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Effect of Polymer Concentration on the Structure and Performance of Polysulfone Flat Membrane for CO_2 Absorption in Membrane Contactor

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Abstract

In this study, polysulfone (PSF) flat membrane prepared via non-solvent phase inversion method was employed in gas-liquid membrane contactor module to absorb CO_2. Two polymer concentrations of 16 wt% and 18 wt% were used in the dope solution of fabricated membranes. The membranes were characterized in terms of morphological structure and contact angle. Scanning electron microscopy (SEM) analysis demonstrated that PSF membrane with polymer concentration of 16 wt% in the dope solution has a porous layer with a combination of finger-like, sponge-like and macrovoid structures, but the other membrane has a sponge-like structure. Also, characterization results through atomic force microscopy (AFM) and contact angle measurement demonstrated that the porosity, surface roughness and hydrophobicity of the PSF membranes decreased with an increase in polymer concentration. Evaluation of mass transfer resistance displayed that the resistance of the PSF membrane with polymer concentration of 18wt% in the dope solution is higher than that of the other membrane. In addition, decreasing the polymer concentration significantly improved CO_2 absorption flux. At the absorbent flow rate of 9.7 ml/min, the CO_2 absorption flux of PSF membrane with 16 wt% polymer concentration was 2.17 times higher than the absorption flux of the PSF with 18 wt% polymer concentration.

Keywords: *CO_2 Absorption, Polysulfone, Polymer Concentration, Flat Membrane Contactor*

1. Introduction

Over recent decades, there has been an increase of greenhouse gases concentration in the atmosphere due to the growth of human activities. The largest source of greenhouse gas emissions comes from burning fossil fuels such as coal, fuel oil and natural gas for electricity production in thermal power plants as well as heat generation in industrial, commercial and residential sectors. Other fundamental sources of greenhouse gas generation are petroleum processing and use of petroleum based fossil fuels such as gasoline and diesel in transportation systems [1-3].

Some consequences of global warming, caused by emission of greenhouse gases to the atmosphere, could be environmental hazards such as more droughts and floods, less ice and snow, more extreme weather

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incidents and rising sea levels. Among greenhouse gases such as water vapor, carbon dioxide, methane, nitrous oxide, ozone and CFCs, CO_2 is regarded as the most serious component considering its concentration in the atmosphere and its function in enhanced greenhouse effect [4, 5]. Therefore, it is essential to develop efficient separation processes to remove CO_2 from industrial off gas mixtures.

Nowadays, molecular sieve based adsorption, cryogenic distillation systems, physical or chemical absorption and membrane applications are common approaches applied for CO_2 removal [6-8]. The conventional processes extensively used in this field are CO_2 capturing by absorption into aqueous solutions using gas/liquid contacting devices such as packed towers, bubble columns, venturi scrubbers and tray columns [9-11]. However, the most commercial one is packed column using alkanolamines as absorbent solutions. Some operational problems associated with these contacting devices such as flooding, channeling, entrainment, foaming and also some drawbacks such as large size, low specific gas-liquid interfacial area, high capital and operating cost restrict their applications [12].

Application of membrane-based gas separation is another technique for the recovery of CO_2. Despite the development achieved by decreasing the thickness and increasing the selectivity of membranes used for this purpose, their low permeability and low mass transfer rate have limited their commercialization [13-15].Thus, by taking advantage of both membrane separation and gas-liquid absorption, a novel approach has recently emerged as membrane contactor to overcome the aforementioned problems. In this way, the role of the membrane is just a stationary interface between gas and liquid phases and offers no selectivity between the species of gas streams [16]. Hence, a membrane contactor serves as a modular system with high interfacial area per unit volume, easy scale-up with independent control of gas and liquid streams and high selectivity with high mass transfer flux provided by liquid absorbent [17, 18]. On the other hand, in addition to the gas phase and liquid phase mass transfer resistances, the membrane contactor module has the drawback of extra membrane mass transfer resistance, which reduces its performance. However, as the diffusivity of gas phase is higher than the liquid phase, completely gas-filled membrane pores ensured by hydrophobic membranes with optimized pore size can minimize the membrane resistance[19-21].

