Preparation of polydimethylsiloxane/polypropylene composite membranes for degassing of water with high running stability

Yan Chen^{a,b}, Zhiqian Jia^{a,*}

^aLaboratory for Membrane Science and Technology, College of Chemistry, Beijing Normal University, Beijing 100875, PR China, emails: zhqjia@bnu.edu.cn (Z.Q. Jia), yc2718@ic.ac.uk (Y. Chen) ^bDepartment of Chemical Engineering, Imperial College London, UK

Received 15 October 2019; Accepted 4 November 2020

ABSTRACT

Polydimethylsiloxane (PDMS)/polypropylene (PP) composite membranes were prepared by dip-coating method. The influence of crosslinking time of PDMS solution, immersion time, and multi-coating on the PDMS layer thickness, dissolved oxygen removal and stability of PDMS/ PP composite membranes were studied. The results showed that, with the increased crosslinking time and immersion time, the PDMS layer thickness and stability of the PDMS/PP membranes increased, while the deoxidization rate and mass transfer coefficient reduced. It was found that, multiple coatings of PDMS solution greatly increased the long-term running stability (>1,760 min) with only a slightly reduced deoxidization rate and mass transfer coefficient (~3.8%), demonstrating great potential in water degassing of PDMS/PP composite membranes.

Keywords: Degassing; Membrane; Dissolved oxygen; Composite membrane; Polydimethylsiloxane; Polypropylene

1. Introduction

Dissolved oxygen (DO) is defined as non-compound oxygen existing in water or other liquids [1]. Removing dissolved oxygen from water is important for many industries, such as food processing, power plants, semiconductor manufacturing, and pharmaceutical and biotechnology [1]. In the power industry, dissolved oxygen (>0.5 mg/L) presented in the feed water of boiler may react with iron, leading to corrosion or even explosion of boilers and pipes [2]. As for the semiconductor manufacturing industry, dissolved oxygen in the water can result in formation of natural oxide layer on the surface of silicon wafers, deteriorating the performance of products. Several effective physical methods have been developed to remove DO in water, such as thermal degassing and vacuum degassing, but such methods have high costs and cumbersome steps [3]. Chemical methods have also been utilized, such as chemical reduction by hydrazine or sodium sulfite. However, hydrazine is highly toxic, and the addition of sodium sulfite requires further ion exchange, which makes expenses high [4].

In recent years, membrane separation technology has become an effective degassing method for degassing, since it is environmental-friendly and energy-saving [5,6]. In the membrane degassing process, gas components in the liquid phase diffuse into a vacuum through a membrane, which acts as a barrier between the gas and liquid phase [1]. Compared with traditional physical methods, membrane degassing possesses a large surface area per unit volume and high mass transfer efficiency [6]. So far, both porous and non-porous membranes have been investigated to remove DO from water [7,8]. Microporous polypropylene (PP) hollow fiber membrane is a commonly used as degassing membrane due to its porosity and thus low gas transfer resistance [7,9,10]. For small pores (<0.1 µm), the pores remain dry and gas-filled. In order to improve the degassing performance, the design of the PP membrane module (e.g., woven fabric) and device were also

^{*} Corresponding author.

^{1944-3994/1944-3986 © 2021} Desalination Publications. All rights reserved.

reported [11]. However, the long-term deoxygenation performance of PP membrane is always challenging since PP membrane tends to lose stability due to its relatively low hydrophobicity [12]. Polyvinylidene fluoride has also been used as a degassing membrane due to its strong hydrophobicity [5]. Non-porous polydimethylsiloxane (PDMS) is stable, permeable and hydrophobic, and has been used for degassing [13–17], in which PDMS is often coated as a top-layer on different porous support materials, forming a composite membrane [18]. Although the factors affecting the polymerization of PDMS, such as the concentration of PDMS solution, the ratio of catalyst and a crosslinking agent, have been explored before for various membranes processes [19,20], the improvement of long-term stability in degassing has seldom been addressed. In this work, PDMS was coated on the surface of PP membranes by a dip-coating method, and the influence of crosslinking time of PDMS solution, immersion time, and multi-coating on the thickness of the PDMS layer, DO removal and stability of PDMS/PP composite membrane were studied, and a model was used to describe the mass transfer process.

