
S-B-S flat sheet	70	Toluene	100	30	1–1.4	9	5000	[33]
PDMS coiled geometry	2.4	Chloroform	1000	40	1	40	4890	[38]
PDMS straight hollow fiber	2.4	Chloroform	1000	40	1	20	1670	[38]
PVDF hollow fiber	3	Benzene	120	35	19	14	540	[42]
PDMS tubing	335	Dichloromethane	650	27	Helium	36	4000	[46]

PDMS tubing	335	Bromoethane	570	27	Helium	42	6500	[46]
PDMS tubing	335	Chloroform	460	27	Helium	54	9000	[46]
PDMS tubing	335	Acetone	2500	27	Helium	20.4	680	[46]
Oligosilylstyrene–PDMS flat sheet	22	1,2 Dichloroethane	120	30	5	7.2	1020	[47]
Oligosilylstyrene–PDMS flat sheet	22	Chloroform	170	30	5	6.1	1060	[47]
Oligosilylstyrene–PDMS flat sheet	22	<i>p</i> -Xylene	30	30	5	2.8	1400	[47]
Oligosilylstyrene–PDMS flat sheet	22	Cumene	30	30	5	1.6	900	[47]
Oligosilylstyrene–PDMS flat sheet	22	Toluene	110	30	5	11	3400	[47]
PDMS flat sheet	127	Trichloroethane	300	30	1 ± 0.3	40	8100	[50]
PVDF hollow fiber	0.3	Styrene	140	25	19	3.8	1050	[50]
PDMS tubing	330	Trichloroethylene	0.25	20	Argon/methane	0.017	4780	[53]
PDMS composite spiral-wound	3.5	1,1,2-Trichloroethane	2100	30	4	210	450	[59]
PDMS spiral-wound	3.5	Chloroform	1100	30	4	150	470	[59]
Polyolefin + PDMS	0.5 + 3.5	1,1,2-Trichloroethane	2000	30	4	170	3670	[59]
NBR sheet	200	Benzene	350	30	2.3	12	23000	[63]
NBR sheet	200	Chloroform	250	30	2.3	90	27000	[63]
SBR sheet	300	Benzene	80	30	2.3	15	44000	[63]
SBR sheet	300	Chloroform	250	30	2.3	47	21000	[63]
Silicalite-filled silicone composite	n.a.	Tetrahydrofuran	44000	50	2	980	205	[67]
PDMS hollow fiber (tube feed)	25	Trichloroethylene	900	25	20	9.6	360	[68]
PDMS hollow fiber (shell feed)	25	Trichloroethylene	900	25	20	3	140	[68]
EPDM flat module	130	Dichloromethane	1000	25	3	1.5	380	[69]
EPDM composite flat	5	Dichloromethane	1000	25	3	8.5	610	[69]

C_0 : feed solute concentration (ppm); α : separation factor; n.a.: not available; BA-co-AA: *n*-butyl acrylate-co-acrylic acid; S-B-S: styrene and butadiene copolymer; NBR: nitrile-butadiene copolymer; SBR: styrene-butadiene. *Note*: Flux data were converted into g/(m² h) if they were in mole/(m² h) or other units in original data.

Table 2
PV membrane materials used for VOCs removal

Polymer	Structure	Reference
Polydimethylsiloxane (PDMS)	$(-\text{Si}(\text{CH}_3)_2-\text{O}-)_n$	[15,46]
Nitrile–butadiene copolymer (NBR)	$(-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CN})-)_n$	[63]
Polyvinylidene fluoride (PVDF)	$(-\text{CH}_2-\text{CF}_2-)_n$	[62]
Styrene–butadiene (SBS)	$(-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-)_n$	[63]
Polyolefin (PO)	$(-\text{CH}_2-\text{CH}_2-)_n$	[59]
Polyoctenamer	$(-\text{CH}_2)_3-\text{CH}=\text{CH}-(\text{CH}_2)_3-)_n$	[62]
Poly[bis(phenoxy)phosphazene] (BPOP)	$(-\text{N}=\text{P}((-\text{O}-\text{C}_6\text{H}_5)_2)-)_n$	[24]
Polyether-block-polyamides (PEBA)	$(-\text{C}(=\text{O})-\text{PA}-\text{C}(=\text{O})-\text{C}-\text{PE}-\text{O}-)_n$	[62]
Polyurethane (PUR)	$(-\text{CONHR}'\text{NHCOORO}-)_n$	[62]
Block copolymer styrene (PS) butadiene	$(-\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2-)_m(-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-)_n-$ $(-\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2-)_m$	[33]

zeolite (1-silicalite) was blended into PDMS in order to improve the separation factor for the removal of organic compounds from water [25–27]. The silicalite was believed to create preferential permeation pathways for organic compounds while posing a barrier for water permeation. However, bulky organic molecules may be partly excluded from entering the zeolite pores, thereby reducing permeation in the membrane. Also, there is a certain limit to the amount of filler which can be accommodated in the polymer matrix. Beyond that limit, the physical properties of the filled-PDMS fall off dramatically, resulting in a weak film. For example, PDMS has a glass transition temperature (T_g) of -125°C which is lower than almost all other kinds of polymers. This contributes to its molecular mobility and flexibility, both of which are advantageous for organic compound permeation in the membrane. When silicalite is incorporated in the membrane, the membrane becomes brittle and less rubbery. This phenomenon was also observed in grafting functional groups onto the PDMS backbone structure [26].

Lee et al. [28] studied the effect of irradiation treatment on polyethylene (PE) membranes for treating an aqueous 10 ppm chlorobenzene solution. The PE was a partially crystalline material at temperatures below 105°C . The crystalline phase does not absorb penetrants. Irradiation-induced cross-linking between PE molecules reduced the degree of crystallinity. The permeability of chlorobenzene in PE exposed to a moderate irradiation dose of about 35 megaröntgen was found to be 40% larger and the total flux showed a 50% increase relative to the non-irradiated sample.

Yamaguchi et al. proposed a pore-filling membrane that consisted of a porous substrate and a filling polymer in the pores of the substrate [29–31]. They found that a membrane produced by plasma-grafting poly(laurylacrylate) into a porous high density polyethylene (HDPE) membrane showed a higher TCE selectivity and flux than the reference membrane [29]. In an experiment with a 0.05 wt.% TCE aqueous solution at 25°C , the pore-filled HDPE membrane produced a permeate TCE concentration of nearly 90 wt.% with a TCE flux of about $90\text{ g}/(\text{m}^2\text{ h})$. The polymerized filling in the membrane pores was believed to prevent the membrane from swelling in organic/organic separations. Mishima and Nakagawa [32] also used a grafting technique to introduce 1H-, 1H-, 9H-hexadecafluorononyl methacrylate (HDFNMA) into a PDMS membrane and then evaluated this membrane for the separation

of aromatic and halogenated hydrocarbons from water by PV. Their experiments showed that a 7.0 wt.% degree of grafting gave a higher permselectivity for toluene.

