This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Membrane Air Stripping: A Process for Removal of Organics from Aqueous Solutions

Hassan Mahmud; Ashwani Kumar; Roberto M. Narbaitz; Takeshi Matsuura

To cite this Article Mahmud, Hassan , Kumar, Ashwani , Narbaitz, Roberto M. and Matsuura, Takeshi(1998) 'Membrane Air Stripping: A Process for Removal of Organics from Aqueous Solutions', Separation Science and Technology, 33: 14, 2241 — 2255

To link to this Article: DOI: 10.1080/01496399808545725

URL: http://dx.doi.org/10.1080/01496399808545725

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, 33(14), pp. 2241–2255, 1998

REVIEW

Membrane Air Stripping: A Process for Removal of Organics from Aqueous Solutions

---

HASSAN MAHMUD and ASHWANI KUMAR*
INSTITUTE OF CHEMICAL PROCESS AND ENVIRONMENTAL TECHNOLOGY
NATIONAL RESEARCH COUNCIL CANADA
MONTREAL ROAD, OTTAWA, ONTARIO K1A 0R6, CANADA

ROBERTO M. NARBAITZ
DEPARTMENT OF CIVIL ENGINEERING
UNIVERSITY OF OTTAWA
OTTAWA, ONTARIO K1N 6N5, CANADA

TAKESHI MATSUURA
INDUSTRIAL MEMBRANE RESEARCH INSTITUTE
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF OTTAWA
OTTAWA, ONTARIO K1N 6N5, CANADA

ABSTRACT

The membrane air-stripping (MAS) process using microporous polypropylene hollow fiber membranes has shown potential for the removal of volatile organics from aqueous streams over conventional treatment processes, particularly in reducing the size of the equipment. This paper reviews the theoretical aspects and experimental investigations on the performance of these membranes in terms of overall mass transfer capabilities in the removal of organics from aqueous solutions. The reported findings of the effect of pH, ozone, chlorine, influence of packing density and possible fouling on the performance of these hollow fibers membranes are presented. The fate of the stripped air is discussed. Other possible applications as well as the future research needs are highlighted, along with a critical assessment of the reported work.

---

* To whom correspondence should be addressed.

www.dekker.com

Key Words. Organic contaminants; Membrane air stripping; Hollow fiber

INTRODUCTION

An estimated 1.6 to 5.0 million tons of volatile organic chemicals (VOCs) enter the environment each year (1), which causes a significant pollution burden. The main types of water contaminated with VOCs are groundwater and industrial wastewater. Contamination of water supplies by VOCs is an established problem (2, 3). It could be attributed to one or more of the following sources: improper disposal of common industrial solvents, leaking storage tanks, municipal or industrial landfill leachates, and others. Although contaminated groundwater normally contain parts per billion (ppb) levels of VOCs, even these levels render them unfit for human consumption. Cleanup of these contaminated groundwater aquifers is difficult, expensive, and very slow. Additionally, contamination of drinking water by halogenated hydrocarbons produced as by-products of chlorination is a concern. Since many common organic solvents are VOCs, industrial wastewater laden with these solvents is also of concern. Use of naphtha in the oil sand recovery process is another source of contamination of water/air by organics. Furthermore, it is a wasted resource that could be recovered for reuse.

Conventional treatment methods for removal of VOCs include air stripping, adsorption, advanced oxidation, anecrobic/aerobic biological treatment, and distillation. All these techniques have some disadvantages (4). Adsorption is effective and economic only at low VOC concentrations due to the high cost of the adsorbent and of its regeneration or disposal. On the other hand, distillation is economic at higher VOC concentrations. The effectiveness of advanced oxidation is compound-dependent, and it can also form new products which are more harmful than the original ones. Some of these techniques also result in the release of gaseous VOC emissions, thereby only transferring the contaminants to another phase (5). Among conventional techniques, packed-tower aeration (PTA) is the most economical and hence the most widely used process for removal of VOCs from water. It is considered the best available technology (BAT) for removal of VOCs from drinking water by the US Environmental Protection Agency (6). However, the contaminants are simply transferred from the water to the air phase during the stripping process, and the exhaust air may requires further treatment before release to the atmosphere. Gas-phase granular activated carbon (GAC) adsorption is currently employed in conjunction with air stripping to control the gas-phase emissions from PTA. Gas-phase GAC adsorption of off-gases has several limitations. The contaminants are once again only transferred from the gas to the solid phase. The presence of moisture in exhaust stripper air competes with VOCs for adsorption sites on the GAC, thereby reducing their effective adsorption capacity for VOCs and increasing GAC usage. The regeneration or disposal of the contaminated carbon is costly and adds significantly to the overall cost of VOC removal from contaminated water (7, 8). Although air stripping with off-gas treatment is much more expensive than air stripping alone, its costs are comparable to those of liquid-phase GAC adsorption (9). As the contaminated sites are often located in urban centers, tall PTA towers are sometimes considered aesthetically undesirable and more compact alternative technologies are selected. In addition to the above limitations, in some cases PTA suffers from severe fouling problems due to iron and manganese precipitation on the packing (10). Some groundwaters are known to foul packed towers in a matter of months.