2. Experiment

2.1. Materials

PP hollow fiber membranes with an average pore diameter of 0.05 μ m, an outer diameter of 0.5 mm, an inner diameter of 0.4 mm, and an effective length of 34 cm were provided by Tianjin Blue Cross Membrane Technology Co., Ltd., (Tianjin, China). 20 pieces of PP membranes with an effective area of 96.08 cm² were sealed in a module. Silicone rubber (average molecular weight of 5,000), tetraethyl orthosilicate (TEOS) and dibutyltin dilaurate were bought from Jinan Xingfeilong Huagong Co., Ltd., (China). *n*-Heptane was from Beijing Chemical Works, (Beijing, China).

2.2. Preparation of PDMS/PP composite membrane

PDMS (10%) was dissolved in *n*-heptane and stirred for 4 h. Then, the crosslinking agent TEOS and the catalyst dibutyltin dilaurate were added into the solution with a mass ratio of PDMS/TEOS/catalyst = 10/1/0.35 [21–23]. During the cross-linking reaction, the viscosity of the polymer solution was measured at intervals with the NDJ-1 viscometer.

A dip-coating method was used to prepare the PDMS/ PP composite membrane. First, both ends of 20 pieces of pristine PP membranes were sealed with epoxy, and then the sealed membranes were dipped into PDMS solution for a certain time, air-dried in a fume hood for 24 h, and dried in an oven at 90°C for 5 h to obtain PDMS/PP composite membranes.

Multiple coating was tried to improve the stability of composite membranes. As an example, the sealed PP membranes were dipped in the PDMS polymer solution (with a crosslinking time of 135 min) for 30 s, and then airdried in a fume hood for 24 h. Then the dried composited membrane was immersed in the PDMS solution (crosslinking time of 120 min) for 30 s, and air-dried in a fume hood for 24 h and then dried in an oven at 90°C. The as-obtained composite membranes were marked as 135/30 + 120/30. We also prepared membranes marked as 135/15 + 135/15, 135/15 + 120/15, and 135/10 + 120/10 + 120/10, etc.

2.3. Deoxygenation

Fig. 1 showed the schematic of membrane degassing. The feed deionized water with DO of 8.41 mg/L flowed through the lumens of the membrane module at a flow rate of 0.04 m/s unless otherwise noted. Vacuum (-0.1 MPa) was applied to the shell-side of the module.

2.4. Characterization

The morphology of membranes was characterized by a field-emission scanning electron microscope (FESEM, S-8010, Hitachi, Japan), and the sample was sprayed with Au before observation. The infrared spectra were recorded on a Fourier-transform infrared spectrophotometer (FTIR, Affinity-1, Shimadzu, Japan). The DO content of deionized water was measured by a JPSJ-605F dissolved oxygen analyzer (INESA Scientific Instrument Co., Ltd., China). The deoxidization rate is the ratio of DO removed from the feed water to the original DO in the water.

3. Results and discussion

3.1. Mass transfer model

For the membrane desorption process, the mass transfer rate in an infinitesimal element can be described as:

$$dN = K_L (C - C^*) dA \tag{1}$$

where K_L is the overall mass transfer coefficient; *A* is the surface area of the membrane; *N* is the desorption rate; *C*^{*} is the DO concentration in liquid phase in equilibrium with the gas phase in the shell-side of the membrane module, which follows Henry's law:

$$C^* = \frac{P}{H} \tag{2}$$



Fig. 1. Schematic of membrane degassing. (1) Feed tank; (2) peristaltic pump; (3) rotameter; (4) hollow fiber membrane module; (5) outlet tank; (6) vacuum pump.

where *H* is the Henry's constant (73.8 MPa L/mol at room temperature). Under the vacuum condition in the shell-side, C^* is nearly equal to zero. Thus:

$$dN = K_L (C - C^*) dA = K_L C dA = n K_L 2\pi r C dL$$
(3)

where n is the number of membranes in the module. Meanwhile, the decrease rate of oxygen in the liquid phase after passing through the infinitesimal element is:

$$dN = q_L dC \tag{4}$$

Thus:

$$\frac{nK_L 2\pi rCdL}{q_L} = \frac{dC}{C} \tag{5}$$

Integrate the entire membrane module:

$$\int_{0}^{L} \frac{nK_{L} 2\pi r dL}{q_{L}} = \int_{C_{\rm in}}^{C_{\rm out}} \frac{dC}{C}$$

$$\tag{6}$$

Hence, K_1 is expressed as:

$$K_{L} = \frac{q_{L} \ln \frac{C_{in}}{C_{out}}}{2n\pi rL}$$
(7)

The reciprocal of the overall mass transfer coefficient is the overall resistance, which consists of the resistance of the liquid film, the membrane resistance, and the resistance of the gas film. The gas film resistance can be neglected for vacuum degassing.