As noted above, the alteration of existing membranes, such as PDMS, is one method for improving PV separations. Preparation of totally new membranes is another approach to improve PV operations. Dutta and Sikdar [33] studied a block copolymer membrane made from styrene and butadiene (S-B-S) for the removal of chlorinated hydrocarbon VOCs from water. The polystyrene block phase has a high glass transition temperature of 95 °C and provides mechanic strength while the polybutadiene block provides good selectivity for the organic compounds relative to water. A thin film of this copolymer coated on a porous polytetrafluoroethylene (PTFE) support yielded an organic-water separation factor on the order of 5000 for TCA, TCE, and PCE.

Hoshi [34] developed a copolymer membrane of *n*-butyl acrylate-co-acrylic acid (BA-co-AA) by a cross-linking method in order to overcome the drawback of weak mechanic strength when long chain ester residues were introduced to obtain higher affinity for VOCs such as TCE. In another study [20], polyurethane membrane 1,6-diisocyanatohexane-polytetramethyleneglycol (HMDI-PTMG) and 1,6-diisocyanatohexane-polycaprolactone diol (HMDI-PCL) were used for the removal of phenol from water by PV. A PTMG molecular weight of 3000 in the membrane produced a phenol flux reaching about 70 g/(m² h) and a phenol concentration in the permeate of 30 wt.% with a separation factor of 50.

Jou et al. [35] looked into the surface modification of a ceramic substrate with a polyvinyl acetate (PVAc) grafting layer for TCE removal. Good membrane structural integrity and high chemical and physical resistance were observed after modification. The mass transfer resistance from the membrane was found to be negligible compared to the resistance caused by concentration polarization on the feed side of the membrane when separating TCE and chloroform from aqueous solution.

4. Modules

There are three common types of commercial membrane modules used for VOC removal from aqueous solutions, i.e. plate-and-frame, hollow fiber, and spiral-wound. Plate-and-frame modules, which consist of stacks of alternating permeate and feed layers were an early favorite because of the relatively simple design. The most basic form of the plate-and-frame module, a single feed chamber and a single permeate chamber separated by a flat sheet membrane, can be used to test different membranes by simply swapping out the flat sheet membrane. Further, it allows for the use of membrane materials which cannot be conveniently produced as hollow fibers or spiral-wound elements. The disadvantages of the plate-and-frame design are that the ratio of membrane area to module volume is low compared to spiral-wound or hollow fiber modules, dismounting is time-consuming and labor-intensive, and higher capital costs are associated with the frame structures.

Hollow fiber modules can be configured for liquid flow on the “shell” side (outside of the fibers) or on the lumen side (bore feed, inside the hollow fibers) of the hollow fibers [36]. These “tubes” have diameters on the order of 100 μm. As a result, they have a very high surface area to module volume ratio. This makes it possible to construct compact modules

with high surface areas. The drawback is that the liquid flow inside the hollow fibers is normally within the range of laminar flow regime due to its low hydraulic diameter. The liquid boundary-layer mass transfer resistance is likely to be substantial in this membrane module. However, because of laminar flow regime, the modeling of mass transfer in a hollow fiber module is relatively easy and the scale-up behavior is more predictable than that in other modules. Another problem with a hollow fiber module is that a whole unit has to be replaced if failure occurs unless the defective fiber(s) can be plugged. The alternative to lumen feed is shell-side feed. Shell-side feed has the advantage that turbulence can be introduced to lower the mass transfer resistance, however short circuiting and maldistribution of flow can occur.

In simplistic terms, a spiral-wound module is like a plate-and-frame module rolled into a cylinder with liquid flow entering along the end of the cylinder and leaving at the other end. Permeate spirals to the center of the cylinder where it is collected via a central pipe. Porous spacers separate the layers of membranes. Feed spacers create a gap allowing liquid feed to flow between the active membrane surfaces while permeate spacers create a gap allowing the permeate vapor to flow to the central receiving tube. The feed spacer also acts to enhance turbulence, thereby reducing the liquid boundary-layer mass transfer resistance. One potential drawback to spiral-wound modules lies in the permeate path length. A permeating component that enters the permeate envelope farthest from the perforated permeate tube must spiral inward several feet. Depending upon the path length, permeate spacer design, and permeate flux, significant permeate-side pressure drops can be encountered, thereby reducing the mass transfer driving force. Another limitation of spiral-wound modules is that the feed spacer acts as a sieve for particles and may become blocked with particulate matter.

Apart from the conventional modules used in most studies on VOCs removal, there are also some new and interesting derivative forms of membrane modules. Vane et al. [37] pioneered a vibrating flat sheet PV module for VOC removal from water. Their module was a plate-and-frame system comprised of circular plates with open channel flow. The entire stack of membrane plates vibrated rotationally about the axis of the stack at approximately 60 Hz. A 10-fold increase in the overall mass transfer coefficient of TCA, TCE, and PCE was achieved relative to a non-vibrating module.

Schnabel et al. [38] compared the effectiveness of a coiled hollow fiber membrane module with that of a straight hollow fiber PDMS membrane in parallel alignment. The positive effect of Dean vortices generated by flow through the coiled fibers on the efficiency of chloroform solution PV was evident. A two-fold increase in chloroform flux from 20 to 44 g/(m² h) at 40 °C, corresponding to a separation factor increase from 1700 to 4900, was achieved in their study.

5. Physical properties of VOCs

The physical properties of VOCs such as diffusivity in water, affinity for specific membrane material, permeability in membrane and saturation vapor pressure are all very important for designing and evaluating PV systems. When PV is used to remove VOCs from surfactant-based soil remediation fluids, knowledge of the water-surfactant VOC partition

coefficient is critical for proper system design. These physical properties are also important in defining issues such as the limiting mass transfer step, cross-over effects from multiple VOCs, etc.

VOC diffusivity in water is a function of VOC molecular size, solution viscosity and temperature. The Wilke–Chang equation is widely used for calculating the diffusivity D_i of organic compounds in water:

$$D_i = 7.4 \times 10^{-8} \frac{(\psi_j M_j)^{1/2} T}{\mu V_i^{0.6}} \quad (5)$$

where i represents the organic species and j signifies solvent (water in this case), D_i has units of cm^2/s , V_i is molar volume ($\text{cm}^3/(\text{g mol})$) of solute, M_j molecular weight of solvent j , μ viscosity of the solvent or solution ($10^{-2} \text{ g}/(\text{cm s})$, i.e. cP), T is absolute temperature (K), and the dimensionless constant ψ_j is 2.6 when water is the solvent. This equation is valid for non-dissociating compounds and is generally accurate to within 10%.