Recently, CO_2 removal using this technology has been extensively investigated by different membrane configurations, but most of them were devoted to hollow fiber membrane contactors [22-24] with a few exceptions of flat sheet ones [25-27]. Khaisri *et al.* [28] compared the performance of a gas absorption membrane system in both physical and chemical absorption studies using three common hydrophobic membranes including polytetrafluoroethylene (PTFE), polypropylene (PP) and polyvinylidene fluoride (PVDF). They found that the CO_2 absorption performance can be ranked as PTFE > PVDF >PP. Although PTFE is regarded as the most hydrophobic membrane and displays good absorption performance, it is considerably expensive which restricts its application. Lu *et al.* [29] evaluated CO_2 absorption using amino-acid salt solution through PP hollow fiber membrane contactor. Their results demonstrated that the overall mass transfer coefficient with the composite solution is evidently higher than that of the single solution. Lv *et al.* [30] assessed the efficiency of super hydrophobic PP hollow fiber membrane contactors for CO_2 absorption with MEA solution. In addition to the membrane material, its structure is an important factor in the success of membrane contactor technology. Therefore, some researches have focused on the fabrication of new membranes with modified structures using other types of membrane materials such as polyetherimide and polysulfone [31, 32]. They found that the structure of membrane depends on the phase inversion process where the fingerlike macrovoid in the membrane structure enhances the membrane porosity and reduces the membrane tortuosity. Simons *et al.* [33] investigated the separation of CO_2 from CH_4 in two hollow fiber membrane contactors using PP and polyphenylene oxide (PPO) membranes and amine absorbent. They concluded that performance of PP membranes outperforms the performance of PPO membranes in terms of productivity and selectivity. Ghasem *et al.* fabricated polyethersulfone hollow fiber membranes with a good hydrophobicity for the separation of CO_2 from a gas mixture using the membrane contactor module [34]. Polysulfone (PSF) membrane has been employed in different membrane separation processes and is a good candidate for membrane gas absorption due to its relatively strong hydrophobicity, good chemical resistance and high heat resistance. Rahbari *et al.* fabricated a PSF membrane with high permeability and low mass transfer resistance and applied it to CO_2 absorption in a hollow fiber contactor[35].

To the best of our knowledge, no research has been done on the absorption of CO_2 using PSF flat sheet membrane contactors. Also, the effect of polymer concentration in the dope solution on the performance of PSF flat membrane contactors for CO_2 absorption has not yet been reported in the literature. Therefore, the present work focuses on the CO_2 absorption rates in the synthesized PSF flat sheet membranes using distilled water as absorbent. Also, the effects of liquid flow rates on CO_2 absorption fluxes and the contribution of mass transfer resistance of separate phases in overall mass transfer resistance is investigated.

2. Theory

2-1. Mass transfer equations

According to film theory, overall mass transfer in membrane contactor module has been considered as resistance in series model, which takes place in three steps including mass transfer from the bulk gas phase into membrane surface, mass transfer through the membrane pores and mass transfer from the membrane–liquid interface into bulk liquid phase. Fig. 1 shows schematically the concentration profile across the hydrophobic microporous membrane, and the following equation can be used to express CO_2 flux (mol/m^2.s) through a flat sheet membrane [36]:

$$\begin{aligned} J_i &= K_l\left(C_i^{id} - C_{il}\right) = k_{ig}\left(C_{ig} - C_{img}\right) \\ &= k_{im}\left(C_{img} - C_{ieg}\right) = k_{il}\left(C_{ie} - C_{il}\right) \end{aligned} \tag{1}$$

where K_l is an overall mass transfer coefficient of the liquid phase (m/s); k_{ig}, k_{im} and k_{il} are the mass transfer coefficients (m/s) in the gas, membrane and the liquid phases for the species CO_2, respectively; C_{ig} and C_{il} are CO_2 concentrations (mol/m^3) in the gas and liquid phase, respectively; C_{img}, C_{ieg} and C_{ie} are CO_2 concentrations at the gas-membrane interface, the gas-liquid interface and the liquid-gas interface, respectively; and C_i^{id} is CO_2 concentration in the liquid phase ideally in equilibrium with its concentration in the gas phase.

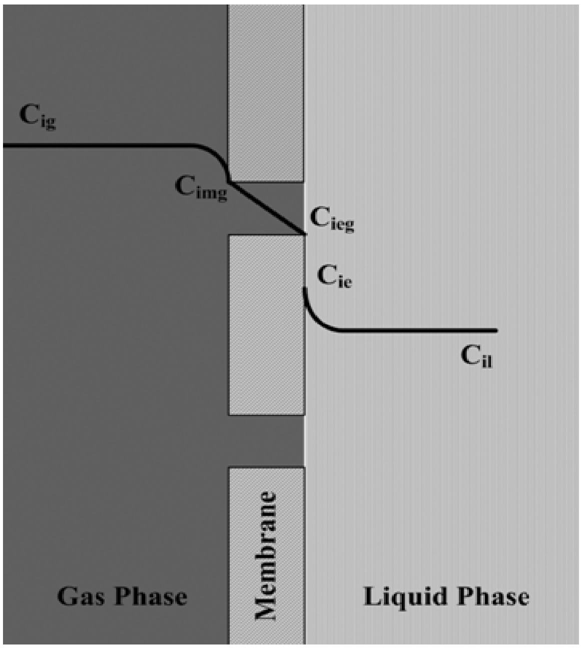


Figure 1. Concentration profile across the hydrophobic microporous membrane.

Based on the resistance in series model, the overall liquid phase mass transfer coefficient (K_l) can be described by the following equation[36]:

$$1/K_l = 1/k_{il} + 1/(k_{im}H_e) + 1/(k_{ig}H_e) \tag{2}$$

where H_e is dimensionless Henry's law constant for CO_2. Individual mass transfer coefficients of the liquid phase, the membrane and the gas phasecan be predicted by equations which have been presented in the literature [37-39].