3.2. Preparation and characterization of PDMS/PP membranes

As shown in Fig. 2a, as the PDMS crosslinking reaction proceeded, the viscosity of the PDMS solution increased. During the first 120 min, the viscosity increased slowly, while it grew rapidly after reacting for 160 min, which might make the coating difficult to control [12,19,24,25]. Considering the processability, the solution with viscosity of about 11.6 cP was used to obtain a continuous and smooth PDMS layer on PP membranes.

Fig. 2b gives the FTIR spectra of PDMS/PP composite membranes obtained at various immersion time. The bands around 2,838–2,950 cm⁻¹ are attributed to the stretching vibration of -CH₂ and -CH₂- of PP. 1,259 cm⁻¹ is ascribed to the bending vibration of Si-CH_{3'} and 1,015 cm⁻¹ is the asymmetric stretching vibration of Si-O-Si, and 794 cm⁻¹ is the C-H stretching of the silicone Si-C [22], indicating the successful coating of PDMS on PP membranes. Meanwhile, as the immersion time increased, the PDMS adsorption intensity increased while the PP adsorption declined. Fig. 3a shows that, the surface of pristine PP membranes possessed lots of pores. For PDMS/PP membranes, the surface was smooth and no pores could be observed (Fig. 3b). In the cross-section of PDMS/PP membranes (Fig. 3c), a PDMS layer around 10 µm in thickness could be observed on the PP membrane surface.

3.3. Deoxidization with pristine PP membranes

The deoxidization performance of the pristine PP membranes was studied firstly. As illustrated in Fig. 4a, as the flow rate of feed water rose from 0.04 to 0.12 m/s (Re from 15.83 to 47.89), the mass transfer coefficient of the membrane increased from 6.11 \times 10⁻⁶ to 1.27 \times 10⁻⁵ m/s, while the deoxidization rate decreased from 40.7% to 30.4%. For microporous PP membranes, the mass transfer is always controlled by the resistance in the liquid phase because gas transfer through the membrane by gas-phase diffusion (10⁴ times faster than the liquid phase diffusion), and thus this resistance is negligible. The overall mass transfer can thus be estimated by the liquid film transfer coefficient, which could also be calculated by the Sherwood number (Sh = $K_1 d_1/D$), herein d_1 is the inner diameter of PP membrane, D is the oxygen diffusivity in water $(1.98 \times 10^{-9} \text{ m}^2/\text{s})$ at 274 K). The relationship between Sh, Reynolds number



Fig. 2. (a) Effect of crosslinking time on the viscosity of PDMS solution and (b) FTIR spectra of membranes obtained at various immersion time.



Fig. 3. Scanning electron microscopy images of membranes. (a) Surface of pristine PP membrane, (b) surface of PDMS/PP composite membrane, and (c) cross-section of PDMS/PP membrane.

(Re), Schmidt number (Sc) can be expressed by the semiempirical equation:

$$Sh = C \operatorname{Re}^{\alpha} \operatorname{Sc}^{0.333}$$
(8)

where *C* and α are determined empirically. Based on the fitting linear regression obtained from Fig. 4b, the correlation equation was Sh = 0.14Re^{0.65} Sc^{0.333}. The increase in the flow rate enhanced the liquid turbulence, leading to an increased mass transfer coefficient. Meanwhile, as the average residence time of water decreased, the contact between the water and membrane became insufficient, so that the dissolved oxygen could not be removed effectively, leading to a declined deoxidization rate.

Fig. 4c shows that, when the operating temperature increased from 20.5°C to 26.5°C at a fixed flow rate, the deoxidation rate rose from 62.4% to 69.5% remarkably. When the velocity was fixed, the oxygen diffusivity in the water rose rapidly with the increase in temperature, leading to an increase in the mass transfer coefficient (neglecting the change of the Henry coefficient). However, a high temperature makes the micropores of membranes wet easily, causing tiny droplets to form on the surface of the membranes.