VOC permeability through a non-porous membrane is defined as the product of solubility and diffusivity:

$$P_m = SD \quad (6)$$

This equation was used in explaining permeability of VOCs in membranes. In work by Ji et al. [18], both the liquid and vapor permeabilities of VOCs were examined. Toluene was shown to have the highest intrinsic liquid permeability of $4.32 \times 10^{-8} \text{ m/s}$ in PDMS and the lowest permeability in PUR. The solubilities of the organic compounds in the membranes accounted for the observed trend in intrinsic liquid permeability and separation factor: toluene > TCE > methylene chloride. Similarly, Visvanathan et al. [39] investigated TCA and TCE removal efficiencies from water using a composite dense PDMS permselective active layer supported by a thick porous poly(ether sulfone) layer. They found preferential passage of TCE relative to TCA in the membrane. The authors attributed the preferential permeation of TCE to the lower molecular volume and polarity of TCE. Mishima and Nakagawa [32] compared the behaviors of different chlorinated hydrocarbons and solvents in PDMS and found that PCE and toluene have higher solubilities than ethyl butanoate (EBU) in PDMS because of their higher octanol–water partitioning coefficients (P_{ow}). Hoshi et al. [40] studied the diffusivity of phenol in PUR membranes, estimating a phenol diffusivity of $2.5 \times 10^{-12} \text{ m}^2/\text{s}$ at 60°C .

Molecule structure also affects organic compound permeability in membranes. Dotremont et al. [41] studied the influence of structure characteristics such as the number and position of chlorine atoms, branching degree, presence of double bond, etc. on the permeabilities of chlorinated hydrocarbons in PDMS polymers. According to their work, a double bond increased permeability of organic compounds by reducing polarity of molecules. A long chain decreased the permeability, but it was not as critical for smaller molecules that were more likely affected by other operating factors. Branching yielded a negative effect on permeability in hydrophobic zeolite-filled membranes. As for the effect of chlorine position, this parameter must be judged on an individual basis. A list of VOCs most often studied in PV research is provided in Table 3.

Table 3
Physical properties of common VOCs in PV studies

Material	M_W	Solubility in water (wt.%) ^a	Molar volume (cm ³)	Saturation pressure (mmHg) (25 °C)	Reference
Dichloromethane	85	1.945	64.5	430	[46]
Chloroform	119.5	0.78	81.1	199	[46]
Bromoethane	108.9	0.897	75.3	460	[46]
Acetone ^a	58	All proportions	73.9	283	[46]
Benzene	78	0.17	89	122	[63]
1,1,1-Trichloroethane	133	0.44	99.2	100	[64]
1,1,2-Trichloroethane	133	0.45	92.4	22.4	[59]
Trichloroethylene	132	0.1	90.4	74	[53]
Tetrachloroethylene	166	0.015	102	18	[65]
Toluene	92	0.05	106	25.6	[59]
Chlorobenzene	112.5	0.05	102	10	[66]

^a Acetone was excluded from EPA VOC list on June 1995.

6. Process parameters

Understanding the effects of PV operational variables is critical for VOC removal from water. In fact, it is hard to evaluate a PV process just by examining organic compound flux or separation factors alone without considering related parameters like feed temperature, feed concentration, permeate pressure, module geometry, feed flow dynamics, etc. A change in one parameter sometimes results in a change in the separation efficiency via several mechanisms at the same time. For example, an increase in feed temperature will result in increased diffusivity in both the liquid layer and the membrane, decreased liquid viscosity, raised vapor pressure, and altered membrane sorption properties. Extensive studies have been performed and reported examining the roles of these variables. Generally, the effect of process parameter variations has been reported in terms of flux and separation factor changes. Evaluation of PV data reported in the literature can be difficult due to the variety of units encountered. For the purpose of simplifying the comparison, units of g/(m² h) will be used for flux, parts per million (ppm or mg/l) for liquid concentration, and Torr for downstream permeate pressure.

6.1. Temperature

Temperature is a key factor in influencing VOC separation by PV. Temperature affects all of the constituent steps of solute transport outlined in Section 2.1 as well as the driving force for mass transfer. For VOC removal from water, temperature impacts PV performance through altered vapor–liquid partitioning of the VOCs (Henry's Law constants), via changes in the diffusion coefficients of the VOCs in both the aqueous phase and the membrane material, and through altered sorption behavior in the membrane. The effect of temperature on the first mass transfer step, diffusion through the liquid boundary-layer, can be calculated by the Wilke–Chang equation or other diffusivity equations. The effect of temperature on the permeability of solutes in the membrane (i.e. the effect on diffusivity and sorption in the membrane) can, in part, be explained by the frequency and amplitude of polymer molecular

motion that are greater at higher temperature and the fact that thermal motion of polymer chains in the amorphous region will produce larger free volume.

The usual temperature range examined in the literature was 20–70 °C. When feed temperature is raised, both VOC flux and water flux will increase. The separation factor will change accordingly depending on the relative change of the VOC flux to that of the water flux. For example when temperature was increased from 20 to 55 °C, benzene flux increased from 8 to over 15 g/(m² h), which caused a decrease in the separation factor from about 1000 to less than 100 [42]. In this case, the separation factor decreased due to an increase in water flux which outpaced the increase in benzene flux. In research done by Hollein et al. [12], the influence of temperature on acetone–water separation was examined with an silicone composite (SC) membrane. A temperature increase from 20 to 68 °C resulted in an increase in the total acetone and water flux from 200 to 1300 g/(m² h) for a 2 wt.% acetone–water solution.

Yeom et al. [15] performed an experiment of PV separation of dichloroethane from water and observed that when the temperature was changed from 30 to 45 °C, both organic compound and water fluxes increased and the net result was a decreased separation factor, similar to the benzene–water behavior mentioned previously. However, when they carried out similar experiments on chloromethane, which is more hydrophobic than dichloroethane, the organic flux showed an increase of about 33% when temperature increased from 30 to 45 °C, but water flux decreased 5–15%. The decrease in water flux was attributed to water cluster formation that curtailed the increase in diffusion at higher temperatures. Thus the separation factor for chloromethane increased with an increase in temperature. Arrhenius-type relationships can be used in describing the effect of temperature on flux as follows [43]:

$$J_i = J_0 \exp\left(\frac{E_a}{RT}\right) \quad (7)$$

where J_i (g/(m² h)) represents the flux of species i , J_0 (g/(m² h)) is a constant, E_a (J/mol) the activation energy, R (J/(mol K)) the universal gas constant, and T is the absolute temperature in Kelvin (K). When the value of E_a is high, the flux will be more susceptible to changes in temperature. E_a values of 34.4 [44] and 32.0 kJ/mol [12] were reported for water permeation in PDMS and SC, respectively. In the same reports, E_a was reported to be 34.7 kJ/mol for *p*-cresol [44] and 30.1 kJ/mol for acetone [12]. In experiments reported by Dutta and Sikdar [33] with SBS block copolymer membranes, TCA flux increased from 22 to 39 g/(m² h) when temperature was increased from 30 to 50 °C and E_a was 23.4 kJ/mol for TCA and 51.5 kJ/mol for water.