2-2. Application of Wilson plot

An alternative technique to evaluate the membrane resistance is the Wilson plot [40].The gas phase mass transfer resistance can be neglected if pure CO_2 is used as the feed gas in physical gas absorption membrane systems [37] and the mass transfer resistance of the liquid phase is dependent on the liquid velocity(u).Thus, a graph of $1/K_l$ versus $1/u^{\alpha}$, known as Wilson plot, yields a straight line with an intercept giving the membrane mass transfer coefficient. The empirical α value of the graph is a constant result in the best straight line.

3. Experimental

3-1. Materials

Polysulfone beads (PS Mn: 22,000 Da), used as the membrane substrates polymer, were purchased from Sigma-Aldrich. N,N-dimethylformamide(DMF) with purity more than 99.5%, used as the solvent, was purchased from Dae Jung, Korea. Sodium dodecyl sulfate (SDS, Merck) was used in the precipitation bath of fabricated membranes.

3-2. Synthesis of PSF flat sheet membranes

The non-solvent phase inversion method was used to fabricate flat PSF membranes. Two dope solutions containing different concentrations of polymer (16 wt% and 18 wt% PSF) balanced with DMF were prepared at room temperature. The solutions were allowed to mix for at least 8 h until the homogeneous polymer dope solutions were completely formed and then degassed at room temperature for 12 h. The polyester non-woven fabric with a thickness of about 100 μm was attached to a clean glass plate, and the dope solution was then spread onto the polyester fabric using a casting knife. The precipitation bath for initiating the phase inversion contained distilled water, 0.1 wt% SDS and 2 wt% DMF. The prepared membranes were immediately immersed in the precipitation bath for 30 min and then washed. After that, the membranes were stored in water bath for at least 1 day to leach out the residual solvents and additives completely. Finally, in order to dry the membranes, two sheets of filter paper were placed on both sides of the fabricated membranes for 24 h at room temperature.

3-3. Membrane characterizations

3-3-1. SEM and AFM observation

Surface and cross-section observation of fabricated flat membranes was carried out by scanning electron microscopy (SEM model: KYKY-EM3200) operating at 24 KV. The samples were coated with a gold layer before the surface scanning. Also, the membranes were fractured in liquid nitrogen for the cross-section microscopy.

Atomic force microscopy (AFM model: Easyscan2 Flex) was used to determine the surface morphologies and the roughness of the PSF membranes. The scan size of $5\,\mu m \times 5\,\mu m$ was selected for imaging the membrane surfaces at atmospheric pressure. For each membrane, the reported roughness value is the average of roughness values of three scanned images. The mean roughness value (S_a) measured by an AFM is defined as [41]:

$$S_a = \frac{1}{LW}\int_0^L \int_0^W |f(x,y)|\, dxdy \qquad (3)$$

where $f(x,y)$ is the surface relative to the center plane, L and W are the surface dimensions. Based on the pore size distribution function (F_r) obtained by AFM data, the mean pore size of the membranes (r_{ave}) can be estimated through Eq. 4 [41]:

$$r_{ave} = \frac{\int_{r_{min}}^{r_{max}} r\, F_r\, dr}{\int_{r_{min}}^{r_{max}} F_r\, dr} \qquad (4)$$

3-3-2. Measurement of membrane porosity and contact angle

The volume of pores divided by the total membrane volume is defined as the membrane porosity (ε) which can be calculated by measuring the dry mass (m_{dry}) and wet mass (m_{wet}) of membranes and using Eq. 5 [42]:

$$\varepsilon = \frac{\frac{m_{wet}-m_{dry}}{\rho_w}}{\frac{m_{wet}-m_{dry}}{\rho_w} + \frac{m_{dry}}{\rho_P}} \times 100 \qquad (5)$$

where ρ_P is the polymer density (1.25 g/cm^3 for polysulfone) and ρ_w is the water density.

A simple method to determine the membrane ability for preventing the liquid phase penetration into membrane pores is contact angle measurement [43]. The sessile drop method was applied by a contact angle goniometer (Dataphysics OCA 15, Germany) to measure the contact angle of distilled water on fabricated flat sheet membranes. For each sample, the volume of a single water drop created on the membrane surface was 4 µl. After repeating the contact angle measurement three times, the average value of contact angles was calculated.