3.4. Effect of crosslinking time and immersion time on composite membranes

During the dip-coating of PDMS solution on PP membranes, when the immersion time was fixed, as the crosslinking time of the PDMS increased from 90 min to 180 min, the thickness of PDMS layer increased (Fig. 5a). Similarly, when the crosslinking time was fixed, as the immersion time rose from 30 to 90 s, the PDMS layer thickness also rose. Generally, the thickness of the PDMS layer was relatively low, mostly between 5–10 μ m, which was beneficial for the permeation of oxygen [24]. Figs. 5b and c show that, at the flow rate of 0.04 m/s (Re = 15.83), the deoxidization rate and mass transfer coefficient of the composite membranes were significantly reduced as the crosslinking time and immersion time increased due to the rising thickness of the PDMS layer [14,25].

The stability of pristine PP and PDMS/PP composite membranes in long-term operation is given in Fig. 5d. Although the deoxidization rate of the pristine membrane was high at first, it decreased to only a half after working for only 240 min. In contrast, for the PDMS/PP membranes, although the initial deoxidation rate was relatively lower, it maintained its initial value for a longer time (e.g., more than 450 min for the membrane of 135/90). With the rising PDMS crosslinking time and immersion time, the stability of composite membrane increased, such as 135/90 > 135/60 > 135/30, 120/60 > 120/30, etc. It seemed that, thick PDMS layer can cover the PP pores and reduce the permeating of water through the pores, improving the running stability.

3.5. Effects of multi-coating on composite membranes

To further improve the stability of membranes, multicoating was applied to manufacture the PDMS/PP composite membrane. Table 1 shows that, for the total immersion time of 30 s, in comparison of the single dip-coating (i.e., 120/30, 135/30), twice- or multiple dip-coating (i.e., 135/15 + 120/15, 135/15 + 135/15, 135/10 + 120/10 + 120/10) increased the thickness of PDMS layer by about 160%–470%, while the deoxidization rate and mass transfer coefficient declined only 3.1%–31.2%, and the stability time (>1,500 min) increased more than 460%. For the total immersion time of 60 s, compared with the single dip-coating(135/60), twice coating(135/30 + 120/30) increased the thickness of PDMS layer by about 245%, while the deoxidization rate and mass transfer coefficient declined only 3.8%, and the stability time (>1,760 min) increased more than 319%.

The reason is that, during the long single dip-coating time, the PDMS solution intrudes into the PP pores, blocks the pores, and forms a continuous film on the PP membrane surface [18]. In contrast, in the twice- or multi-coating method, the immersion time is short for each coating. Although the thickness of the PDMS layer increased apparently, the intrusion of PDMS solution into the PP pores and the pores blocking are not serious, leading to slightly decreased deoxidization rate and mass transfer coefficient. It seemed that the PDMS in the PP pores mainly contribute to the mass transfer resistance. In addition, the PDMS layer after multi-coating is probably more continuous with fewer defects, resulting in excellent stability in the long-term running.

The oxygen mass transfer coefficient of the composite membrane is also compared with other membranes



Fig. 4. Pristine PP membranes (a) Effects of flow rate, (b) mass transfer correlation of Sh and Re, and (c) effects of temperature.

Table 1 Comparison of single, twice- and multi-coating methods

Total immersion time (s)	Crosslinking and immersion time (min)	PDMS Thickness (µm)	Deoxidization rate (%)	Mass transfer coefficient (×10 ⁻⁶ m/s)	Stability time (min)
30	120/30	5.8	33.3	4.69	220
	135/30	6.7	31.3	4.43	320
	135/15 + 120/15	16.2	30.7	4.39	1,500
	135/15 + 135/15	19.1	23.4	3.12	_
	135/10 + 120/10 + 120/10	35.8	22.1	2.92	_
60	135/60	6.7	28.4	3.91	420
	135/30 + 120/30	23.2	27.3	3.73	1,760

reported in the literature (Table 2). Generally, porous PP membranes displayed higher mass transfer coefficients due to the porous membrane structure. In this work, although degassing was conducted at relatively low flow rates, the oxygen transfer performance of PDMS/PP membranes is comparable or acceptable in comparison with other membranes. In addition, the PDMS/PP membranes display good stability in long term-running, which is important for practical applications.

