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

Fouling and Cleaning of Gas-Filled Membranes for Cyanide Removal

Binbing Han[a]; Zhisong Shen[ab]; S. Ranil Wickramasinghe[a]
[a] Department of Chemical Engineering, Colorado State University, Fort Collins, CO, USA [b] Department of Environmental Engineering, Jiangsu Institute of Microbiology, Wuxi, P.R. China

To cite this Article Han, Binbing , Shen, Zhisong and Wickramasinghe, S. Ranil(2005) 'Fouling and Cleaning of Gas-Filled Membranes for Cyanide Removal', Separation Science and Technology, 40: 6, 1169 — 1189
To link to this Article: DOI: 10.1081/SS-200053315
URL: http://dx.doi.org/10.1081/SS-200053315

Separation Science and Technology, 40: 1169–1189, 2005

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1081/SS-200053315

Fouling and Cleaning of Gas-Filled Membranes for Cyanide Removal

Binbing Han
Department of Chemical Engineering, Colorado State University, Fort Collins, CO, USA

Zhisong Shen
Department of Chemical Engineering, Colorado State University, Fort Collins, CO, USA and Department of Environmental Engineering, Jiangsu Institute of Microbiology, Wuxi, P.R. China

S. Ranil Wickramasinghe
Department of Chemical Engineering, Colorado State University, Fort Collins, CO, USA

Abstract: Results of an experiment on the removal of cyanide from two industrial wastewaters by using gas-filled hollow fiber membranes in a pilot plant in China are presented. The plant was operated in batch mode using 1000 L of feed solution. The plant contained 10 hollow fiber modules with a total effective membrane surface area of 180 m^2. The strip stream consisted of a 10% NaOH solution. The overall mass transfer coefficient for cyanide was determined experimentally. A decrease in the overall mass transfer coefficient with time was observed for real wastewaters due to fouling of the membrane. In particular, the presence of particulate matter in the wastewater can lead to a significant decrease in the overall mass transfer coefficient and, hence, the rate of cyanide removal. Various cleaning strategies were investigated in order to regenerate the membrane. The gas-filled membranes were stable for over two months of continuous operation when they were used with industrial wastewaters.

Keywords: Cyanide, gas-filled membrane, wastewater, membrane fouling, membrane cleaning

Received 29 April 2004, Accepted 10 January 2005

Address correspondence to S. Ranil Wickramasinghe, Department of Chemical Engineering, Colorado State University, Fort Collins, CO 80523-1370, USA. Fax: +1 970 491 7369; E-mail: wickram@engr.colostate.edu

INTRODUCTION

Cyanide is widely used in many industries. However due to its high toxicity, cyanide removal from liquid waste streams is essential (1). According to the United States Environmental Protection Agency (U.S. EPA), the final cyanide concentration in wastewaters must be reduced to less than 5.0 mg/L for facilities discharging less than 10,000 gal/day or 1.9 mg/L for facilities discharging more than 10,000 gal/day, respectively (2). Further, recovery and reuse of cyanide from wastewater streams may bring significant economic benefits. Several different cyanide removal processes have been developed (1, 3–23). Among them, alkaline chlorination (1) is the most commonly used process in practice. However this process suffers from several problems: 1) it is less effective for the removal of iron cyanides; 2) cyanide cannot be recovered and reused; and 3) more severely, chloramines and free chlorine remain in solution leading to the production of secondary contaminants.

The use of gas-filled microporous membranes to remove and recover cyanide from wastewaters may overcome these problems (15–23). Figure 1 is a schematic diagram of a gas-filled microporous membrane-based absorption process for cyanide removal. A hydrophobic microporous membrane, e.g., polypropylene (PP) or polytetrafluoroethylene (PTFE), is used to separate two aqueous streams: the feed solution (wastewater) and the strip solution. The membrane pores remain gas filled as long as the pressure difference between these two aqueous phases is less than the critical pressure known as the breakthrough pressure. The wastewater containing cyanide flows on one side of the membrane while the strip solution containing reactive NaOH flows on the other side. The protonated form of cyanide, or prussic acid (HCN), is a weak acid with a pKa of 9.31. Since HCN is volatile, it will vaporize at the wastewater/membrane interface, diffuse across the gas-filled pores, and enter the strip solution. In the reactive strip solution HCN will react with NaOH to form NaCN,

$$HCN + NaOH \longleftrightarrow NaCN + H_2O \quad (1)$$

This reaction is very fast, thus the HCN concentration in the strip solution is essentially zero. Consequently, HCN will continue to transfer from the wastewater to the strip solution providing there is excess NaOH present in the strip solution. From the preceding description, it can be seen that the use of gas-filled microporous membranes offers a number of advantages. The cyanide can be recovered and reused; no secondary pollutants are produced; the energy and chemical requirements are low; and the equipment is simple to operate (15–23).

Cyanide removal using gas-filled membranes was conducted at both the laboratory and pilot plant scales using artificial and real wastewaters (15–23).

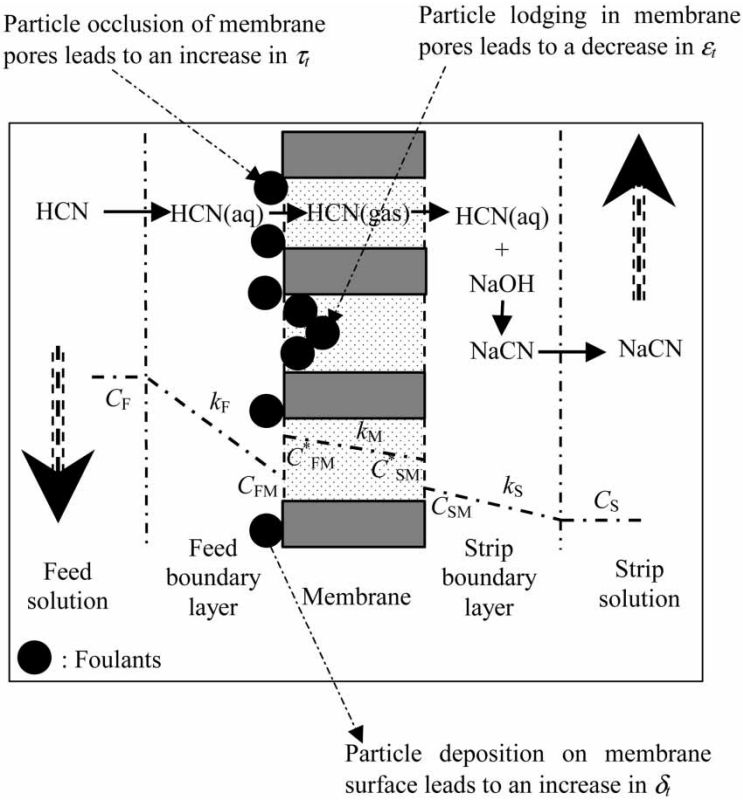

Figure 1. Illustration of HCN removal by a gas-filled membrane absorption.