3-4. CO_2 absorption experiment

Fig. 2 shows a schematic representation of the experimental setup employed to capture CO_2 using a flat sheet membrane contactor.The membrane contactor module consisted of two flow field plates and a membrane interposed between them. In this study, the serpentine channels were formed on the flow field plates for directing gas and liquid streams. The width and the depth of the channels were 1.0 mm. Pure CO_2 as the feed gas was used on one side of the membrane, and distilled water as the liquid absorbent was used on the other side of the membrane in the constructed module. To obtain the best performance, all experiments were conducted in a counter current mode operation. The equipment used in the gas line of the setup consists of a CO_2 gas cylinder, a pressure regulator, a mass flow controller (MFC), a pressure gauge and a needle valve. At the start-up stage, the gas was first transferred to the module and liquid was then allowed to flow to the module in order to prevent the phenomena of membrane wetting. Gas flow rates were controlled by a mass flow controller (Dwyer GFC-1107, USA) at 298.15 K and atmospheric pressure. A peristaltic pump (Thomas SR25, Germany) with variable flow rates of 3-12 ml/min was applied for directing distilled water in the liquid line. A differential pressure of 2-4 psig between the gas and the liquid phase was employed using a pressure gauge and a needle valve in the liquid line to avoid the dispersion of gas bubbles into the liquid. At steady state condition, reached after at least 20 min of each run operation, the average value of mass transfer fluxes for three CO_2 loaded samples taken under the same operating conditions, were calculated. For the calculation of the overall absorption flux of CO_2, its content in the outlet absorption liquid was measured by the chemical titrimetric method in which Sodium hydroxide solution was used as a titrant with phenolphthalein as an indicator [33]. Therefore, the overall mass transfer coefficient of liquid phase was calculated through Eq. 6 [44]:

$$r_{ave} = \frac{\int_{r_{min}}^{r_{max}} r\, F_r\, dr}{\int_{r_{min}}^{r_{max}} F_r\, dr} \qquad (6)$$

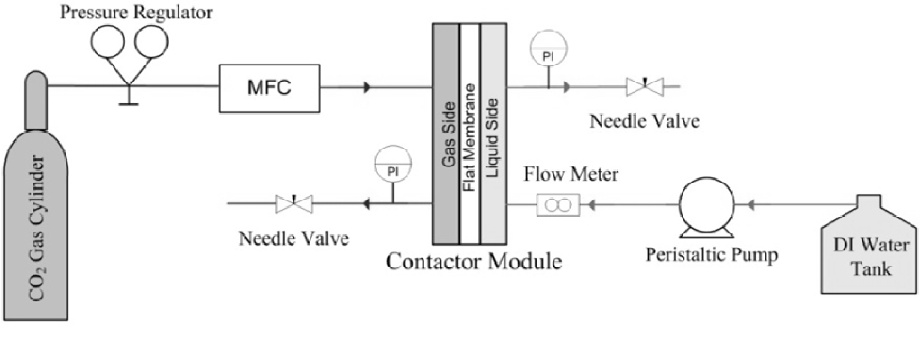


Figure 2. Experimental setup of CO_2 absorption using membrane contactor module.

where Q_L is liquid volumetric flow rate (m^3/s); A_m is membrane mass transfer surface area (m^2); $C_{il,out}$ and $C_{il,in}$ are CO_2 concentrations in the outlet and inlet liquid respectively (mol/m^3). Two fabricated PSF membranes were separately placed in the contactor module and their results were compared.

4. Results and discussions

4-1. Characterization results of PSF membranes

The membranes were characterized in terms of mean pore size, porosity, roughness and water contact angle measurement. These results for both samples are listed in Table 1.

The cross-section and surface SEM images of PSF flat sheet membranes with various polymer concentrations (samples PSF-16 and PSF-18) are shown in Fig. 3. As it is clear in Figs. 3a and 3c, PSF-16 membrane showed a thin skin layer and a porous supported layer with finger-like, sponge-like and macrovoid structures. This can be attributed to different starting conditions for phase separation at layers far from the surface in solvent-non solvent exchange. The membrane transport properties are dependent on both skin and support layers. This structure is expected to provide lower mass transfer resistance and higher gas permeability, favorable for gas absorption application. Also, the lower polymer concentration can be regarded as the other reason for the macrovoid formation in PSF-16 membrane due to faster precipitation in the phase inversion process [45]. In contrast, the PSF-18 membrane displayed a sponge-like structure due to the high polymer concentration which increased the viscosity of polymer, leading to a phase separation delay and the formation of smaller pore size. Kimmerle *et al.* reported that high viscosity of the polymer dopes generated the membranes with sponge-like structure [46]. According to Figs. 3b and 3d, it seems that by increasing the polymer concentration in the dope solution from 16 wt% to 18 wt%, the porosity and mean pore size of the membrane decreased which is also confirmed by the data represented in Table 1.

The 3D AFM images of PSF-16 and PSF-18 membranes were displayed in Fig. 4. In these pictures, the dark sections represent the depressions (membrane pores) and the bright ones are representatives of nodules. Besides, the roughness of the substrate is assigned to the height of the surface's lumps [47]. It is obvious that there was a change in surface morphology of the membranes and the surface roughness of PSF-16 membrane was higher than that of PSF-18 membrane as presented in Table1.

Table 1. Characteristics of fabricated PSF flat membranes.