Aerobic biological processes are also gaining importance for removal of organics from contaminated water. However, a part of the VOCs is air stripped during the biodegradation process (11).

In summary, existing conventional processes for VOCs removal, even with modifications, still suffer from: 1) transfer of contaminants from one phase to another, creating yet another removal/disposal problem; 2) generation of undesirable by-products/intermediates which only compound the problem; and 3) specific contaminant concentration levels for some of the processes. These limitations of existing or modified conventional processes have led to a search for alternative VOC removal methods capable of avoiding these problems.

Separation of VOCs from liquid streams by membrane air stripping is considered to be an alternative that may help overcome some of the shortfalls of PTA. Membrane air stripping (MAS) may be used over a wide range of VOC concentration levels. MAS could be usefully applied for water pollution reduction, groundwater cleanup, and for organic recovery and reuse from industrial and petroleum wastewater streams.

Several studies during recent years have indicated that air stripping with microporous polypropylene hollow-fiber membranes is a promising technique for the removal of organic compounds from water which may offer significant advantages over PTA in size of installation. The purpose of this paper is to review these studies and suggest directions for future research.

MEMBRANE AIR-STRIPPING PROCESS

The MAS process is characterized by the imposition of a barrier (membrane), generally made of polymeric materials, between contaminated water and a sweeping air phase. The characteristics of the membrane selected for a particular application are dependent on the organic compounds to be separated. Two membrane configurations have been tested so far for membrane air-stripping: a) microporous plate and frame membranes and b) microporous hollow-fiber membranes. Both configurations have some advantages and disadvantages. However, membrane efficacy requires large contact surface areas (12, 13). Given the higher surface-to-volume ratio of the hollow-fiber membrane configuration and its compactness, it appears to be the better choice. With this configuration, a typical MAS system consists of one or more hollow-fiber membrane module(s) used in conjunction with contaminated water and stripping air pumping systems. The contaminated water is pumped through the lumen of the hollow fibers while dried stripping air is passed counter or cocurrently through the exterior (shell side) of the fibers. Mass transfer of the contaminants to be removed occurs across the membrane barrier from the lumen side to the shell side..

In packed-tower air-stripping, mass transfer of VOCs from the liquid phase to the air phase takes place through intimate direct contact between the two phases, while mass transfer in hollow fibers occurs at the interface of the air-filled membrane pores and the liquid-filled fiber lumen. The concentration gradient between the two phases acts as the driving force for this transfer. The concentration gradient is maintained by constantly sweeping away the VOCs crossing the barrier into the stripping air, thereby maintaining an essentially near zero VOC concentration on the shell side.

Some advantages of membrane air-stripping over conventional packed tower air-stripping are (14): a) high surface-to-volume ratio (more compact installations), b) no loading and flooding limitations, and c) reduction of dispersed phase backmixing. In addition to the above operational advantages, the modular nature of membrane air-stripping drastically reduces scale-up problems (15). The main disadvantage is that the overall mass transfer coefficient (K_L) for membrane-based stripping is usually lower than that for conventional processes due to the mass transfer resistance created by the membrane (16). However, in view of the higher effective surface-to-volume ratio (a) of the hollow fiber configuration, the value of K_La is much higher than that reported for conventional processes. Thus, the overall volume specific rate of stripping (mass of contaminants removed per unit time per unit volume of process equipment) for a hollow-fiber membrane unit is likely to be several times larger than that for conventional packed tower systems.

PERMEATE TRANSPORT

In microporous membrane air stripping using hydrophobic polypropylene hollow fibers, the water will not wet the membrane pores, which are filled with air. Due to the high contact angle between the aqueous (nonwetting) phase and the membrane as a result of the difference of the surface tensions, a certain minimum pressure (breakthrough pressure) is required to force the aqueous phase through the membrane pores. The breakthrough pressure for a membrane depends on the pore size of the membrane, the surface tension of the nonwetting phase, and its contact angle on the membrane (17).