However these previous studies were limited to short run times, usually of less than 2 hours. Further, no information is available on membrane fouling and appropriate cleaning strategies. Nevertheless, membrane cleaning will be essential in the design of a viable commercial process. Extended operation may result in membrane fouling if particulate matter is present in the feed solution. These particles may deposit on the membrane surface and block the membrane pores. Further, the long-term stability of gas-filled membranes is not well documented; although, Zhang and Cussler report that their gas-filled membranes were stable for several months in laboratory scale studies (24).

In this paper, the long-term performance of gas-filled membranes for cyanide removal was investigated using two real wastewater streams. One of the wastewater streams was obtained from a caffeine manufacturing process while the other was obtained from a benzonitrile (a pesticide) manufacturing process. These two wastewaters are denoted as caffeine and

benzonitrile wastewater, respectively. In the caffeine wastewater, there was only one volatile component, i.e., cyanide. However in the benzonitrile wastewater a high concentration of volatile benzonitrile was also present. Cyanide removal was studied using a 1000 L pilot scale plant operated in a batch mode for up to 2 months. The plant used 10 hollow fiber modules with a total effective membrane surface area of 180 m^2. Experimental results obtained indicate that the gas-filled membrane could be stable for at least 2 months. Further, the degree of membrane fouling depended strongly on the composition of the feed stream. A dilute acid solution was effective in regenerating the fouled membranes.

THEORY

The HCN flux, J, from the feed to strip solution may be described by the following equation,

$$J = K_t([\mathrm{HCN}]_{\mathrm{F},t} - [\mathrm{HCN}]_{\mathrm{S},t}) \approx K_t[\mathrm{HCN}]_{\mathrm{F},t} \tag{2}$$

where K_t is the overall mass transfer coefficient at time t and $[\mathrm{HCN}]_{\mathrm{F},t}$ and $[\mathrm{HCN}]_{\mathrm{S},t}$ are the HCN concentrations in the bulk feed and strip solution at time t, respectively. It is assumed that excess base is present in the strip solution, thus the HCN concentration in the strip solution, $[\mathrm{HCN}]_{\mathrm{S},t}$, is always essentially zero. Equation (2) indicates that the HCN flux may be predicted if the overall mass transfer coefficient and the bulk HCN concentration in the feed solution are known.

A mass balance around the feed reservoir results in the following differential equation,

$$\frac{d([\mathrm{HCN}]_{\mathrm{F},t}V_{\mathrm{F},t})}{dt} = -K_tA([\mathrm{HCN}]_{\mathrm{F},t} - [\mathrm{HCN}]_{\mathrm{S},t}) \approx -K_tA[\mathrm{HCN}]_{\mathrm{F},t} \tag{3}$$

In Eq. (3), the left hand side gives the rate of change of HCN in the bulk feed solution while $V_{\mathrm{F},t}$ is the volume of the feed solution at time t. The right hand side of Eq. (3) gives the rate of transfer of HCN from the feed to the strip solution while K_t is the overall mass transfer coefficient for HCN at time t. Since it is assumed there is excess base, $[\mathrm{HCN}]_{\mathrm{S},t}$ is zero. In deriving Eq. (3) it also is assumed that the recirculation rate is fast relative to the rate of mass transfer (25), consequently the HCN concentration in the hollow fiber modules does not change significantly in one pass.

Previous studies indicated that when the activities of the feed and strip solutions are different, for example if the salinity of the feed solution is high, the water vapor pressure will be different for the two solutions (22, 23). Consequently, water will transfer between the two solutions due to

osmotic distillation. We assume that the change in volume of the feed solution due to osmotic distillation is given by the following expression,

$$V_{F,t} = V_{F,0} + \alpha t \tag{4}$$

where $V_{F,0}$ is the initial feed volume, α is the average rate of volume change, and t is the time. Since α is small, the volume of the feed solution in the hollow fibers does not change significantly in one pass. Substituting Eq. (4) into Eq. (3) and then integrating Eq. (3) from $t = 0$ to t gives,

$$\ln\left(\frac{[HCN]_{F,t}}{[HCN]_{F,0}}\right) = -\int_0^t \left(\frac{K_t A + \alpha}{V_{F,0} + \alpha t}\right) dt \tag{5}$$

The overall mass transfer coefficient, K_t, will decrease with time due to membrane fouling. However for short run times (for example two hours or less) we may assume the mass transfer coefficient is approximately constant and may be represented by an average mass transfer coefficient, $\overline{K}_t$. Equation (5) may be integrated to obtain Eq. (6) where K_t has been replaced by $\overline{K}_t$,

$$\ln\left(\frac{[HCN]_{F,t}}{[HCN]_{F,0}}\right) = -\left(\frac{\overline{K}_t A + \alpha}{\alpha}\right) \ln\left(\left[1 + \frac{\alpha t}{V_{F,0}}\right]\right) \tag{6}$$

For $|\alpha t / V_{F,0}| < 1$,

$$\ln\left(\left[1 + \frac{\alpha t}{V_{F,0}}\right]\right) = \frac{\alpha t}{V_{F,0}} - \left(\frac{\alpha t}{V_{F,0}}\right)^2 + \cdots \tag{7}$$

Further, for small $\alpha t / V_{F,0}$ the series expansion in Eq. (7) may be truncated after the first term and substituted into Eq. (6) resulting in,

$$\ln\left(\frac{[HCN]_{F,t}}{[HCN]_{F,0}}\right) = -\left(\frac{\overline{K}_t A + \alpha}{V_{F,0}}\right) t \tag{8}$$

Thus plotting $\ln([HCN]_{F,0}/[HCN]_{F,t})$ vs. t should yield a straight line with a slope of $(\overline{K}_t A + \alpha)/V_{F,0}$. For a given total membrane surface area, A, and an initial feed volume, $V_{F,0}$, $\overline{K}_t$ can be calculated if α is known. Equation (8) is not applicable for a long-term operation (more than a few hours) as K_t may vary significantly with time. For long-term operation, we may split the whole operation period into a series of successive short-runs, and apply Eq. (8) for each short time period. In the absence of volume change, $\alpha = 0$ and Eq. (8) are identical to the equation used in previous cyanide removal studies (15–22). In this case, plotting $\ln([HCN]_{F,0}/[HCN]_{F,t})$ vs. $At/V_{F,0}$ should yield a straight line with a slope of $\overline{K}_t$.