Membrane	Mean Pore Size r_{ave} (nm)	Porosity ε (%)	Roughness S_a (nm)	Water Contact Angle θ (°)
PSF-16	155.46	69.64	14.26	73.5
PSF-18	129.29	64.22	7.38	69.6

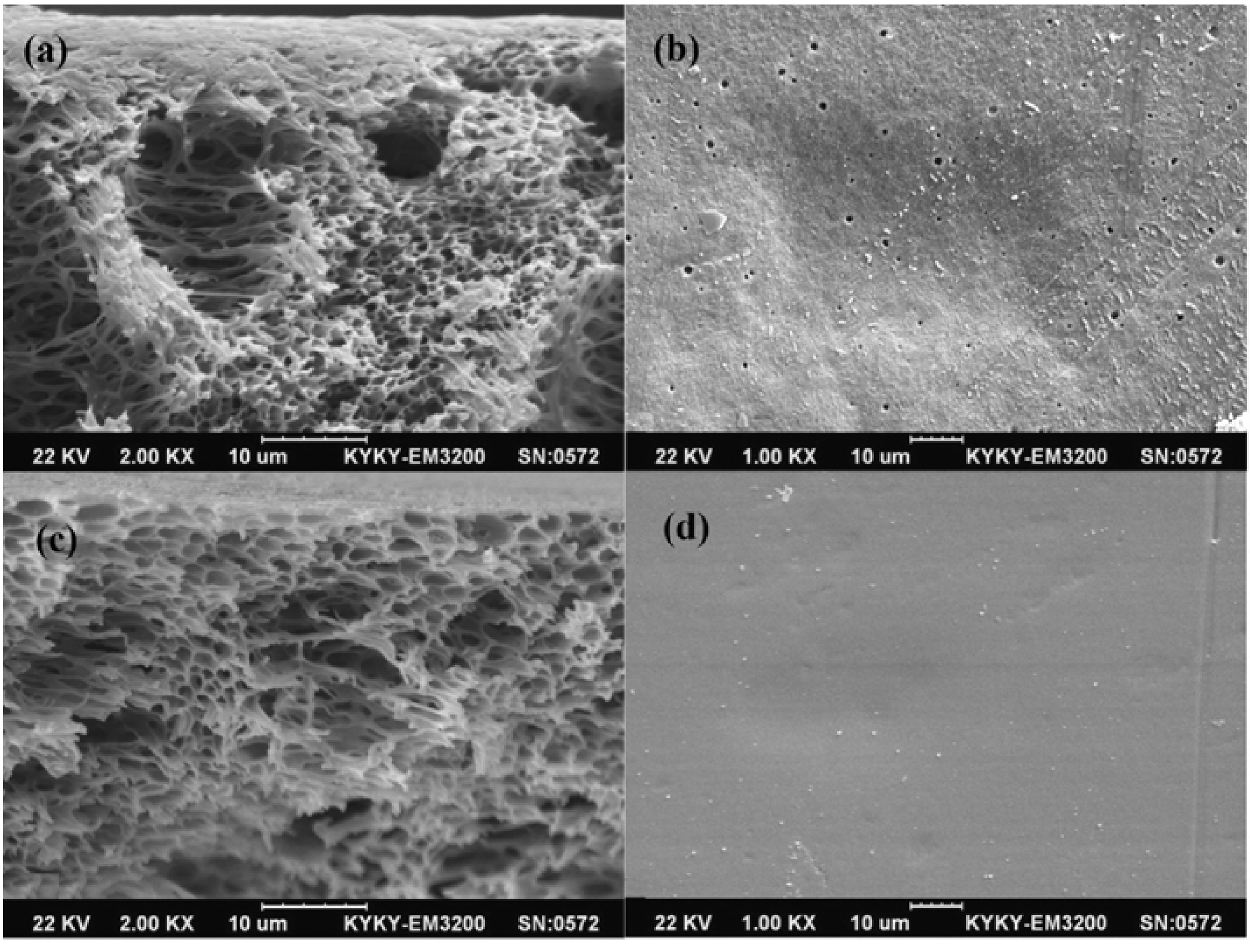
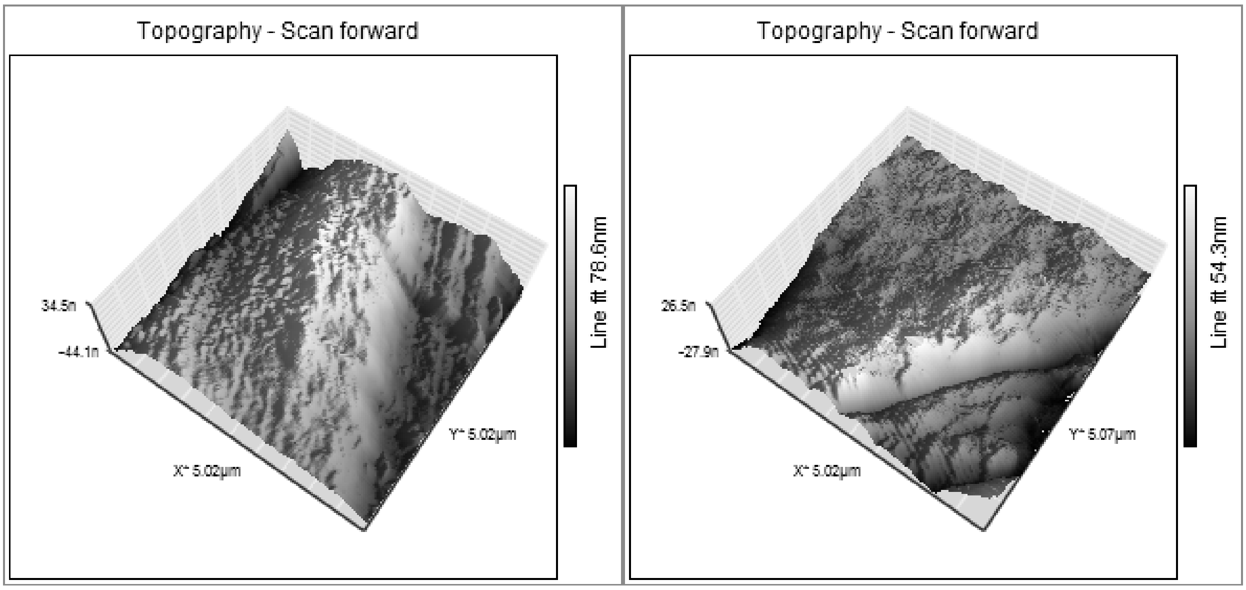