4. Conclusion

PDMS was coated on porous PP membranes by dip-coating method for degassing. As the crosslinking time of PDMS solution and immersion time increased, the thickness of PDMS layer and stability of the PDMS/PP composite membranes increased, while the deoxidization rate and mass transfer coefficient declined. Multiple coatings of PDMS solution greatly enhanced the long-term stability



Fig. 5. Effect of crosslinking time and immersion time on the thickness of PDMS layer (a), deoxidization rate (b), mass transfer coefficient (c), and stability (d) of PDMS/PP composite membranes.

Table 2 Comparison of oxygen mass transfer coefficient of different membranes

Membrane	o.d./i.d. (µm)	Flow rate (m/s)	Mass transfer coefficient (×10–6 m/s)	References
Polypropylene	400/300	0.12	30	[11]
Polypropylene	500/400	0.04	6.1	This work
Polypropylene	500/400	0.12	13	This work
Silicon rubber microtube	320/200	0.09	39	[14]
Polyethylene composite	289/258	3.5	32	[26]
PDMS/PP (135/30)	513/400	0.04	4.43	This work
PDMS/PP (135/15 + 120/15)	532/400	0.04	4.39	This work

(>1,760 min) with only a slightly reduced deoxidization rate and mass transfer coefficient (~3.8%), demonstrating great potential in degassing as well as aeration applications of PDMS/PP composite membranes.

Acknowledgments

This study was supported by the National Natural Science Foundation of China and the Qinghai Qaidam Saline Lake Chemical Science Research Joint Fund (No. U1607109).

References

- T. Li, P. Yu, Y.B. Luo, Deoxygenation performance of polydimethylsiloxane mixed-matrix membranes for dissolved oxygen removal from water, J. Appl. Polym. Sci., 132 (2015) 41350.
- [2] Z.Z. Zhu, Z.L. Hao, Z.S. Shen, J. Chen, Modified modeling of the effect of pH and viscosity on the mass transfer in hydrophobic hollow fiber membrane contactors, J. Membr. Sci., 250 (2005) 269–276.
- [3] V. Sinha, K. Li, Alternative methods for dissolved oxygen removal from water: a comparative study, Desalination, 127 (2000) 155–164.

- [4] J.-S. Moon, K.-K. Park, J.-H. Kim, G. Seo, Reductive removal of dissolved oxygen in water by hydrazine over cobalt oxide catalyst supported on activated carbon fiber, Appl. Catal., A, 201 (2000) 81–89.
- [5] T. Li, P. Yu, Y.B. Luo, Preparation and properties of hydrophobic poly(vinylidene fluoride)-SiO₂ mixed matrix membranes for dissolved oxygen removal from water, J. Appl. Polym. Sci., 131 (2014) 40430, https://doi.org/10.1002/app.40430.
- [6] X.Y. Tan, K. Li, Investigation of novel membrane reactors for removal of dissolved oxygen from water, Chem. Eng. Sci., 55 (2000) 1213–1224.
- [7] T.O. Leiknes, M.J. Semmens, Vacuum degassing using microporous hollow fiber membranes, Sep. Purif. Technol., 22–23 (2001) 287–294.
- [8] J. Li, L.-P. Zhu, Y.-Y. Xu, B.-K. Zhu, Oxygen transfer characteristics of hydrophilic treated polypropylene hollow fiber membranes for bubbleless aeration, J. Membr. Sci., 362 (2010) 47–57.
- [9] X.Y. Tan, G. Caper, K. Li, Analysis of dissolved oxygen removal in hollow fibre membrane modules: effect of water vapour, J. Membr. Sci., 251 (2005) 111–119.
- [10] S. Karoor, K.K. Sirkar, Gas absorption studies in microporous hollow fiber membrane modules, Ind. Eng. Chem. Res., 32 (1993) 674–684.
- [11] Z.-G. Peng, S.-H. Lee, T. Zhou, J.-J. Shieh, T.-S. Chung, A study on pilot-scale degassing by polypropylene (PP) hollow fiber membrane contactors, Desalination, 234 (2008) 316–322.
- [12] W. Wei, S.S. Xia, G.P. Liu, X.H. Gu, W.Q. Jin, N.P. Xu, Interfacial adhesion between polymer separation layer and ceramic support for composite membrane, AICHE J., 56 (2010) 1584–1592.
- [13] A.K. Zulhairun, Z.G. Fachrurrazi, M. Nur Izwanne, A.F. Ismail, Asymmetric hollow fiber membrane coated with polydimethylsiloxane–metal organic framework hybrid layer for gas separation, Sep. Purif. Technol., 146 (2015) 85–93.
- [14] A. Ito, K. Yamagiwa, M. Tamura, M. Furusawa, Removal of dissolved oxygen using non-porous hollow-fiber membranes, J. Membr. Sci., 145 (1998) 111–117.
- [15] H. Adelnia, H.C. Bidsorkhi, A.F. Ismail, T. Matsuura, Gas permeability and permselectivity properties of ethylene vinyl acetate/sepiolite mixed matrix membranes, Sep. Purif. Technol.,146 (2015) 351–357.
- [16] G.P. Liu, W. Wei, W.Q. Jin, N.P. Xu, Polymer/ceramic composite membranes and their application in pervaporation process, Chin. J. Chem. Eng., 20 (2012) 62–70.
- [17] W. Wei, S.S. Xia, G.P. Liu, X.L. Dong, W.Q. Jin, N.P. Xu, Effects of polydimethylsiloxane (PDMS) molecular weight on performance of PDMS/ceramic composite membranes, J. Membr. Sci., 375 (2011) 334–344.