In aqueous solution HCN can dissociate as follows,

$$HCN \longleftrightarrow H^+ + CN^- \qquad pKa = 9.31 \tag{9}$$

If the pH of the aqueous feed solution is much less than 9.31, HCN will be the dominant component. However if the pH of the feed is more than 8.5, less than 85% of the cyanide will be present as HCN. Since HCN is the species that volatizes and diffuses through the membrane pores, if the pH of the feed is higher than 8.5, the actual undissociated HCN concentration in the feed solution should be used. As analytical methods determine the total cyanide present (22, 23), it is necessary to express the undissociated HCN concentration in terms of the total cyanide, $[CN]_T$, which is denoted as,

$$[CN]_T = [HCN] + [CN^-] \tag{10}$$

Further,

$$\frac{[H^+][CN^-]}{[HCN]} = 10^{-9.31} \tag{11}$$

Combining Eqs. (10) and (11) leads to,

$$[HCN] = [CN]_T \frac{10^{-pH}}{10^{-pH} + 10^{-9.31}} \tag{12}$$

Equation (12) should be substituted into Eq. (8) if the pH of the feed is above 8.5.

The overall mass transfer coefficient may be calculated from individual mass transfer coefficients as,

$$\frac{1}{K} = \frac{1}{k_F} + \frac{1}{k_M} + \frac{1}{k_S} \tag{13}$$

where k_F, k_M, and k_S are the three individual mass transfer coefficients that describe the transfer of HCN across the feed side concentration boundary layer, through the membrane, and across the strip side concentration boundary layer, respectively (18). In the studies conducted here the feed stream always flowed inside the hollow fibers.

Previous investigators have shown that the lumen side mass transfer coefficient may be estimated by the following equation (16, 18, 24),

$$\frac{k_F d}{D_F} = 1.64\left(\frac{d^2 \nu_F}{l D_F}\right) \tag{14}$$

where d and l are the inside diameter and the length of the hollow fibers respectively; D_F is the diffusion coefficient of the volatile species in the

feed, and ν_F is the velocity of the liquid phase through the hollow fiber lumen. We do not expect membrane fouling to significantly affect the diffusivity of HCN in the feed stream. Further, though deposition of particulate matter on the membrane surface could lead to a narrowing of the inside diameter of the hollow fibers, changes in d and ν_F are expected to be minor. Therefore the lumen side mass transfer coefficient is assumed to be independent of time.

Equation (14) was originally developed by Lévêque (26) for heat transfer in tubes. Though numerous assumptions are involved in the derivation of Eq. (14), see Castino and Wickramasinghe (27), the mass transfer analog has been used by Kenfield (18), Shen et al. (20–22), and Yang and Cussler (28) to predict the mass transfer coefficient inside the fibers.

The membrane mass transfer coefficient may be predicted by the equation,

$$k_M = \frac{\varepsilon D_M H}{\delta \tau} \tag{15}$$

where ε and δ are the void fraction and membrane thickness of the hollow fiber membrane; τ is the tortuosity of the membrane pores; D_M is the diffusion coefficient of the HCN in the gas phase within the membrane pores; and H is the partition coefficient of HCN, which relates the concentration of HCN in the gas phase to that in the liquid phase (18). In Eq. (15) each of the independent variables could be a function of time. However we expect ε, δ, and τ to vary the most with time. Deposition of particulate matter in the membrane pores could lead to complete pore blockage and, therefore, a change in the effective porosity of the membrane. Deposition of particulate matter on the membrane surface could lead to the formation of a "dynamic membrane," which will lead to an increase in the effective membrane thickness. In addition, deposition of particulate matter in the membrane pores could lead to partial occlusion of the pores and, hence, a change in the tortuosity factor (see Fig. 1). The tortuosity factor accounts for the pore geometry. Tortuosity factors ranging from 2–12 have been reported (29, 30).

The strip side mass transfer coefficient for a reactive strip solution is more difficult to predict. Cussler (30) showed that the form of the mass transfer correlation depends on whether the reaction, for example the reaction between HCN and NaOH, is fast or instantaneous. Astarita et al. (31) showed that the presence of a chemical reaction may significantly accelerate the rate of mass transfer. For cyanide removal Kenfield et al. (18) and Shen et al. (17) showed that in the presence of excess NaOH, the strip side mass transfer coefficient is much larger than is the feed side mass transfer coefficient. Thus, for cyanide removal, k_S may be ignored and the overall mass transfer coefficient simplified to,

$$\frac{1}{K} = \frac{1}{k_F} + \frac{1}{k_M} \tag{16}$$

We shall use these equations to analyze the experimental results.

EXPERIMENTAL

Two different cyanide-containing wastewaters, one containing caffeine and the other benzonitrile, were investigated. Table 1 gives further details of these wastewater streams. The strip solution consisted of a 10% NaOH solution. Hydrophobic microporous polypropylene hollow fibers, OD 450 μm, average wall thickness 60 μm, pore size 0.05–0.2 μm, and average porosity 35%, were used in this study. Table 2 gives further details of these hollow fibers. The hollow fibers were packed into module housings of two different dimensions as described in Table 3.

The pilot scale experimental set up is shown in Fig. 2. The cyanide-containing wastewater is pumped from a reserve tank into the wastewater feed tank through a polypropylene fine filter (pore size less than 5 μm). The strip solution is also pumped from a reserve tank through a polypropylene fine filter and then into the strip tank. From the feed tank, the wastewater is pumped through the lumen side of the hollow fiber modules at 15 $m^3 hr^{-1}$ while the strip solution is introduced into the shell side of the modules at the same flow rate. This arrangement can maximize the rate of mass transfer by avoiding bypassing and channeling on the feed side (25). The feed and strip solutions are recycled. The volume of the feed and strip solutions was 1000 and 500 L respectively. The temperature was 18 $\pm$ 2°C. The hollow fiber membrane unit contained 20 modules divided into two groups of 10 housed in a stainless steel frame 2000 × 900 × 1500 mm^3 as shown in Fig. 3. At any given time one group of 10 modules was in operation while the other group was being cleaned or in standby mode. Tables 2 and 3 give further details of the fibers and modules.