The mass transfer of VOCs will occur from the liquid phase to the air phase across the membrane. The equations describing the relationship and the dependency of this mass transfer and other parameters have been well explained by several researchers (18–20). The relationships are shown below with minor adjustments to make them clearer.

First, a VOC diffuses from the bulk aqueous solution across the liquid boundary layer to the membrane surface. Second, it diffuses through the air-filled pores. This diffusion step does not exist in packed-tower air stripping. Third, it diffuses through the air boundary layer outside the membrane into the stripping air. Thus the overall mass transfer coefficient includes the effects of three separate mass transfers created in these three steps. The overall mass transfer resistance thus stands as follows:

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{k_m H} + \frac{1}{k_a H} \tag{1}$$

where K_L = overall mass transfer coefficient (m/s)
k_L = liquid-phase mass transfer coefficient (m/s)
k_m = membrane mass transfer coefficient (m/s)
k_a = air-phase mass transfer coefficient (m/s)
H = nondimensional Henry's law constant

The driving force for mass transfer across the interface is proportional to the concentration difference between the phases. At equilibrium conditions the concentration of the gas phase, X, is related to the concentration in the liquid phase, C^*, by the nondimensional Henry's law constant H, in which

$$H = X/C^* \tag{2}$$

where C^* = equilibrium concentration in the liquid phase (ppm)
X = concentration of the component in the air phase (ppm)
H = nondimensional Henry's law, i.e., the ratio of the mass concentrations

Mass transfer across a single hollow fiber is given by

$$\frac{dC}{dt} = -\frac{v dC}{dz} - K_L a(C - C^*) \tag{3}$$

where v = water velocity inside the hollow fiber (m/s)

K_L = overall mass transfer coefficient (m/s)
a = surface-to-water volume ratio (m^2/m^3)
z = distance from hollow fiber inlet (m)
C = concentration of the component in the liquid phase (ppm)
t = time (s)

Under steady-state conditions the above relation becomes

$$-v dC/dz = K_L a(C - C^*) \tag{4}$$

with the boundary conditions are $C = C_{in}$ in the aqueous influent ($z = 0$) and $C = C_{out}$ in the aqueous effluent ($z = L$), where L is the length of the hollow fiber.

An overall mass balance (over a module length) yields the following relationship:

$$Q_w C_{in} + Q_g X_{in} = Q_w C_{out} + Q_g X_{out} \tag{5}$$

where Q_w = water flow rate (m^3/s)
Q_g = air flow rate (m^3/s)
X_{in} = organics concentration in incoming air (ppm)
X_{out} = organics concentration in outgoing air (ppm)

Assuming that X_{in} is zero, and integrating over the length of the stripper for the boundary conditions, the following equation can be derived:

$$\int_{C_{in}}^{C_{out}} \frac{dC}{(1 - R)C + RC_{out}} = \frac{-K_L a}{v} \int_0^L dz \tag{6}$$

where a = effective surface-to-water volume ratio within the module (m^2/m^3).

The nomenclature used by the authors of Refs. 18 and 19 stripping factor as $R = Q_w/Q_g H$ is the reverse of that conventionally used in PTA calculations (i.e., $R = Q_g H/Q_w$). It seems that these authors (18, 19) have used R as a lumped parameter, apparently without using it as a critical design parameter as in PTA design. This is likely due to the single pass nature of PTA compared to the multiple pass nature of hollow-fiber membrane stripping in a batch system. In a PTA system, if R is less than 1, the level of removal will be limited to a certain value, proportional to the value of R (21). In batch hollow-fiber systems, due to the multiple passes, the level of removal is not limited by the values of R less than 1.

Solving this equation for the ratio of influent and effluent concentrations for a single pass through the module, the expression becomes

$$\frac{C_{\text{in}}}{C_{\text{out}}} = \frac{\{\exp[(K_{\text{L}}a/v)(1 - R)] - R\}}{(1 - R)} = M \tag{7}$$

where M is the ratio of influent and effluent concentrations for a single pass through the module. The above relationship shows that organic removal should be enhanced by increasing the mass transfer coefficient, the length of the module, or the ratio of surface area to volume within the module itself. Lowering the velocity should also improve the removal efficiency. The surface-to-volume ratio, a, for a hollow-fiber module is constant and depends on the inner diameter, d, of the fiber as follows:

$$a = \frac{4\pi ndL}{\pi nd^2L} = \frac{4}{d} \tag{8}$$

where n = number of fibers
d = inner diameter of the hollow fiber (m)