6.2. Permeate pressure

PV operation is carried out by applying vacuum or a sweep gas to the permeate-side of the membrane, which creates a chemical potential difference between the permeate-side and the feed side. In most cases, vacuum is preferred over use of a sweep gas. The range of vacuum pressures explored for VOC separation from dilute aqueous solution is from nearly zero to about 100 Torr. In simplistic terms, the permeate pressure impacts PV performance through the driving force term in Eq. (1) and does not impact the mass transfer coefficient. Thus, the effect of permeate pressure on performance is less complex than the effect of

temperature. However, the relative response of the flux of each compound will be different resulting in separation factor changes. In addition, although permeate pressure control is fairly straightforward in bench-scale systems, control and knowledge of permeate pressure throughout larger-scale PV systems is quite complicated. For example, as was mentioned in Section 4, permeate pressure in modules can be a function of distance from the vacuum distribution point.

The relationship between permeate-side pressure and solute flux can be expressed by rewriting Eq. (1) in terms of partial pressures as follows [18,45]:

$$J_i = J_{i0}(C'_i \gamma'_i P_i^0 - P_i'') \quad (8)$$

where J_i ($\text{cm}^3(\text{STP})/(\text{cm}^2 \text{ s})$) is the permeation flux of species i , J_{i0} ($\text{cm}^3(\text{STP})/(\text{cm}^2 \text{ s cmHg})$) the pressure-normalized permeation flux of species i through the membrane, C'_i the mole fraction of species i at the upstream surface of the membrane, P_i^0 (cmHg) the saturation vapor pressure of pure i at the feed temperature, γ'_i the activity coefficient of i in the feed, and P_i'' (cmHg) is the partial pressure of i on the permeate-side of membrane. For typical VOCs, the activity coefficient in water is quite large. Likewise, the pure component vapor pressure is high. As a result, even at low VOC concentrations, the product $C'_i P_i^0 \gamma'_i$ is relatively large. Thus, permeate pressure has only a modest effect on VOC flux under most conditions. This is generally not the case for water flux. First, $C'_w P_w^0 \gamma'_w$ is approximately equal to P_w^0 in dilute aqueous VOC solutions because both C'_w and γ'_w approach 1. Second, P_w^0 ranges from only 18 Torr at 20 °C to 150 Torr at 60 °C. As a result, a permeate partial pressure of water below 6 Torr is necessary to avoid impacting water flux at 20 °C while permeate partial pressures of water up to 50 Torr are not likely to cause reduced water fluxes at 60 °C. Despite high VOC–water separation factors, the permeate from such a separation may still be mostly water, especially on a mole basis (because the molecular weight of water is several times smaller than that of most VOCs). If permeate pressure is raised and approaches the vapor pressure of water, water transport may be reduced so significantly that convective flow practically ceases, stagnating the permeate. When this occurs, VOC mass transfer resistances on the permeate-side of the membrane may become limiting.

These general observations are borne out in the experimental data. Ji et al. [18] found that within a permeate pressure range of 0.1–15 Torr (at 30 °C), the flux of TCA and toluene were not affected by the permeate pressure variation. When pressure was further increased over 15 Torr, the mass transfer coefficients of the two VOCs were reduced. At low pressure, the convective flow from the membrane–vapor interface into the bulk permeate was the main mode of organic mass transport, and when pressure was increased, VOC diffusion became dominant and would bring the coupling phenomenon of the mass transfer. Similarly, Hollein et al. [12] found that an increase in permeate-side pressure from near 0–70 Torr resulted in a linear decrease in acetone flux from 0.3 to 0.16 $\text{kg}/(\text{m}^2 \text{ h})$ and a decreasing water flux in a gradually accelerating mode when the permeate pressure was less than 50 Torr, followed by an almost level-off zone between 50 and 70 Torr.

6.3. Feed concentration

When the VOC concentration is increased in solution, the VOC flux usually increases accordingly. This can be explained by the increase in driving force in the right hand term of

Eq. (1). Usually, the VOC partial pressure at the permeate-side of the membrane is negligible (i.e. under moderate vacuum) and, therefore, the local flux is a linear function of the feed side concentration. For systems with a low single-pass VOC removal, the liquid concentration is simply the feed concentration. However, in cases where an appreciable single-pass removal is observed, the log-mean liquid feed concentration can be used to represent the average liquid concentration of VOC:

$$C_{lm} = \frac{C_f - C_r}{\ln(C_f/C_r)} \quad (9)$$

where C_{lm} , C_f and C_r represent the log-mean, feed and residual concentrations, respectively. If solute partitioning between the feed liquid and the membrane is ideal and there is no membrane swelling from VOC sorption, then a linear relationship between organic compound flux and concentration will be observed. Water flux usually remains constant when membrane swelling is negligible. Both increased and decreased water flux were observed in several studies when the VOC concentration was increased. When VOC concentration in the membrane polymer is high, plasticization of polymer and mass transfer coupling of different organic compounds may occur and should be taken into account. In general, the influence of feed concentration on separation factor is not as critical as the effects of feed temperature and permeate pressure.

Nguyen and Nobe [46] conducted PV experiments with aqueous solutions containing dichloromethane, bromoethane, and chloroform using an silicone tubing membrane. The feed concentration of the VOCs was varied from 0.002 to 0.06 wt.%. In this concentration range, the organic compounds did not cause membrane swelling and a linear relationship between solute flux and feed concentration was observed. Similarly, Dutta and Sikdar [33] found that water flux (about 22 g/(m² h)) and separation factor for an SBS membrane were independent of the aqueous concentration of TCA, TCE, and toluene in the feed liquid.

When membrane swelling due to VOC sorption is substantial, the water flux typically increases as VOC concentration increases due to a reduced diffusion resistance to water transport in the membrane. Mishima and Nakagawa [32] found that when the benzene feed concentration was increased from 0.01 to 0.03 wt.% at 25 °C, the PDMS membrane showed swelling and the water flux increased from 70 to 120 g/(m² h). When the authors repeated the experiment with a grafted membrane, water flux was no longer a function of benzene concentration.