During operation 30–50 mL samples of the wastewater and strip solution were removed and the cyanide concentration was determined. The cyanide concentration was measured using silver nitrate titration for concentrations above 10 mg/L and colorimetric analysis for concentrations below 10 mg/L (32). In addition, the pH in both solutions was also measured.

The pilot plant was run until the cyanide concentration in the feed solution fell below the required value for direct discharge (<0.5 mg/L).

Table 1. Details of the wastewaters tested

Wastewater	$[CN^-]$ (mg/L)	Color	Turbidity (NTU)	pH	Salinity (%)	Other major volatile components
Caffeine	500–2000	Colorless	<1	2–3	<1	None
Benzonitrile	3000–4000	Light yellow	20∼40	9.5–10	25–30	C_6H_5CN, NH_3, C_6H_6

Table 2. Details of the hollow fibers. All the membrane properties were provided by the manufacturer

Outside diameter	Wall thickness	Pore size	Porosity	Gas penetrability	Breakthrough pressure	Manufacturer
450 μm	50–70 μm	0.05–0.2 μm	30%–40%	7.2 $cm^3/cm^2 \cdot s \cdot cmHg$	0.25 MPa	Hangzhou Hualu Membrane Engineering Co., Ltd., Zhe Jiang Province, P.R. China

Table 3. Details of hollow fiber modules

	Hollow fiber		Module			
No.	Length (cm)	Number	ID (cm)	Length (cm)	Housing material	Comments
A	82.5	16,000	8	112	ABS	Used in pilot scale experiments. 10 modules are used in this study in parallel
B	18	200	1.2	32	Glass	Used in laboratory scale experiments

Then the feed and strip solutions were replaced with fresh solutions and the next run started.

Membrane cleaning was investigated at both the laboratory and pilot scales. For the laboratory experiments, small laboratory scale modules were used. Table 3 gives details of these membrane modules (module B). Real wastewaters contain a number of other dissolved species. Further, the wastewaters tested here contained suspended particles. The effect of suspended particulate matter on membrane fouling was investigated by preparing an

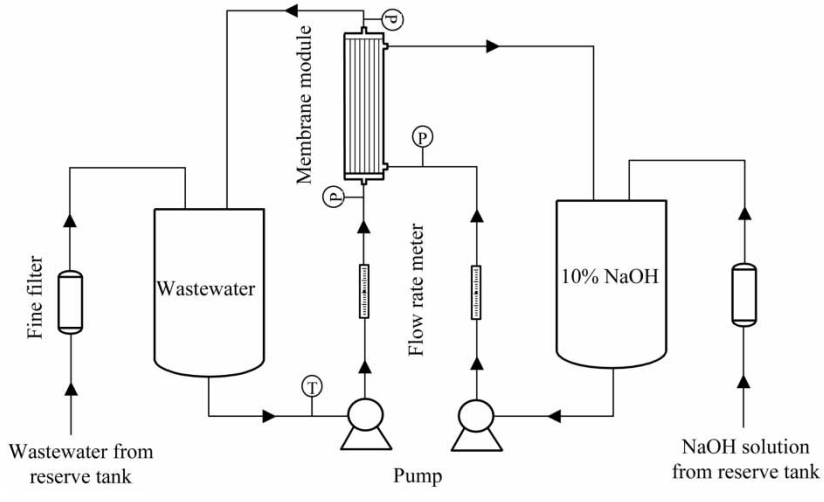

Figure 2. Pilot scale experimental set up.

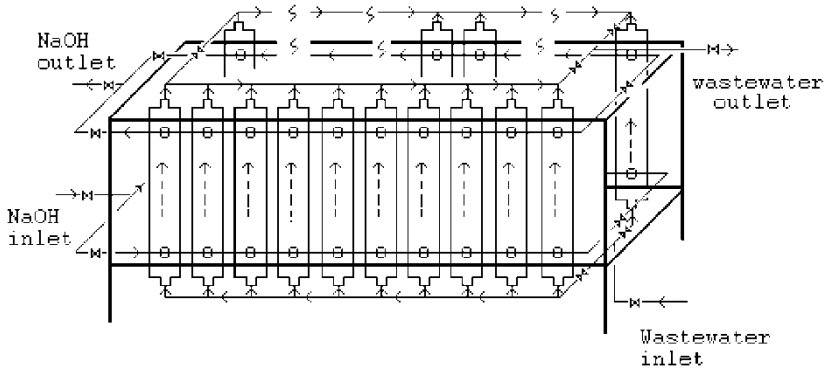

Figure 3. Schematic diagram of membrane unit.

artificial feed stream consisting of standard hydrazine sulfate–hexamethylene tetramine turbidity solution in deionized water (DI) water. The turbidity of this test solution was 400 Nephelometric Turbidity Units (NTU). No cyanide was present.

Laboratory scale experiments were conducted using an artificial cyanide solution consisting of 500 mg L^{-1} cyanide in DI water at pH 4.0. The strip solution contained 0.4% NaOH. The overall mass transfer coefficient, K_{0M}, was determined using the artificial cyanide solution at a flow rate of 42.4 mL/s for the feed and strip solutions. Next the 400 NTU test solution was run through the lumen of the hollow fibers for 5 hours, after which the overall mass transfer coefficient for the fouled membrane, K_{MF}, was determined using the same artificial cyanide solution.

Four cleaning strategies were investigated: use of dilute acid solution (1%–2%, flow rate 42.4 mL/s), compressed air (0.1 MPa) sparging in forward (lumen to shell side) mode, compressed air (0.1 MPa) sparging in backward (shell to lumen side) mode, and use of an ethanol solution (50%, flow rate 42.4 mL/s). For the dilute acid and ethanol, the solutions were pumped through the lumen of the hollow fibers for 20 minutes. Gas sparging was conducted for 1 hour.

After membrane cleaning, the overall mass transfer coefficient, K_{MC}, was measured again using the artificial cyanide solution. The percentage recovery of the mass transfer coefficient, η, is defined as,

$$\eta\,(\%) = \frac{K_{MC} - K_{MF}}{K_{0M} - K_{MF}} \times 100\% \tag{17}$$

Based on the laboratory scale experiments, the best cleaning strategy was chosen and verified at the pilot scale using the two real wastewaters.

RESULTS

Mass transfer results for the real wastewaters from the pilot plant are given in Fig. 4. In this figure, $\ln([HCN]_{F,0}/[HCN]_{F,t})$ is plotted against At/V_F, as suggested in Eq. (8) by assuming $\alpha = 0$. Consequently, the effects of osmotic distillation were ignored. The results in Fig. 4 are for run times of 2 hours.