- [18] I.F.J. Vankelecom, B. Moermans, G. Verschueren, P.A. Jacobs, Intrusion of PDMS top layers in porous supports, J. Membr. Sci., 158 (1999) 289–297.
- [19] M.A. Mazo, A. Nistal, A.C. Caballero, F. Rubio, J. Rubio, J.L. Oteo, Influence of processing conditions in TEOS/PDMS derived silicon oxycarbide materials. Part 1: microstructure and properties, J. Eur. Ceram. Soc., 33 (2013) 1195–1205.
- [20] S. Roy, N.R. Singha, Polymeric nanocomposite membranes for next generation pervaporation process: strategies, challenges and future prospects, Membranes, 7 (2017) 53, https://doi. org/10.3390/membranes7030053.
- [21] G.R. Wu, X.X. Chen, Y.L. Li, Z. Jia, Preparation of submicron PAF-56 particles and application in pervaporation, Microporous Mesoporous Mater., 279 (2019) 19–25.
- [22] Z.Q. Jia, S. Hao, M.C. Jiang, PAF-11/poly (dimethylsiloxane) mixed matrix pervaporation membranes for dealcoholization of aqueous solutions, J. Chem. Technol. Biotechnol., 93 (2018) 3276–3283.
- [23] G.R. Wu, X.Y. Lu, Y.L. Li, Z.Q. Jia, X.Z. Cao, B.Y. Wang, P. Zhang, Two-dimensional covalent organic frameworks (COF-LZU1) based mixed matrix membranes for pervaporation, Sep. Purif. Technol., 241 (2020) 116406, https://doi.org/10.1016/j. seppur.2019.116406.
- [22] Z.Y. Dong, G.P. Liu, S.N. Liu, Z.K. Liu, W.Q. Jin, High performance ceramic hollow fiber supported PDMS composite pervaporation membrane for bio-butanol recovery, J. Membr. Sci., 450 (2014) 38–47.
- [23] D.Y. Liu, G.P. Liu, L. Meng, Z.Y. Dong, K. Huang, W.Q. Jin, Hollow fiber modules with ceramic-supported PDMS composite membranes for pervaporation recovery of bio-butanol, Sep. Purif. Technol., 146 (2015) 24–32.
- [24] F.J. Xiangli, Y.W. Chen, W.Q. Jin, N.P. Xu, Polydimethylsiloxane (PDMS)/ceramic composite membrane with high flux for pervaporation of ethanol-water mixtures, Ind. Eng. Chem. Res., 46 (2007) 2224–2230.
- [25] M.-C. Kim, R.H.W. Lam, T. Thorsen, H.H. Asada, Mathematical analysis of oxygen transfer through polydimethylsiloxane membrane between double layers of cell culture channel and gas chamber in microfluidic oxygenator, Microfluid. Nanofluid., 15 (2013) 285–296.
- [26] T. Ahmed, M.J. Semmens, M.A. Voss, Oxygen transfer characteristics of hollow-fiber, composite membranes, Adv. Environ. Res., 8 (2004) 637–646.