An increase in VOC concentration will most likely cause an increase in water flux or no effect at all. However, a few studies have found that an increase in VOC concentration has resulted in a lower water flux. For example, Lau et al. [47] observed that an increase in chloroform concentration resulted in the expected increase in chloroform flux, but a decrease in water flux. When the chloroform mole fraction in the feed liquid was increased from 0.5×10^{-5} to 10×10^{-5} chloroform flux increased from 2 to 30 g/(m² h) and water flux decreased from 37 to 18 g/(m² h) yielding an increase in the separation factor from 1170 to 1800. Organic compound and water permeation through the membrane was believed to act as two competing processes with one hindering the other.

One application of PV is as a unit operation in a soil remediation process. As VOCs usually have little solubility in water, surfactants are sometimes introduced in the contaminated soil to improve the apparent solubility of organic compounds so that a higher removal

efficiency is achieved in the soil. Groundwater drawn from contaminated sites remediated with surfactants can be treated with PV to separate VOC contaminants while the surfactant is retained in the PV retentate for subsequent reconcentration and reuse. In this situation, a portion of the organic compounds will partition into surfactant micelles and the concentration of the organic compounds in the aqueous phase outside the micelles (extramicrocellular aqueous phase) may be significantly lower than the total VOC concentration in feed. As a result, the observed VOC flux and separation factor for a given total VOC concentration (sum of micellar and extramicrocellular concentrations) in the presence of surfactant will be smaller than for the same VOC concentration in the absence of surfactant. Abou-Nemeh et al. [48] reported that 0.3 wt.% sodium dodecyl sulfate (SDS) increased the solubility of TCE in water from 900 to 3500 ppm while the single-pass fraction of TCE removed by the hollow fiber PV module dropped from 95 to 89%. Similarly, Jiang et al. [49] found that when non-ionic surfactant Triton X-100 was 40 times the critical micelle concentration ($40 \times \text{CMC}$), where $1 \times \text{CMC} = 0.15 \text{ g/l}$, TCA had apparent aqueous solubility up to 4500 ppm but its flux was 40% lower than without surfactant due to viscosity increase and TCA partitioning into micellar phase. When surfactant was in the range $(0.25\text{--}4) \times \text{CMC}$, no appreciable impact on PV performance was observed. In another study [50] on TCA–water binary system with presence of $8.8 \times \text{CMC}$ ($1 \times \text{CMC} = 2.36 \text{ g/l}$) SDS under turbulent flow regime they showed similar potential of using PV for recovering VOCs from soil remediation fluids. Hitchens et al. [51] also found a decline in the removal efficiency of toluene from surfactant-based remediation fluids by PV due to the existence of surfactant micelles and partitioning of toluene into the micelles.

6.4. Flow velocity

Feed liquid velocity is a critical factor in PV efficiency when the liquid boundary-layer resistance limits VOC mass transfer. Boundary-layer resistance can be very severe in circumstances where the solute diffusivity is low in water and the membrane resistance is small compared to the total mass transfer resistance. In this circumstance, an increase in feed fluid velocity will increase the VOC mass transfer rate from the bulk solution to the membrane surface, thus the total mass transfer rate is enhanced. This issue has been studied rather extensively [33,38,41,52]. In most of these studies, the mass transfer resistances associated with partitioning of molecules from the aqueous phase into the membrane and then desorption and diffusion of the molecules into the vapor permeate phase are generally neglected. As a result, the overall mass transfer coefficient (K^{ov}), can be related to the liquid boundary-layer mass transfer coefficient (k^{b}), membrane permeability (P_{m}), and membrane thickness (l) as follows:

$$\frac{1}{K^{\text{ov}}} = \frac{1}{k^{\text{b}}} + \frac{l}{P_{\text{m}}} \quad (10)$$

where the inverse of a mass transfer coefficient is the resistance to mass transfer, thus the overall mass transfer resistance is the sum of the individual resistances in series.

When resistance from the liquid boundary-layer is much larger than that from the membrane ($k^{\text{b}} \ll P_{\text{m}}/l$), mass transfer in the boundary-layer becomes rate-limiting. An increase in mass transfer efficiency in this step will lead to an overall improvement in mass transfer.

This situation is commonly encountered in the removal of VOCs from water by PV using hydrophobic membranes. For example, when the flow rate of a TCA solution was increased from 0.03 to 0.11 m³/h, an increase in separation factor from 1300 to 3200 was achieved (135 ppm feed at 30 °C) in experiments by Dutta and Sikdar [33]. This same trend was also found by Jou et al. [35] who calculated the overall mass transfer coefficient of TCE and found two-fold increases in mass transfer rate when the Reynolds number, which is proportional to liquid velocity, was increased from 860 to 2780. This boundary-limiting phenomenon was also demonstrated by Jian and Pintauro [42]. They found the same benzene removal rate by either bore-side feed or shell-side as long as feed velocity was larger than 0.06 m³/h, but at lower velocity, the shell-side had smaller Reynolds number and the separation efficiency was not as good as that of the bore-side feed operation. In an experiment reported by Psaume et al. [53], at a solute concentration of 150 μg/l (0.150 ppm), TCE flux increased substantially from 0.36×10^{-3} to 10.1×10^{-3} g/(m² h) when the Reynolds number increased from 2 to 60. In all their experiments, water flux was constant at 14 g/(m² h). Similarly, Urtiaga et al. [52] found that as the feed liquid velocity was increased from 0.0012 to 0.0063 m³/h, the liquid boundary-layer mass transfer resistance for chloroform was reduced. However, water flux was independent of flow rate and was constant at about 22 g/(m² h) at 30 °C and 40 g/(m² h) at 50 °C.

Eq. (10) can be used to estimate the individual mass transfer resistances associated with the liquid boundary-layer and membrane from experimentally determined values of the overall mass transfer coefficient as a function of membrane thickness or feed liquid velocity, as illustrated in Figs. 1 and 2. By varying either feed velocity or membrane thickness while keeping other factors unchanged, a plot of overall mass transfer resistance versus mass transfer resistance due to the change in velocity or membrane thickness can be constructed. Then an estimation of mass transfer resistance that is not affected by the changing factor can be made by extrapolation of the plot to get the intercept on the ordinate. Understanding that the concentration boundary-layer could be the rate-limiting step is very important to

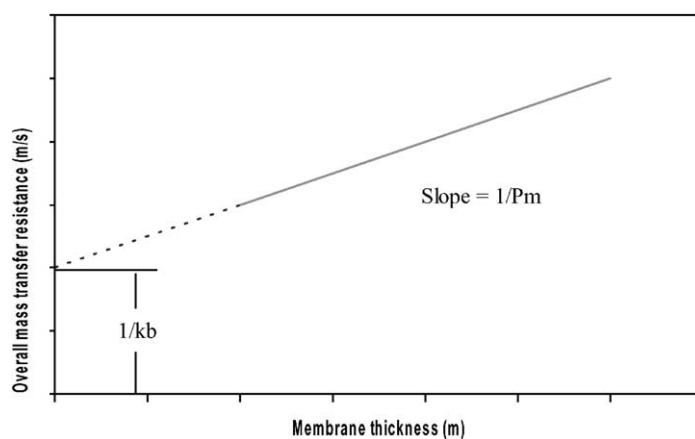


Fig. 1. Plot of overall mass transfer resistance as a function of membrane thickness under constant cross-flow feed flow rate. (Solid line represents the range of experimental results; dotted line represents the extrapolating process.)