For a batch system consisting of a pump that pumps VOC-laden water from a completely mixed reservoir through a hollow-fiber module and back into the reservoir, the appropriate mass balance is

$$\frac{V_{\text{w}}dC_{\text{t}}}{dt} = Q_{\text{w}}(C_{\text{out}} - C_{\text{in}}) = Q_{\text{w}}\left(\frac{1}{M} - 1\right)C_{\text{in}} \tag{9}$$

where V_{w} = volume of the water in the system (m^3)
dC_{t} = change of concentration in the reservoir for the period t (ppm)
C_{t} = concentration in the reservoir after the period t (ppm)

This relationship holds provided: 1) the reservoir concentration and the module inlet concentration are equal, and 2) the time scale required to reach steady state is much smaller than that of concentration change in the reservoir.

The change in volume of the solution in the system with time was not considered during the development of this relationship. This can have a significant effect in cases where the volume of the samples withdrawn is substantial compared to the volume of the reservoir. This can also create headspace in the reservoir, which will contribute to significant losses of VOCs and thus lead to an overestimation of the mass transfer coefficient. Although the exact size of the sample withdrawn was not reported (18), frequent withdrawal of sample for analysis might introduce a significant error in the case of a reservoir of only 500 mL.

Rearranging and integrating the above equation with the boundary conditions of $C_{\text{in}} = C_0$ at time 0 to $C_{\text{in}} = C_{\text{t}}$ at time t, Semmens et al. (18) derived the following key equation:

$$\ln\left(\frac{C_0}{C_t}\right) = \left(\frac{Q_w}{V_w}\right)\left(1 - \frac{1}{M}\right)t = kt \tag{10}$$

Thus, if the concentration of the organics in the water reservoir is monitored over time, a plot of $\ln(C_0/C_t)$ versus time should yield a linear relationship with a slope of k. Substituting the value of M from Eq. (7) in Eq. (10) and solving for K_L, and substituting value of a from Eq. (8), results in the following equation containing all known values:

$$K_L = \left(\frac{vd}{4L}\right)(1 - R)^{-1} \ln\left\{\left[\frac{Q_w}{(Q_w - V_w k)}\right](1 - R) + R\right\} \tag{11}$$

Equation (11) is valid for liquid flow in the lumen side. It has been stated that for these types of systems, the same equation can be used for liquid flow both in the shell side and lumen side by interchanging the surface to volume ratio, a, and its equivalent internal fiber diameter term, $4/d$, respectively (16). Thus the above equation can be rewritten for liquid flow in the shell side as follows:

$$K_L = \left(\frac{v}{aL}\right)(1 - R)^{-1} \ln\left\{\left[\frac{Q_w}{(Q_w - V_w k)}\right](1 - R) + R\right\} \tag{12}$$

where v = water velocity outside the hollow fiber.

MEMBRANE MATERIALS FOR MAS

There is very little information in the literature regarding possible membrane-making materials that can be used for the preparation of membranes for air stripping. Only very limited types of polymeric membranes have been tested. It has been stated by Matson (22) that 1) polymeric membranes of silicone rubber and its various copolymers, e.g., the block polymer formed from polydimethylsiloxane and polycarbonate; and 2) hydrophobic, microporous membranes prepared from nonwetting polymers such as polytetrafluoroethylene (PTFE) and polypropylene (PP) could be suitable for membrane air stripping. Membranes prepared from polytetrafluoroethylene (PTFE) have also been tested by Boswell and Vaccari (23).

Due to their surface hydrophobicity, high chemical resistivity, and low cost (24), polypropylene or silicon-coated polypropylene hollow-fiber membranes have been investigated for the removal of VOCs from water by membrane air stripping (18–20, 25, 26). Zander et al. (20) reported that the value of $K_L a$ measured for hollow-fiber membrane air-stripping systems were at least one order of magnitude greater than those for packed towers. However, a high air pressure drop in the hollow-fiber module was a significant problem, which may increase the energy cost for a full-scale system. It should be noted that the modules tested by Zander et al. (20) were designed primarily for medical purposes, and their design had not been optimized for industrial use.