The data fall on two different straight lines. Consequently, we can conclude that the rate of water vapor transfer due to osmotic distillation is small (23). Further, the variation in K_t over two hours is small, allowing us to replace K_t by $\overline{K_t}$. As indicated by Eq. (8) the slope of the lines in Fig. 4 is equal to $\overline{K_t}$.

Figure 4 indicates that the rate of mass transfer of HCN is much faster for the caffeine wastewater than for the benzonitrile wastewater. In earlier work (22, 23) we show that the lower rate of mass transfer in the benzonitrile wastewater is due to the fact that the pH of the wastewater, 9.5, is higher than the pKa of HCN, which is 9.31. Consequently a significant amount of the HCN will be deprotonated. In addition, the presence of volatile benzonitrile rather than air in the membrane pores will reduce the rate of HCN transfer (25).

Figure 5 shows the variation of the mass transfer coefficient of cyanide with time for caffeine and benzonitrile wastewaters. In these pilot scale experiments, the plant was run continuously without membrane cleaning for 40 hours for the caffeine wastewater and 20 hours for the benzonitrile wastewater. For the caffeine wastewater, the overall mass transfer coefficient of

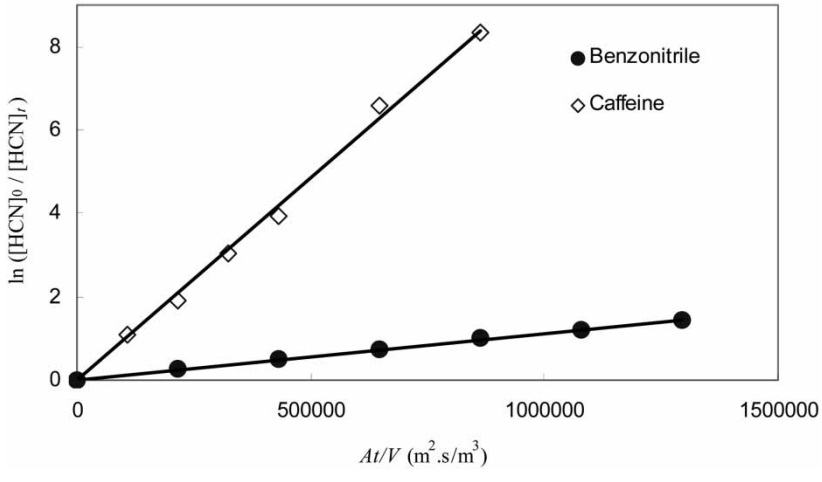

Figure 4. Determination of the average overall mass transfer coefficient for cyanide for the two wastewaters.

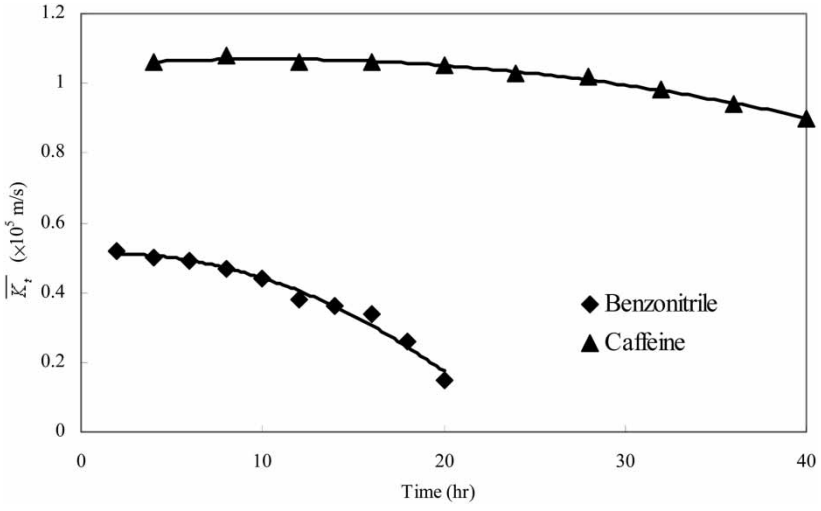

Figure 5. Variation of the overall mass transfer coefficient of cyanide with time for the two wastewaters.

cyanide decreased to 0.9×10^{-5} m/s from 1.06×10^{-5} m/s after 40 hours, i.e., about 15%. However for the benzonitrile wastewater, the mass transfer coefficient decreased from 0.52×10^{-5} m/s to 0.15×10^{-5} m/s within 20 hours, i.e., over 70%. The presence of particulate matter in the benzonitrile wastewater led to greater membrane fouling.

Table 4 lists the membrane-cleaning results for the laboratory scale experiments. The first column gives the overall mass transfer coefficient before membrane fouling (new membrane); the second column gives the overall mass transfer coefficient after membrane fouling (fouled membrane); the third column gives the overall mass transfer coefficient after membrane cleaning (cleaned membrane), and the fourth column gives the percentage recovery in the overall mass transfer coefficient. As can be seen, use of 2%

Table 4. Results of membrane fouling and cleaning using four different methods

Cleaning agent	K_{0M}, m s^{-1}	K_{MF}, m s^{-1}	K_{MC}, m s^{-1}	η, %	Comments
2% HCl	1.265×10^{-5}	0.760×10^{-5}	1.222×10^{-5}	91	Very effective
Forward air sparging	1.180×10^{-5}	0.712×10^{-5}	0.770×10^{-5}	12	Less effective
Back air sparging	1.222×10^{-5}	0.724×10^{-5}	0.816×10^{-5}	18	Less effective
50% ethanol	1.162×10^{-5}	0.700×10^{-5}	1.112×10^{-5}	89	Very effective

HCl or 50% ethanol were the most successful cleaning strategies. Based on practical considerations, the pilot plant modules were cleaned using dilute 1% HCl.

Figure 6 shows the variation of the mass transfer coefficient with time for the caffeine wastewater. In these experiments, the pilot plant was run continuously for 40 hours. After this the membranes were cleaned with 1% HCl for 30 minutes. Results are shown for four different periods of operation, the first 40 hours, 461–500, 961–1000, and 1481–1520 hours. As can be seen, membrane fouling was not a serious problem for the caffeine wastewater. After 1520 hours the mass transfer coefficient was similar to the mass transfer coefficient after 40 hours of operation indicating the effectiveness of the cleaning strategy employed.