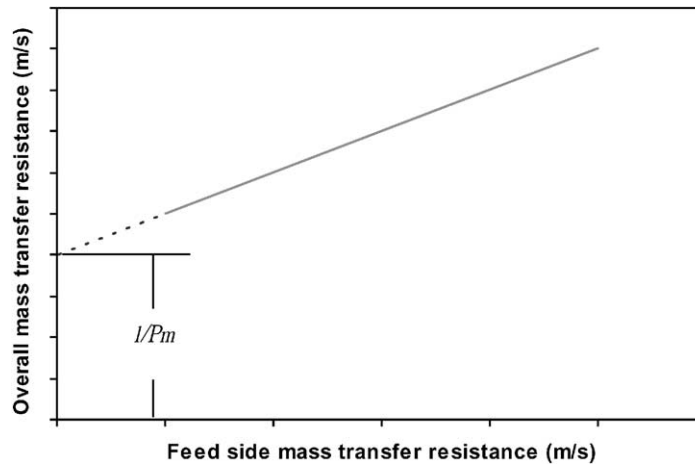


Fig. 2. Plot of overall mass transfer resistance as a function of feed side mass transfer resistance. (Solid line represents the range of experimental results; dotted line represents the extrapolating process.)

the design of a PV system for separating VOCs from water. This aspect of PV research will not be covered in this paper. Numerous works on modeling concentration boundary-layer effects can be found in the literature [8,37,53–58].

6.5. Membrane thickness

The PV membrane shows a mass transfer resistance that is proportional to its thickness. The thickness can only be decreased to a certain limit because of manufacturing techniques and mechanical stability. Therefore, permeation flux is usually inversely proportional to the membrane thickness, assuming the diffusion within the membrane being the rate-determining step. Most studies on VOC removal from water reached a similar conclusion that the total flux will decrease when PV membrane thickness increases while other conditions are kept unchanged. Normally, the separation factor as well as the permeate concentration will increase as the membrane thickness increases because the water flux usually decreases at a faster rate than that of the VOC flux. This effect is a result of water transport being limited by the membrane while VOC transport is at least in part limited by the liquid boundary-layer resistance.

Nijhuis et al. [22] reported that water flux was inversely proportional to the thickness of the membrane when PDMS or EPDM were used for PV of a toluene–water solution. When the thickness of PDMS was increased by a factor of 8 (from 30 to 240 μm), the water flux decreased by almost the same factor ($8.5\times$) from 51 to 6 $\text{g}/(\text{m}^2 \text{h})$. At the same time, toluene flux only decreased from 20 to 13 $\text{g}/(\text{m}^2 \text{h})$. Thus, as suggested above, the VOC flux was affected less than the water flux by an increase in membrane thickness. Similarly, when the thickness of an EPDM membrane increased from 35 to 200 μm ($5.7\times$ increase), the water flux decreased from 0.9 to 0.17 $\text{g}/(\text{m}^2 \text{h})$ ($5.3\times$ decrease) while the toluene flux changed from 8.5 to 3.5 $\text{g}/(\text{m}^2 \text{h})$. Hoshi et al. [34] also observed a faster decrease of water flux than

that of TCE flux when the thickness of their copolymer membrane increased from 40 to 140 μm . The TCE concentration in the permeate increased from 54.6 to 62.7 wt.%, which led to an increase in the separation factor from 610 to 830. Lau et al. [47] showed that selectivity increased for separation of toluene, chloroform, and methylene chloride from respective aqueous solutions when the thickness of the membrane was increased from 20 to 60 μm . The increase in separation factor was most obvious for toluene, from 3500 to about 7000 for a 110 ppm solution.

The general observation that the water flux increased with the decrease of membrane thickness is not always true. In experiments by Yeom et al. [15], when the thickness of PDMS decreased from 100 to 20 μm , chloromethane flux increase of 50 $\text{g}/(\text{m}^2 \text{h})$ was observed with a 100 ppm feed solution at 35 °C and permeate pressure of 5 Torr, but water flux was not increased. This was explained that in chloromethane dilutions the water clustering was very significant due to the very high hydrophobicity attributed to the organic compound and this clustering made water diffusivity smaller.

Closely related with the resistance from the membrane is the resistance from support or backing materials used for improving or maintaining membrane mechanical strength. Usually the resistances from these materials are negligible because of their porous structures. However, additional resistance from materials other than the membrane may also be observed and could be of significance in certain cases. For example, Smart et al. [14] found fiberglass backing brought another 20% resistance to the whole mass transfer as the toluene flux decreased 20% from 88 $\text{g}/(\text{m}^2 \text{h})$ for a flat sheet module. The additional resistance was attributed to the weave of the individual fiberglass fibers, the size of the fibers, the sizing/binding agents on the fibers, or adhesive layer that bonded the non-porous PDMS layer to the fiberglass mat. Blume et al. [59] studied the pervaporative separations of chloroform and 1,1,2-trichloroethane by very thin PDMS (3.5 μm) and polyolefin composite membranes with porous polyester as the support material in a spiral-wound module. The incorporation of another thin layer of polyolefin membrane into the composite PDMS membrane reduced the total flux to only about 1/10 of the original flux for 1,1,2-trichloroethane. Almost all of this flux decline was due to a decline in water flux while the VOC flux was not impacted significantly. Thus, the final VOC removal rates of these two membranes were basically the same, and the concentrations of the solute could be reduced from 0.35 to 0.05% after about 1.5 h of PV treatment.

6.6. Pilot and in-field application

Actual wastewaters and ground waters are more complex than surrogate binary solutions prepared in the laboratory. Aqueous wastes are usually composed of more than two ingredients and might contain different organic compounds, as well as suspended and dissolved solids such as inorganic salts. The performance of a PV system with an actual wastewater usually deviates from the ideal binary system to some extent. The separation effects and selectivity will be affected by additional factors. For example, Kondo and Sato [19] studied the behavior of PEBA in treating wastewater containing phenol. They found the flux and selectivity in pervaporative treatment of the wastewater was less than half of the corresponding binary system. When the feed concentration was 2.5 wt.% (25,000 ppm), the separation factor and phenol flux were 38 and 50 $\text{g}/(\text{m}^2 \text{h})$, respectively, for treating the

wastewater by PV, as compared with 80 and 210 g/(m² h) in a simulated binary system. In the binary system, two consecutive tests of the membrane showed the same pervaporative effect in reducing phenol concentration from 4% to 300 ppm within 120 h. In contrast with the test conducted with real wastewater, 240 h were needed to achieve the same result and the second trial could only reduce phenol concentration to 1121 ppm.