Effect of pH, Ozone, and Chlorine

The effect of pH, ozone, and free chlorine on microporous polypropylene hollow-fiber membranes has been investigated by Castro and Zander (25) using an aqueous mixture of chloroform, bromoform, bromodichloromethane, and dibromochloromethane as feed. Their results showed that these membranes were compatible with low pH (pH 5 to 7) and low chlorine waters but not with waters with higher pH (>7) or high chlorine (≥15 mg/L) concentration. At high pH these membranes exhibited a marked reduction in performance, lower membrane bubble pressures, and a reduction in pore area. Use of these membranes requires pretreatment of high pH wastewaters. At high chlorine concentration there was no substantial reduction in performance, but a reduction in pore area and damage to the epoxy potting material were reported. These membranes were also not found to be suitable for use in treating waters containing ozone.

Influence of Packing Density

Zander et al. (20) observed that the air pressure drops at the shell side across hollow-fiber membrane modules were much higher than those for packed towers. The packing density of the hollow fiber in the modules was thought to be the cause for this high pressure drop. Based on data obtained from three hollow-fiber modules with different packing densities, Schwarz et al. (27) concluded that packing density may not be the only cause for this pressure drop. Proper design of the bundle to prevent fiber blockage of the exit port and avoiding major headloss across the air ports may help reduce the pressure drop.

The effects of packing density on the removal performance of 1,1,2-trichloroethane, trichloroethylene, and carbon tetrachloride from aqueous mixtures have been studied using modules with three different fiber densities (27). The authors could not come to any conclusion as to the variation in removal rates for the three different packing densities as the differences were within the limit of experimental error. This aspect needs to be investigated in more detail. In all the investigations reported above, contaminated water has been pumped through the lumen side and sweeping air through the shell side of the hollow-fiber module. Further study should include reversal of the setup, i.e., pumping water through the shell side and the air through the lumen side of the hollow-fiber module.

Fouling of Hollow-Fiber Membranes

Four types of fouling are considered important when hollow-fiber membranes are used in water treatment applications (27):

1. Suspended solids accumulation. Suspended solids in the water can quickly plug the membrane modules in the case of a pressure-driven process. In air stripping, as it is a concentration-driven process, no solids accumulate at the membrane wall since no water crosses the membrane. Thus, it is not a problem for this process. However, the ends of the hollow fibers can become plugged by influent solids, and pretreatment may be necessary.
2. Biological fouling and slime development. Growth of bacteria on the surface may or may not be a problem depending on the water characteristics and the type of material being stripped.
3. Calcium carbonate deposition. During CO_2 stripping from groundwater, $CaCO_3$ may deposit on the fiber surface if the pH is high. Most groundwater treatment applications acidify the water to a pH of approximately 4 to minimize fouling problem.
4. Iron oxide fouling. Reduced iron found in groundwater is oxidized and precipitates as $Fe(OH)_3$ as oxygen permeates from the sweeping air to the aqueous side of the membrane. This oxidation is strongly dependent on the pH and the ferric ion concentration in the water.

Iron fouling of hollow-fiber membranes has been investigated by Schwarz et al. (27). These workers conducted two separate studies: a) a long-term field study to evaluate the effect of iron fouling on performance and b) a laboratory study to characterize the kinetics of iron fouling. The first study was conducted for 75 days with a commercially available hollow-fiber membrane module. The module had a 3.4 m^2 effective surface area of microporous polypropylene membrane with pores of 0.03 μm diameter covering 40% of the membrane surface. It was stated that iron fouling was the main problem during this field study from the evidenced release of a high concentration of iron from the membrane during its regeneration with acid after 75 days. This type of fouling increases the membrane resistance to mass transfer. Although Yang and Cussler (28) stated in an earlier study that membrane resistance is a negligible factor and that the overall resistance is governed mainly by liquid film diffusion during removal of VOCs by air stripping, in practice, as the membrane becomes fouled, its resistance does become increasingly significant (27).

The second study was conducted to evaluate the factors influencing the rate of iron fouling of polypropylene hollow fibers under controlled conditions (27). It was reported that the velocity of the feed in the hollow fiber plays a greater role in ferric hydroxide accumulation than the feed ferric ion concentration. It was also reported that not all the ferric hydroxide formed accumulates on the fiber but that a portion is transferred to the aqueous system as a precipitate. Thus, in an industrial MAS application with several modules in series, the second and subsequent modules would be more prone to particulate fouling and fiber plugging by the ferric hydroxide formed upstream. Preacidification of water or intermediate filtration between modules must be planned to avoid this potential problem.