Figure 3. SEM images of fabricated PSF flat membranes (a) cross section of 16 wt% PSF (b) surface of 16 wt% PSF (c) cross section of 18 wt% PSF and (d) surface of 18 wt% PSF.



(a) **(b)**

Figure 4. AFM images of fabricated PSF flat membranes (a) 16 wt% PSF (b) 18 wt% PSF.

According to the data reported in Table 1, the effect of polymer concentration on the membrane surface contact angle can be evaluated. It was observed that the contact angle of fabricated membranes increased with a decrease in polymer concentration, hence leading to an increase in hydrophobicity of the PSF-16 membrane. As the hydrophobicity of the membrane increased, the probability of membrane wetting tended to decrease which is a favorable parameter for CO_2 removal efficiency. It is due to the fact that when the membrane is not wetted by the liquid absorbent, CO_2 is not forced to diffuse through the membrane with liquid-filled pores and hence the membrane mass transfer resistance decreases, leading to the enhancement of absorption flux.

4-2. Analysis of CO_2 absorption performance

The CO_2 absorption fluxes of both fabricated PSF membranes were determined at various liquid flow rates in order to evaluate the dependency of the membrane contactor performance on the liquid phase mass transfer resistance. The constant gas flow rate of 1000 ml/min was selected for this test. As shown in Fig. 5, it can be concluded that by increasing the liquid velocity from 0.025 m/s to 0.1 m/s, the CO_2 absorption fluxes of both PSF-16 and PSF-18 membranes increased. This can be attributed to the decrease in thickness of the liquid boundary layer at high flow rates leading to an increase in mass transfer coefficient. Similar trends were also reported for CO_2 absorption flux using water as absorbent in commercial PP and PTFE membrane contactor [35, 48]. It was found that an increase in the liquid flow rate led to the enhancement of the CO_2 mass transfer rate.

Referring to Fig. 5, the results showed that decreasing the polymer concentration in dope solution has contributed to improvement in CO_2 absorption flux. It means that CO_2 mass transfer rate of PSF-16 membrane was greater than that of PSF-18. As an example,at the absorbent flow rate of 9.7 ml/min, CO_2 absorption flux of the PSF-16 membrane was 2.17 times higher than the absorption flux of the PSF-18 membrane.This phenomenon can be ascribed to the modified structure of the PSF-16 membrane; i.e. the increase in the mean pore size and the porosity.The increase in the porosity of the PSF-16 membrane resulted in higher gas-liquid contact area and higher permeability, both of which are preferred factors in membrane contactor. As discussed before, the wettability resistance of the PSF-16 membrane was higher due to the higher contact angle value. Indeed, this factor also improved the membrane performance for CO_2 absorption.

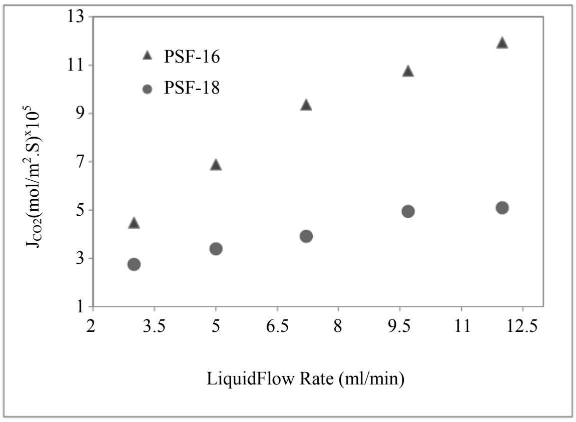


Figure 5. CO_2 absorption fluxes at various liquid flow rates using PSF-16 and PSF-18 membranes.