Figure 7 shows the variation of the mass transfer coefficient with time for the benzonitrile wastewater. Since membrane fouling is more severe for this wastewater, membrane cleaning was initiated after 20 hours of operation. Results are shown for the first 60 hours of operation. As can be seen though, fouling is more severe; after two cleaning cycles the performance is similar to that of a new membrane.

The reciprocal of the overall mass transfer coefficient is the resistance to mass transfer. Figures 8 and 9 plot the change in the resistance to cyanide transfer as a function of time for the caffeine and benzonitrile wastewaters. For the caffeine wastewater the resistance to mass transfer increases slowly with run time. However for the benzonitrile wastewater, after an initial slow increase, the resistance to mass transfer increases rapidly after about 15 hours of operation.

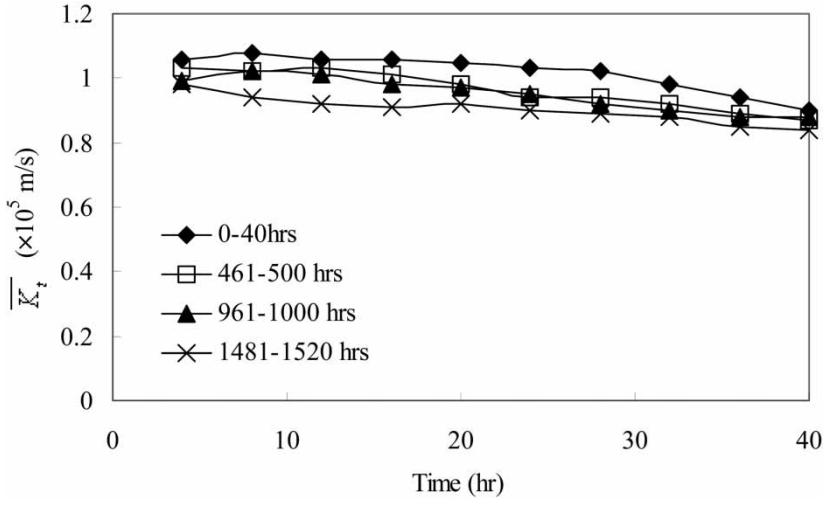

Figure 6. Membrane cleaning results for caffeine wastewater.

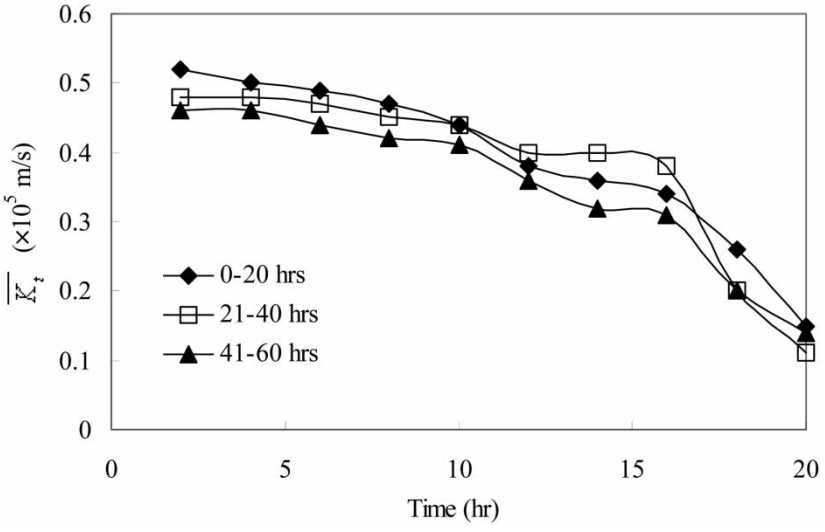

Figure 7. Membrane cleaning results for benzonitrile wastewater.

DISCUSSION

Unlike other membrane-based separation process such as microfiltration and ultrafiltration, few studies have focused on fouling and cleaning of

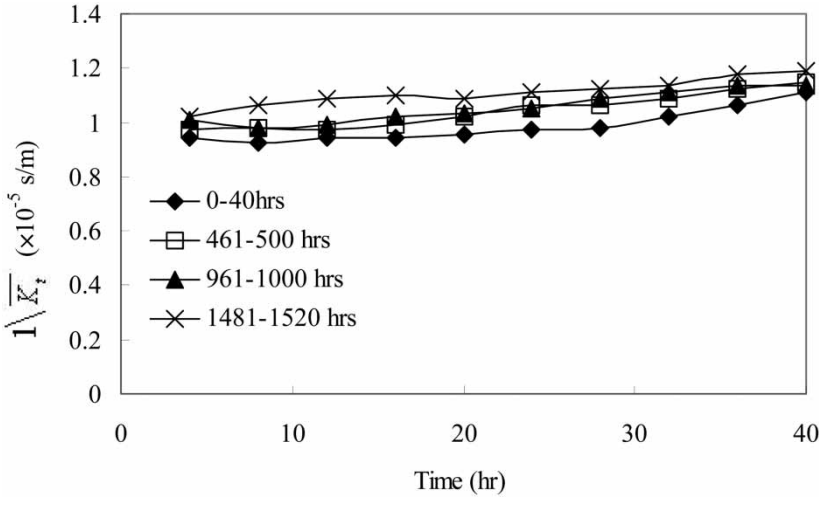

Figure 8. Variation in the resistance to cyanide transfer as a function of time for the caffeine wastewater.

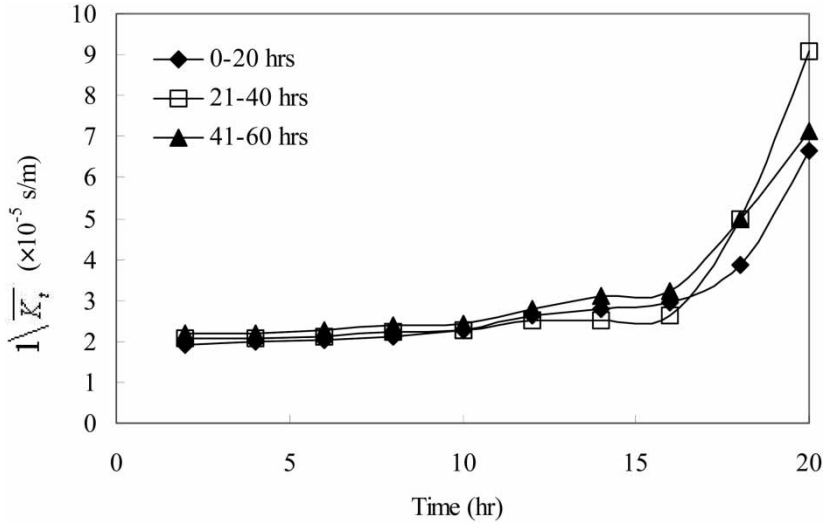

Figure 9. Variation in the resistance to cyanide transfer as a function of time for the benzonitrile wastewater.

gas-filled membranes for simultaneous stripping and absorption. Most previous studies used artificial feed streams that have few suspended solids present. Consequently, blocking of the membrane pores was not a concern. Further, most studies were run for short times, less than 2 hours, thus, a decrease in the mass transfer coefficient with time was not observed. In addition, the membranes used to separate the two aqueous streams are hydrophobic, thus membrane fouling is usually ignored.