MEMBRANE AIR-STRIPPING APPLICATIONS

Possible membrane air-stripping applications can be the removal/concentration of organics from dilute organic/water mixtures like esters, ethers, chlorinated hydrocarbons, and aromatic compounds. This application is very appropriate for environmental, chemical, petrochemical, and biotechnology industries, as they need removal or recovery of organics from dilute solutions. Removal of VOCs has been investigated by many workers in recent years (18–20, 23, 25). Volatile organic chemicals, such as chloroform, 1,1,2-trichloroethane, trichloroethylene, tetrachloroethylene, carbon tetrachloride, bromoform, and bromodichloromethane, have been effectively removed from aqueous mixtures using polypropylene membranes (18, 20, 23, 25).

A detailed comparison was conducted by Zander et al. (20) on the removal of chloroform, bromoform, bromodichloromethane, trichloroethylene, tetrachloroethylene, and carbon tetrachloride using conventional packed air-stripping towers and polypropylene hollow-fiber membrane air-stripping modules. It was reported that although the active length of the membrane was 1.8 ft (0.546 m) compared to a packed tower length of 12 ft (3.7 m), the removal of VOCs for the membrane system ranged from 5 to 95% compared to 20 to 98% for packed towers. A direct comparison was not possible due to size differences, hence a comparison was made based on mass transfer coefficients. It was reported that the overall liquid-phase mass transfer coefficient for a membrane system was generally more than an order of magnitude greater than those measured for a packed tower air-stripping system.

TREATMENT OF AIR-STRIPPING OFF-GAS

The organic contaminants in the stripped air can be vented to the atmosphere, collected by condensation, or subjected to further treatment prior to release. Bhowmick (29) and Bhowmick and Semmens (19) conducted studies to evaluate the possibility of treating VOCs-contaminated stripped air from a hollow-fiber membrane air-stripping process by UV photooxidation in an attempt to develop the closed loop air-stripping process (CLASP). In this process, stripped air from a hollow-fiber membrane air-stripping system treating a synthetic aqueous mixture of five VOCs (chloroform, 1,1,2-trichloroethane, trichloroethylene, tetrachloroethylene, and carbon tetrachloride) was irradiated with ultraviolet light in a photooxidation chamber. The VOCs were destroyed by photolysis and oxidation processes occurring in the gas phase. In this system the production and fate of intermediates was of great interest. It was reported that phosgene, chloroacetylchloride, and chloroacetaldehyde were formed in low concentrations, but there was no problem of ozone formation in large quantities (19) as reported in an earlier study by Bhowmick (29). It was reported that phosgene, which was produced in the greatest amount, was readily photooxidized by radiation at 185 nm (19). It was also suggested that a part of these intermediates might be diverted back to the stripper before being photooxidized. The fate of the intermediates would then be dictated by their stabilities. Phosgene hydrolyzes instantaneously to HCl and CO_2 (30). The effect of this restripping should be investigated in detail. This process appears to offer a number of potential advantages over conventional air stripping with off-gas treatment: no gaseous VOCs emissions, the VOCs are oxidized to harmless end products, no adsorber is required, and no adsorbent regeneration or disposal costs are incurred.

This process can be used for PTA also, but as the PTA process uses a much higher air-to-water ratio during the stripping process than does membrane air stripping (20), a much larger CLASP will be required. An effective oxidation process needs a low air flow rate while effective air stripping requires a high air flow rate (19). Given this inherent conflict in operating parameters, the closed loop configuration for a packed tower air stripping/photooxidation process may not be technically and commercially feasible. The second alternative is to recover the organics through condensation. The recovered organics can be reused and the gas-phase emission problems will be avoided.