4-3. Analysis of membrane resistance

According to resistance in series model presented in Eq. 2, the membrane mass transfer can be determined using the Wilson plot because the gas phase mass transfer resistance can be neglected if pure CO_2 is used as the feed gas. Using Wilson plot for evaluation of mass transfer resistance has been reported in the literature [49]. Yang *et al*. [50] used the Wilson plot and reported a relationship of $1/K_l$ with the reciprocal of fluid velocity to evaluate the liquid stream mass transfer coefficient in designing hollow fiber membrane contactors. Lin *et al*. used Wilson plot for determination of mass transfer resistance during CO_2 absorption by alkanolamine absorbents in PVDF and PP membrane contactors [51].

Fig. 6 shows the Wilson plot for two fabricated PSF membranes and the best straight line to the data of $1/K_l$ versus $1/u^{\alpha}$ was obtained by α equal to 0.93. The contribution of membrane resistance in overall mass transfer resistance can be obtained using the membrane mass transfer resistance calculated from the intercept of the plot. Membrane resistances, equations and regression coefficients of different membranes are reported in Table 2.

Table 2. Equation and membrane resistance obtained by Wilson plot.

Membrane	Equation	R-squared Value	Membrane Resistance (s/m)
PSF-16	$y = 20753\,x + 88837$	0.9951	88837
PSF-18	$y = 24929\,x + 465948$	0.9655	465948

According to these data, the membrane mass transfer resistance of the PSF membrane decreased to approximately 19% of its value when the polymer concentration in dope solution decreased from 18 wt% to 16 wt%. This reconfirms superior performance of PVP-16 membrane against the PSF-18 one in the contactor module which was already proved by the measurement of CO_2 absorption flux. At the liquid velocity of 0.025 m/s, nearly 16% of the total resistance was attributed to the mass transfer resistance of the PSF-16 membrane.So, by neglecting the gas phase resistance, the mass transfer resistance of the liquid phase can be regarded as 84% of the total resistance for the PSF-16 membrane. As it can be seen in Fig. 6, increasing the liquid velocity decreased the overall mass transfer resistance and consequently the contribution of the membrane resistance increased.The results of overall mass transfer resistance for the PSF-16 membrane also revealed that by increasing the liquid velocity from 0.025 to 0.1 m/s, the contribution of the liquid phase resistance decreased to 69% of its value (from 84% to 58%).This can be attributed to the disturbance of the boundary layer in the liquid phase with an increase in the velocity.

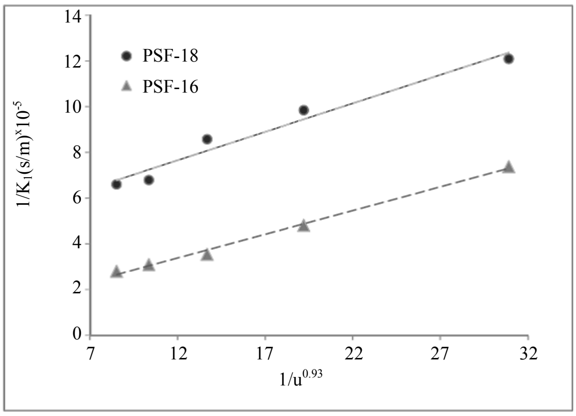


Figure 6. Wilson plot for pure CO_2 absorption using distilled water.

5. Conclusions

The porous PSF membranes with polymer concentrations of 16 wt% and 18 wt% were fabricated via phase inversion method.The CO_2 absorption performance of membranes was investigated in a flat membrane contactor module. As the polymer concentration in the dope solution increased, the mean pore size, porosity and contact angle of the membrane decreased.The PSF-16 membrane showed a combination of finger-like, sponge-like and macrovoid structures while the structure of PSF-18 membrane was sponge-like. An increase in the liquid flow rate resulted in an increase of CO_2 flux for both membranes. The CO_2 absorption flux of the PSF-16 membrane was higher than that of the PSF-18 membrane due to its higher porosity and hydrophobicity.On the other hand, the mass transfer resistance of the PSF-16 membrane was lower than that of the PSF-18 membrane. Therefore, it can be concluded that increasing the polymer concentration in the dope solution has a negative effect on the mass transfer flux of CO_2. All of these results suggest that polysulfone is an appropriate material with the potential to fulfill the demands of carbon dioxide absorption and can be used in membrane contactor applications.

References

[1] Gabelman, A. and Hwang, S.T., "Hollow fiber membrane contactors", J. Membr. Sci., 159(1-2), 61, (1999).

[2] Rufford, T.E., Smart, S., Watson, G.C.Y., Graham, B.F., Boxall, J., Diniz da Costa, J.C. and May, E.F., "The removal of CO_2 and N_2 from natural gas: A review of conventional and emerging process technologies", J. Petro. Sci. Eng.,94–95,123, (2012).

[3] Lampert, K., Ziebik, A. and Stanek, W., "Thermoeconomical analysis of CO_2 removal from the Corex export gas and its integration with the blast-furnace assembly and metallurgical combined heat and power (CHP) plant", Energy,35(2), 1188, (2010).