Dutta and Sikdar [33] found that when their PV module was used in removing VOCs from an actual surfactant-based soil remediation fluid, the flux fell because of the presence of oil and surfactant. In the study of the coupling effects in a ternary system with zeolite-filled membrane, Goethaert et al. [25] found that acetone and isopropyl alcohol showed a similar coupling phenomenon resulting in a decrease in chloroform flux, but acetone experienced higher flux in a ternary system than a binary one.

Pilot and field-scale PV applications for removal of TCA, toluene and PCE were reported [51,60]. In their 75 h pilot study, Hitchens et al. [51] examined the effects of temperature, permeate pressure, and flow rate on VOC mass transfer from a surrogate surfactant solution. They found that addition of a surfactant reduced the removal rate of organic compounds because of the increase in viscosity of the feed solution as well as the partitioning of the organic compounds into the surfactant micelles. At a feed flow rate of 0.5 gallon per minute (40 °C and 25 Torr) the single-pass removal efficiencies for TCA and toluene were reduced from 99.2 and 98.8%, respectively, when no surfactant was present to 93.6 and 88.2%, respectively, in the presence of 1.7 wt.% of an anionic surfactant (DOWFAX 8390). At other operating conditions, similar trends were observed. In a field validation project for separating VOCs from surfactant-based soil remediation fluids, Vane et al. [60] used a vibrating PV system and a series of PDMS coated hollow fiber membrane modules for removing PCE from a soil remediation fluid with a feed PCE concentration range of 35–890 ppm. They achieved 95.8 and 99.9% PCE removal efficiencies for groundwater with and without surfactant, respectively. The projected cost for PV treatment of a surfactant-based soil remediation fluid was on the order of US\$ 20 per 1000 gallons of fluid treated.

Selection of PV for treatment of VOCs in water depends on its cost. In some applications, PV has proven to be an economical alternative for wastewater treatment. The economic driving force for PV application is its lower cost compared with conventional separation processes and better separation. As Baker [61] reported, the treatment of a wastewater containing 10 ppm methylene chloride could cost US\$ 3–4 per gallon. If a PV unit was used in treating 100–300 gallon per day of this wastewater, the discharge can be reduced to 34 ppb and the investment can be expected to pay back in less than 1 year.

7. Summary

As a unique membrane process for VOC separation from dilute aqueous solutions and industrial wastewaters, PV is attracting increasing attention from the environmental remediation industry. The advantage of PV in breaking azeotropic systems or separating components from dilute solutions is sometimes limited by factors such as low permeate flux or competition from other available technologies (though often not as environmentally friendly or energy-efficient as PV). Many bench-scale studies and pilot-scale demonstrations on issues like membrane selection, preparation of PV membrane for a variety of VOCs,

process design, process variable assessment, system analysis, and economic evaluation have been reported in the last decade and much progress has been made as a result of these studies. It should be noted, however, that PV represents a new type of unit operation with the potential to replace a number of conventional separation processes and the decision as to whether or not to use a PV process for a particular task must be weighed against competing conventional separation technologies.

As demonstrated in many studies, the performance of PV for VOC removal can be affected by many process variables and understanding of the dynamics under operating conditions is key to a successful process design and optimization. Permeation flux and selectivity of VOCs are two technical parameters that are of very importance to designers and practitioners alike. Although these two parameters can only be obtained through experiments, they serve as strong indicators for the performance of PV processes. In many practical operations, however, flux and selectivity of a solute in a particular membrane module often negate each other due mainly to the imperfection of membrane materials in discriminating different species in the solution. It is likely that a compromise has to be made in favor of one of these two depending upon the process objective.

Acknowledgements

The authors wish to express their gratitude to USEPA and New Jersey Agriculture Experiment Station at Rutgers University for financial support for this work.

References

- [1] H. Eustache, G. Histi, *J. Membr. Sci.* 8 (1981) 105.
- [2] R. Rautenbach, R. Albrecht, *J. Membr. Sci.* 25 (1985) 1.
- [3] Y.M. Lee, D. Bourgeois, G. Belfort, *J. Membr. Sci.* 44 (1989) 161.
- [4] M.H.V. Mulder, C.A. Smolders, *J. Membr. Sci.* 17 (1984) 289.
- [5] C.M. Bell, F.J. Gerner, H. Strathmann, *J. Membr. Sci.* 36 (1988) 315.
- [6] C. Lipski, P. Côté, *Environ. Prog.* 9 (1990) 254.
- [7] H.O.E. Karlson, G. Trägårdh, *Trends Food Sci. Tech.* 7 (1996) 78.
- [8] H.O.E. Karlsson, G. Trägårdh, *J. Membr. Sci.* 76 (1993) 121.
- [9] F. Lipnizki, S. Hausmanns, P.K. Ten, R.W. Field, G. Laufenberg, *Chem. Eng. J.* 73 (1999) 113.
- [10] J.G. Wijmans, R.W. Baker, *J. Membr. Sci.* 107 (1995) 1.
- [11] J.P.G. Villaluenga, A. Tabe-Mohammadi, *J. Membr. Sci.* 169 (2000) 159.
- [12] M.E. Hollein, M. Hammond, C.S. Slater, *Sep. Sci. Technol.* 28 (1993) 1043.
- [13] R.C. Binning, R.J. Lee, J.F. Jennings, E.C. Martin, *Ind. Eng. Chem.* 53 (1961) 45.
- [14] J. Smart, R.C. Schucker, D.R. Lloyd, *J. Membr. Sci.* 143 (1998) 137.
- [15] C.K. Yeom, H.K. Kim, J.W. Rhim, *J. Appl. Polym. Sci.* 73 (1999) 601.
- [16] J.G.A. Bitter, *Transport Mechanisms in Membrane Separation Processes*, Plenum Press, New York, 1991.
- [17] M.V. Chandak, Y.S. Lin, W. Ji, R.J. Higgins, *J. Appl. Polym. Sci.* 67 (1998) 165.
- [18] W. Ji, S.K. Sikdar, S.T. Hwang, *J. Membr. Sci.* 93 (1994) 1.
- [19] M. Kondo, H. Sato, *Desalination* 98 (1994) 147.
- [20] M. Hoshi, M. Ieshige, T. Saitoh, T. Nakagawa, *J. Appl. Polym. Sci.* 76 (2000) 654.
- [21] K. Jian, P.N. Pintauro, R. Ponangi, *J. Membr. Sci.* 117 (1996) 117.
- [22] H.H. Nijhuis, M.H.V. Mulder, C.A. Smolders, *J. Membr. Sci.* 61 (1991) 99.
- [23] E.E.B. Meuleman, B. Bosch, M.H.V. Mulder, H. Strathmann, *AIChE J.* 45 (1999) 2153.