COMPARATIVE ECONOMICS

A cost comparison between the packed tower and hollow-fiber membrane air stripping was conducted by Schwarz et al. (27) for 99.9% removal of 1500 μg/L trichloroethylene (TCE) from an aqueous mixture. The authors collected the capital cost information for the packed tower and hollow-fiber membrane systems from Peters and Timmerhaus (31) and Rutledge (32), respectively. For this comparison the design of the hollow-fiber membrane system was chosen to minimize membrane and pumping costs. Modules of 0.305 m diameter were used. The packed tower design was based on the mass transfer correlations developed by Onda et al. (33). It was reported that the packed tower method of air stripping remained the least expensive option at the time of the study with a cost of $0.98 per thousand gallons treated compared to $1.37 for the hollow-fiber membrane method. The stripped-air treatment cost was not included in these costs. It was also stated that at the time of their study a fair cost comparison between the long established, well-optimized PTA system and the not optimized, infant hollow-fiber air-stripping technology was difficult. But in other studies the cost of packed tower air stripping were reported much lower than those reported by Schwarz et al. (27). Hand et al. (10) reported \$0.05/1000 gal water treated for 95% removal of VOCs. Dvorak et al. (9) showed that the cost of packed tower air stripping alone for 99.75% TCE removal (with $C_{\text{feed}} = 2000$ μg/L TCE) was \$0.0837/1000 gal whereas with air stripping, including activated carbon off-gas treatment, was \$0.212/1000 gal. Lipski and Côté (34) reported that the treatment cost for trichloroethylene (TCE) ranges from \$0.10/m^3 for air stripping alone to \$0.80/m^3 for treatment trains including stripping with activated carbon off-gas treatment or activated carbon aqueous-phase treatment. These studies showed that PTA is still the cheapest VOC treatment process. However, with the development of optimized, lower air pressure drop hollow-fiber modules, the cost of membrane air stripping can be expected to decrease significantly.

CONCLUSIONS AND RECOMMENDATIONS

The membrane air-stripping process with hydrophobic membranes has shown potential in the removal of volatile organic compounds from aqueous–organic mixtures. So far mostly microporous polypropylene hollow-fiber membrane modules have been investigated for the efficient removal of such VOCs as chloroform, 1,1,2-trichloroethane, trichloroethylene, tetrachloroethylene, carbon tetrachloride, bromoform, and bromodichloromethane. The investigations to date have focused only on contaminated groundwater, and most of them at low VOC concentrations. Further investigation is required with other organics, such as those present in petroleum/oil sands treatment wastewater streams. The possible use of these membranes for treatment of wastewater containing higher VOC concentration levels also needs investigation. The effects of pH, free chlorine, and ozone have been studied, but the effects of feed temperature, air flow, feed flow, and others factors need further investigation. One of the main constraints in the present process is the high air pressure drop on the shell side. There is a need to explore the use of air on the lumen side. Finally, newer membranes need to be developed for improved performance and resistance to fouling.

REFERENCES

1. T. T. Shen and G. H. Sewell, "Control of VOC Emissions from Waste Management Facilities," *J. Environ. Eng.*, *114*, 1392 (1988).
2. R. M. Clark, R. G. Eilers, and J. A. Goodrich, "VOCs in Drinking Water: Cost of Removal," *Ibid.*, *110*(6), 1146–1162 (1984).