The results obtained here indicate that for a commercial gas-filled membrane process, membrane fouling may be significant and may lead to compromised performance. Consequently, it is essential to develop appropriate cleaning strategies. Further membrane fouling is strongly dependent on the other contaminants present in the feed stream. The presence of suspended solids is likely to lead to significant fouling. For the caffeine wastewater membrane fouling is much less severe than for the benzonitrile wastewater. The caffeine wastewater results from a condensation process. Therefore it is relatively pure and contains few suspended solids (turbidity less than 1 NTU). Further, the pH of the feed solution is quite low, around 2–3. Such a low pH may effectively avoid membrane fouling as well.

The benzonitrile wastewater on the other hand, contained a very high salinity (25%–30%), and also had a high pH of 9.5–10. In addition, a significant amount of suspended solids was present as the turbidity was 20∼40. Further, during operation the membranes gradually turned darker in color

indicating adsorption of other species present in the wastewater. After cleaning the color became much lighter.

By using Eqs. (14)–(16), we obtained good predictions of the mass transfer coefficient for a clean membrane (22, 23). For a fouled membrane, the feed side mass transfer coefficient can still be predicted using Eq. (14). However the variation of ε, δ, and τ with time needs to be considered. Estimation of the variation with time of each of these parameters is difficult. However from a practical perspective, the effect of each of these parameters may be lumped together. Thus we define a fouling factor, E, to account for the variation of the membrane mass transfer coefficient with time. Eq. (15) then becomes,

$$k_M = E\frac{\varepsilon D_M H}{\delta\tau} \tag{18}$$

E varies between 0 and 1. E may be estimated from the experimental data and Eqs. (14), (16), and (18). The more severe the fouling, the faster E decreases with time. Figure 10 shows the variation of E with time for caffeine and benzonitrile wastewaters for the experimental results shown in Fig. 5. For the benzonitrile wastewater, E decreased very quickly compared to the caffeine wastewater.

The reciprocal of the overall mass transfer coefficient gives the overall resistance to cyanide transfer. By substituting Eq. (16) with Eq. (15) the

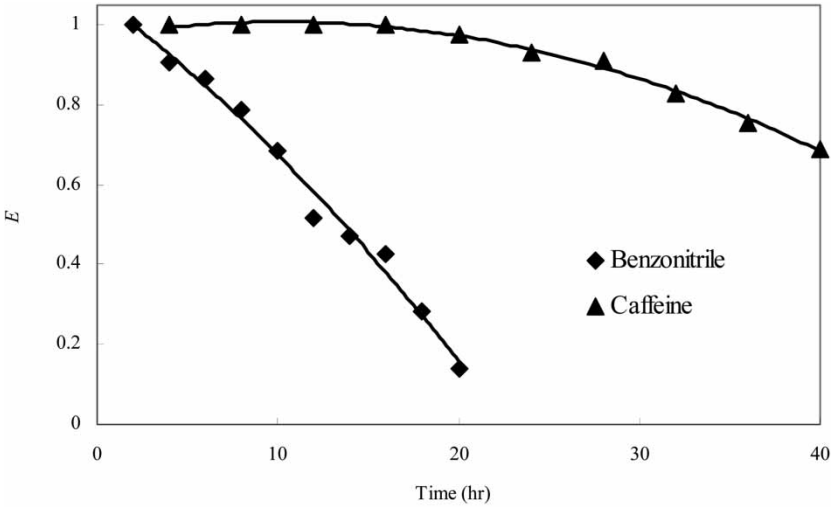

Figure 10. Variation of the fouling factor, E, for caffeine and benzonitrile wastewaters.

overall resistance to cyanide transfer is given by,

$$\frac{1}{K} = \frac{1}{k_F} + \frac{\delta\tau}{\varepsilon D_M H} \tag{19}$$

Comparing Eq. (19) to Figs. 8 and 9, which give the variation in the resistance to cyanide transfer with time, it is likely that the slight increase in the resistance to mass transfer with run time for the caffeine wastewater and for the first 15 hours of operation for the benzonitrile wastewater, is due to deposition of dissolved solutes on the membrane surface and in the pores. This will lead to slight increases in δ and τ with time. In the case of the benzonitrile wastewater, it appears that deposition of dissolved solutes also enhances deposition of suspended solids. The deposition of suspended solids will lead to pore blocking and, hence, a decrease in the porosity, ε. It appears that this effect is particularly severe after 15 hours of operation, i.e., after adsorption of dissolved solutes onto the membrane surface. Unlike microfiltration and ultrafiltration, the transfer of cyanide and other volatile species from the feed to the strip solution will not generate a substantial convective flow through the membrane pores. Consequently, adsorption of dissolved solutes and deposition of suspended solids occurs much more slowly.

Table 4 shows that both 1%–2% HCl and 50% ethanol can be used to regenerate the membranes. Further Figs. 6 and 7 show that 1%–2% HCl can effectively regenerate the membrane fouled by real wastewaters. Although 50% ethanol was an effective cleaning solution, it is expensive compared to 1%–2% HCl solution. Further, operation with dilute HCl solution is simpler from a practical perspective. Thus in the pilot scale experiments, only the dilute HCl solution was used. The results obtained here indicate that extended operation of gas-filled membranes for simultaneous stripping and absorption is likely to require the development of a membrane cleaning procedure. The degree of membrane fouling will depend on the dissolved and suspended solute species present in the feed stream.

CONCLUSION

Cyanide removal from wastewater streams using gas-filled membranes was studied at the pilot scale. Membrane fouling was observed during long-term operation. Membrane fouling strongly depends on the dissolved and suspended solutes present in the wastewater. Further, the fouled membrane can be regenerated using dilute acid solution. The results shown here confirm that gas-filled membranes can be stable for at least 2 months, which is promising for industrial application.