- [24] E.S. Peterson, M.L. Stone, D.G. Cummings, R.R. McCaffrey, *Sep. Sci. Technol.* 28 (1993) 271.
- [25] S. Goethaert, C. Dotremont, M. Kuijpers, M. Michiels, C. Vandecasteele, *J. Membr. Sci.* 78 (1993) 135.
- [26] M. Bennett, B.J. Brisdon, R. England, R.W. Field, *J. Membr. Sci.* 137 (1997) 63.
- [27] J.P. Boom, I.G.M. Pünt, H. Zwijnenberg, R. de Boer, D. Bargeman, C.A. Smolders, H. Strathmann, *J. Membr. Sci.* 138 (1998) 237.
- [28] G.T. Lee, K.R. Krovvidi, D.B. Greenberg, *J. Membr. Sci.* 47 (1989) 183.
- [29] T. Yamaguchi, A. Tominaga, S. Nakao, S. Kimura, *AIChE J.* 42 (1996) 892.
- [30] T. Yamaguchi, S. Yamahara, Shin-ichi Nakao, Shoji Kimura, *J. Membr. Sci.* 95 (1994) 39.
- [31] T. Yamaguchi, T. Suzuki, T. Kai, S. Nakao, *J. Membr. Sci.* 194 (2001) 217.
- [32] S. Mishima, T. Nakagawa, *J. Appl. Polym. Sci.* 75 (2000) 773.
- [33] B.K. Dutta, S.K. Sikdar, *Environ. Sci. Technol.* 33 (1999) 1709.
- [34] M. Hoshi, T. Saitoh, C. Yoshioka, A. Higuchi, T. Nakagawa, *J. Appl. Polym. Sci.* 74 (1999) 983.
- [35] J.-D. Jou, W. Yoshida, Y. Cohen, *J. Membr. Sci.* 162 (1999) 269.
- [36] P. Hunter, S.T. Oyama, *Control of Volatile Organic Compound Emissions*, Wiley, New York, 2000, p. 166.
- [37] L.M. Vane, F.R. Alvarez, E.L. Giroux, *J. Membr. Sci.* 153 (1999) 233.
- [38] S. Schnabel, P. Moulins, Q.T. Nguyen, D. Roizard, P. Aptel, *J. Membr. Sci.* 142 (1998) 129.
- [39] C. Visvanathan, B. Basu, J.C. Mora, *Ind. Eng. Chem. Res.* 34 (1995) 3956.
- [40] M. Hoshi, M. Ieshige, T. Saitoh, T. Nakagawa, *J. Appl. Polym. Sci.* 76 (2000) 654.
- [41] C. Dotremont, S. Goethaert, C. Vandecasteele, *Desalination* 91 (1993) 177.
- [42] K. Jian, P.N. Pintauro, *J. Membr. Sci.* 135 (1997) 41.
- [43] J. Néel, in: R.Y.M. Huang (Ed.), *Pervaporation Membrane Separation Processes*, Elsevier, Amsterdam, The Netherlands, 1991, p. 1.
- [44] P. Wu, R.W. Field, B.J. Brisdon, R. England, S.J. Barkley, *Sep. Purif. Technol.* 22–23 (2001) 339.
- [45] J.G. Wijmans, R.W. Baker, *J. Membr. Sci.* 79 (1993) 101.
- [46] T.Q. Nguyen, K. Nobe, *J. Membr. Sci.* 30 (1987) 11.
- [47] W.W.Y. Lau, J.J. Finlayson, J.M. Dickson, J. Jiang, M.A. Brook, *J. Membr. Sci.* 134 (1997) 209.
- [48] I. Abou-Nemeh, A. Das, A. Saraf, K.K. Sirkar, *J. Membr. Sci.* 158 (1999) 187.
- [49] J.-S. Jiang, L.M. Vane, S.K. Sikdar, *J. Membr. Sci.* 136 (1997) 233.
- [50] J.-S. Jiang, L.M. Vane, S.K. Sikdar, Private communication.
- [51] L. Hitchens, L.M. Vane, F.R. Alvarez, *Sep. Purif. Technol.* 24 (2001) 67.
- [52] A.M. Urriaga, E.D. Gorri, J.K. Beasley, I. Ortiz, *J. Membr. Sci.* 156 (1999) 275.
- [53] R. Psaume, Ph. Aptel, Y. Aurelle, Y.C. Mora, J.L. Bersillon, *J. Membr. Sci.* 36 (1988) 373.
- [54] C. Dotremont, S. Van den Ende, H. Vandommele, C. Vandecasteele, *Desalination* 95 (1994) 91.
- [55] A.S. Michael, *J. Membr. Sci.* 101 (1995) 117.
- [56] B. Raghunath, S.-T. Hwang, *J. Membr. Sci.* 75 (1992) 29.
- [57] X. Feng, R.Y.M. Huang, *Sep. Sci. Technol.* 27 (1992) 2109.
- [58] R.W. Baker, J.G. Wijmans, A.L. Athayde, R. Daniels, J.H. Ly, M. Le, *J. Membr. Sci.* 137 (1997) 159.
- [59] I. Blume, J.G. Wijmans, R.W. Baker, *J. Membr. Sci.* 49 (1990) 253.
- [60] L.M. Vane, L. Hitchens, F.R. Alvarez, E.L. Giroux, *J. Hazard. Mater.* 81 (2001) 141.
- [61] R.W. Baker, *MRS Bull. (March)* (1999) 50.
- [62] J.A. Brydson, *Plastics Materials*, Butterworth, Oxford, 1995.
- [63] J.P. Brun, C. Larchet, G. Bulvestre, B. Auclair, *J. Membr. Sci.* 25 (1985) 55.
- [64] O.T. Love, R.G. Eliers, *J. AWWA* (1982) 413.
- [65] http://www.epa.gov/opptintr/chemfact/s_perchl.txt.
- [66] B. Raghunath, S.-T. Hwang, *J. Membr. Sci.* 75 (1992) 29.
- [67] J. Mencarini Jr., R. Coppola, C.S. Slater, *Sep. Sci. Technol.* 29 (1994) 465.
- [68] A. Das, I. Abou-Nemeh, S. Chandra, K.K. Sirkar, *J. Membr. Sci.* 148 (1998) 257.
- [69] C.C. Pereira, A.C. Habert, R. Nobrega, C.P. Borges, *J. Membr. Sci.* 138 (1998) 227.