3. J. E. Dyksen and A. F. Hess, "Alternatives for Controlling Organics in Groundwater Supplies," *J. Am. Water Works Assoc.*, *74*(8), 394–403 (1982).
4. S. Goethaert, C. Dotremont, M. Kuijpers, M. Michiels, and C. Vandecasteele, "Coupling Phenomena in the Removal of Chlorinated Hydrocarbons by Means of Pervaporation," *J. Membr. Sci.*, *78*, 135–145 (1993).
5. J. Brewer, *Literature Reviews and Research Scoping Study on the Treatment of Volatile Organic Carbon Compounds in the Off-gas from Contaminated Groundwater and Soil Remedial Technologies*, National Groundwater and Soil Remediation Program, Environment Canada, Ottawa 1991.
6. USEPA, *Fact Sheet, Drinking Water Regulations Under the Safe Drinking Water Act*, Office of Drinking Water, US Environmental Protection Agency, Washington, DC, 1990.
7. M. Kosuko, M. E. Mullins, K. Ramanathan, and T. N. Rogers, "Catalytic Oxidation of Groundwater Stripping Emissions," *Environ Prog.*, *7*(2), 136–142 (1988).
8. F. R. McGregor, P. J. Piscaer, and E. M. Aieta, "Economics of Treating Waste Gases from an Air Stripping Tower Using Photochemically Generated Ozone," *Ozone*, *10*, 339–352 (1988).
9. B. I. Dvorak, D. F. Lawler, G. E. Speitel Jr., D. L. Jones, and D. A. Boadway, "Selecting among Physical/Chemical Processes for Removing Synthetic Organics from Water," *Water Environ. Res.*, *65*(7), 827–838 (1993).
10. D. W. Hand, J. C. Crittenden, and J. I. Gehin, "Design and Evaluation of an Air-Stripping Tower for Removing VOCs from Groundwater," *J. Am. Water Works Assoc.*, *78*(9), 87–97 (1986).
11. L. M. Freitas dos Santos, "Biological Treatment of VOC-Containing Wastewaters: Novel Extractive Membrane Bioreactors vs. Conventional Aerated Bioreactor," *Trans. Inst. Chem. Eng.*, *73*(B), 227–234 (1995).
12. R. E. Kesting, *Synthetic Polymeric Membranes*, McGraw-Hill, New York, NY, 1971.
13. T. Matsuura, *Synthetic Membranes and Membrane Separation Processes*, CRC Press, Boca Raton, FL, 1993.
14. R. D. Noble and S. A. Stern, *Membrane Separations Technology. Principles and Applications* (Membrane Science and Technology Series, 2), Elsevier Science, New York, NY, 1995.
15. A. K. Guha, P. V. Shanbhag, C. H. Yun, D. Trivedi, D. Vaccari, and K. K. Sirkar, "Novel Membrane-Based Separation and Oxidation Technologies," *Waste Manage.*, *13*, 395–401 (1993).
16. Q. Zhang and E. L. Cussler, "Microporous Hollow Fibers for Gas Absorption," *J. Membr. Sci.*, *23*, 321–345 (1985).
17. N. P. Tirmizi, B. Raghuraman, and J. Wiencek, "Demulsification of Water/Oil/Solid Emulsions by Hollow-Fiber Membrane," *AIChE J.*, *42*(5), 1263–1275 (1996).
18. M. J. Semmens, R. Qin, and A. Zander, "Using a Microporous Hollow-Fiber Membrane to Separate VOCs from Water," *J. Am. Water Works Assoc.*, *81*(4), 162–167 (1989).
19. M. Bhowmick and M. J. Semmens, "Batch Studies on a Closed Loop Air Stripping Process," *Water Res.*, *28*(9), 2011–2019 (1994).
20. A. K. Zander, M. J. Semmens, and R. M. Narbaitz, "Removing VOCs by Membrane Stripping," *J. Am. Water Works Assoc.*, *81*(11), 76–81 (1989).
21. R. E. Treybal, *Mass Transfer Operations*, 3rd ed., McGraw-Hill, New York, NY, 1980.
22. S. L. Matson, "Method and System for Removing Radon from Radon Containing Water," US Patent 5,100,555 (1992).
23. S. T. Boswell and D. A. Vaccari, "Plate and Frame Membrane Air Stripping," in *Proceedings of the 21st Annual Conference on Water Policy and Proceedings of the 21st Annual*

Conference on Water Policy Management Solving Problems 1994, ASCE, New York, NY, 1994, pp. 726–729.
24. *Encylopedia of Polymer Science and Engineering, Vol. 13*, Wiley, New York, NY, 1988, pp. 464–530.
25. K. Castro and A. K. Zander, "Membrane Air-Stripping: Effect of Pretreatment," *J. Am. Water Works Assoc.*, *87*(3), 50–61 (1995).
26. M. Bhowmick and M. J. Semmens, "A Novel Closed Loop Air Stripping Process," in *Hazardous and Industrial Wastes—Proceedings of the Mid-Atlantic Industrial Waste Conference 1993*. Technomic Publishing, Lancaster, PA, 1993, pp. 136–145.
27. S. E. Schwarz, M. J. Semmens, and K. J. Froelich, "Membrane Air Stripping: Operating Problems and Cost Analysis," in *45th Purdue Industrial Waste Conference Proceedings*, Lewis Publishers, Chelea, MI, 1991.
28. M. C. Yang and E. L. Cussler, "Designing Hollow-Fiber Contactors," *AIChE J.*, *32*(11), 1910–1916 (1986).
29. M. Bhowmick, "A Novel Closed Loop Air Stripping Process," Ph.D. Thesis, University of Minnesota, 1992.
30. N. N. Greenwood and A. Earnshaw, *Chemistry of Elements*, Pergamon Press, New York, NY, 1984.
31. M. S. Peters and K. D. Timmerhaus, *Plant Design and Economics for Chemical Engineers*, 3rd ed., McGraw-Hill, New York, NY, 1980.
32. F. Rutledge, Personal communication with Schwarz et al., 1991.
33. K. Onda, H. Takeuchi, and Y. Okumoto, "Mass Transfer Coefficients between Gas and Liquid Phase in Packed Columns," *J. Chem. Eng. Jpn. 1*, 56–62 (1968).
34. C. Lipski and P. Côté, "The Use of Pervaporation for the Removal of Organic Contaminants from Water," *Environ. Prog.*, *9*, 254–261 (1990).

Received by editor May 8, 1997
Revision received March 1998