NOMENCLATURE

A	membrane surface area
D	diffusion coefficient
d	inside diameter of hollow fibers
E	fouling factor
H	Henry's law constant
J	flux
K	overall mass transfer coefficient
k	individual mass transfer coefficient
l	length of hollow fibers
t	time
v	velocity
V	volume

Greek Symbols

α	average rate of change of the feed volume
ε	membrane porosity
δ	membrane thickness
τ	tortuosity of membrane pores
ν	kinematic viscosity of liquid
η	rate of recovery in mass transfer coefficient of cyanide

Subscripts

F	feed
0M	fresh membrane
i,j	component
M	membrane
MF	membrane fouling
MC	membrane cleaning
S	strip solution
t	time
0	initial

REFERENCES

1. U.S. Environmental Protection Agency (U.S. EPA). In *Treatment of Cyanide Heap Leaches and Tailings*; US EPA: Washington, DC, 1994. EPA 530-R-94-037.
2. U.S. Environmental Protection Agency (U.S. EPA). In *Code of Federal Regulations: Effluent Guidelines and Standards; Electroplating Point Source Category Pretreatment Standards for Existing Sources*; US EPA: Washington, DC, 1981. Final Rule and Amendments, Title 40 CFR Part 413.

3. Hassan, S.Q., Vitello, M.P., Kupferle, M.J., and Grosse, D.W. (1991) Treatment technology evaluation for aqueous metal and cyanide bearing hazardous wastes (F007). *J. Air Waste Manage*, 41: 710.
4. Pak, D. and Chang, W. (1997) Oxidation of aqueous cyanide solution using hydrogen peroxide in the presence of heterogeneous catalyst. *Environ. Technol*, 18: 557.
5. Riveros, P.A., Koren, D., McNamara, V.M., and Binvignat, J. (1998) Cyanide recovery from a gold mill barren solution containing high levels of copper. *Cim. Bulletin*, 91: 73.
6. Kunz, R.G. and Giannelli, J.F. (1976) Activated carbon adsorption of cyanide complexes and thiocyanate ion from petrochemical wastewaters. *Carbon*, 14: 157.
7. Adhoum, N. and Monser, L. (2002) Removal of cyanide from aqueous solution using impregnated activated carbon. *Chem. Eng. Process*, 41: 17.
8. Monser, L. and Adhoum, N. (2002) Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. *Sep. Purif. Technol.*, 26: 137.
9. Goldblatt, E. (1956) Recovery of cyanide from waste cyanide solutions by ion exchange. *Ind. Eng. Chem.*, 48: 2107.
10. Kurama, H. and Catalsarik, T. (2000) Removal of zinc cyanide from a leach solution by an anionic ion-exchange resin. *Desalination*, 29: 1.
11. Gurol, M.D. and Bremen, W.M. (1985) Kinetics and mechanism of ozonation of free cyanide species in water. *Environ. Sci. Technol*, 19: 804.
12. Novak, F. and Sukes, G. (1981) Destruction of cyanide waste-water by ozonation. *Ozone: Sci. Eng.*, 3: 61.
13. Kim, B.R., Podsiadlik, D.H., Kalis, E.M., Hartlund, J.L., and Gaines, W.A. (1998) Photochemical destruction of cyanide in landfill leachate. *J. Environ. Eng.—ASCE*, 124: 1108.
14. Patil, Y.B. and Paknikar, K.M. (2000) Biodetoxification of silver-cyanide from electroplating industry wastewater. *Lett. Appl. Microbiol.*, 30: 33.
15. Short, A.E. (1990) *The GM-IX Process: A Pilot Plant for Recovering Zinc Cyanides from Plating Rinsewaters*; University of Minnesota: Minneapolis MS Thesis.
16. Semmens, M.J., Kenfield, C.F., and Qin, R. (1987) A gas membrane-ion exchange process for cyanide recovery. *Met. Finishing*, 11: 47.
17. Shen, Z., Huang, J., and Qian, G. (1997) Recovery of cyanide from wastewater using gas-filled membrane absorption. *Water Environ. Res.*, 69: 363.
18. Kenfield, C.F., Qin, R., Semmens, M.J., and Cussler, E.L. (1988) Cyanide recovery across hollow fiber gas-membranes. *Environ. Sci. Technol.*, 22: 1151.
19. Short, A.E., Haselmann, S.F., and Semmens, M.J. (1997) The GM-IX process: a pilot study for recovering zinc cyanides. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.*, 32: 215.
20. Shen, Z., Huang, J., and Sun, L. (1999) The treatment of praziquantel wastewater using coagulation and membrane separation integrated process. *Chinese J. Environ. Pollut. Technol.*, 12: 101.
21. Shen, Z., Qian, G., Wang, M., Chen, J., and Wang, N. (1998) The thermal efficiency in the gas membrane process. *Chinese J. Membr. Sci. Technol.*, 18: 46.
22. Shen, Z., Han, B., and Wickramasinghe, S.R. (2004) Cyanide removal from wastewater using gas-membranes: pilot-scale study. *Water Environ. Res.*, 76 (1): 15–22.
23. Han, B., Shen, Z., and Wickramasinghe, S.R. Cyanide removal from industrial wastewaters using gas-membranes. *J. Membr. Sci.,* in press, online available.

24. Zhang, Q. and Cussler, E.L. (1985) Hollow fiber gas-membranes. *AIChE J.*, 31: 1548.
25. Sirkar, K.K. (1992) Other new membrane processes. In *Membrane Handbook*; Ho, W.S.W. and Sirkar, K.K., Eds.; van Nostrand Reinhold: New York.
26. Lévêque, A. (1928) Les lois de la transmission de chaleur par convection. *Ann Mines*, 13: 201.
27. Castino, F. and Wickramasinghe, S.R. (1996) Washing frozen red blood cell concentrates using hollow fibres. *J. Membr. Sci.*, 110: 169.
28. Yang, M.C. and Cussler, E.L. (1986) Designing hollow fiber contactors. *AIChE J.*, 32: 1910.
29. Zhang, Q. and Cussler, E.L. (1985) Microporous hollow fibers for gas absorption II. mass transfer across the membrane. *J. Membr. Sci.*, 23: 333.
30. Cussler, E.L. (1984) *Diffusion: Mass Transfer in Fluid Systems*; Cambridge University Press: New York.
31. Astarita, G., Savage, D.W., and Bisio, A. (1983) *Gas Treating with Chemical Solvents*; Wiley: New York.
32. American Public Health Association (APHA). In *Standard Methods for the Examination of Water and Wastewater*, 20th Ed.; APHA: Washington, 1998.