[4] Yeon, S.H., Lee, K.S., Sea, B., Park, Y.I. and Lee, K.H.,"Application of pilot-scalemembrane contactor hybrid system for removal of carbon dioxide from flue gas", J. Membr. Sci., 257(1-2), 156, (2005).

[5] Dunne, J.A., Jackson, S.C. and Harte, J., Greenhouse Effect, in: Encyclopedia of Biodiversity (2nd Edition), S.A. Levin Ed., Academic Press, (2013).

[6] Guo, W., Feng, F., Song, G., Xiao, J. and Shen, L., "Simulation and energy performance assessment of CO_2 removal from crude synthetic natural gas via physical absorption process", J. Nat. Gas. Chem.,21(6), 633, (2012).

[7] Naim, R. and Ismail, A.F.,"Effect of fiber packing density on physical CO_2 absorption performance in gas–liquid membrane contactor", Sep. Purif. Technol., 115, 152, (2013).

[8] Zhang, Y., Sunarso, J., Liu, S. and Wang, R., "Current status and development of membranes for CO_2/CH_4 separation: A review", Int. J. Greenh. Gas. Con.,12, 84, (2013).

[9] Pineda, I.T., Lee, J.W., Jung, I. and Kang, Y.T., "CO_2 absorption enhancement by methanol-based Al_2O_3 and SiO_2 nanofluids in a tray column absorber", Int. J. Refrig., 35(5), 1402, (2012).

[10] Lin, C.C. and Chen, B.C., "Carbon

dioxide absorption in a cross-flow rotating packed bed", Chem. Eng. Res. Des.,89(9), 1722, (2011).

[11] Yi, F.,Zou, H.K., Chu, G.W., Shao, L., and Chen, J.F., "Modeling and experimental studies on absorption of CO_2 by Benfield solution in rotating packed bed", Chem. Eng. J., 145(3), 377, (2009).

[12] Cheng, H.H., and Tan, C.S., "Removal of CO_2 from indoor air by alkanolamine in a rotating packed bed", Sep. Purif. Technol.,82, 156, (2011).

[13] Favre, E., "Membrane processes and postcombustion carbon dioxide capture: Challenges and prospects", Chem. Eng. J., 171(1-2), 782, (2011).

[14] Ismail, A.F., Kusworo, T.D. and Mustafa, A., "Enhanced gas permeation performance of polyethersulfone mixed matrix hollow fiber membranes using novel Dynasylan Ameo silane agent", J. Membr. Sci., 319, 306, (2008).

[15] Favre, E., "Carbon dioxide recovery from post-combustion processes: Can gas permeation membranes compete with absorption?", J. Membr. Sci., 294(1-2), 50, (2007).

[16] Bottino, A., Capannelli, G., Comite, A., Di Felice, R. and Firpo, R., "CO_2 removal from a gas stream by membrane contactor, separation and purification technology", Sep. Purif. Technol., 59(1), 85, (2008).

[17] Khaisri, S., deMontigny, D., Tontiwachwuthikul, P. and Jiraratananon, R., "CO_2 stripping from monoethanolamine using a membrane contactor", J. Membr. Sci., 376(1-2), 110, (2011).

[18] Scholes, C.A., Simioni, M., Qader, A., Stevens, G.W. and Kentish, S.E., "Membrane gas–solvent contactor trials of CO_2 absorption from syngas", Chem. Eng. J., 195–196, 188, (2012).

[19] Modigell, M., Schumacher, M., Teplyakov, V.V. and Zenkevich, V.B., "A membrane contactor for efficient CO_2 removal in biohydrogen production", Desalination, 224(1-3), 186, (2008).

[20] Zhang, H.Y., Wang, R., Liang, D.T. and Tay, J.H., "Modeling and experimental study of CO_2 absorption in a hollow fiber membrane contactor", J. Membr. Sci., 279(1-2), 301, (2006).

[21] Nguyen, P.T., Lasseuguette, E., Medina-Gonzalez, Y., Remigy, J. C., Roizard, D. and Favre, E., "A dense membrane contactor for intensified CO_2 gas/liquid absorption in post-combustion capture", J. Membr. Sci., 377(1-2), 261, (2011).

[22] Marzouk, S.A.M., Al-Marzouqi, M.H., El-Naas, M.H., Abdullatif, N. and Ismail, Z.M., "Removal of carbon dioxide from pressurized CO_2–CH_4 gas mixture using hollow fiber membrane contactors", J. Membr. Sci., 351(1-2), 21, (2010).

[23] Cai, J.J., Hawboldt, K. and Abdi, M.A., "Contaminant removal from natural gas using dual hollow fiber membrane contactors", J. Membr. Sci., 397–398, 9, (2012).

[24] Zhang, Y. and Wang, R., "Novel method for incorporating hydrophobic silica nanoparticles on polyetherimide hollow fiber membranes for CO_2 absorption in a gas–liquid membrane

contactor", J. Membr. Sci., 452, 379, (2014).

[25] Lin, S.H., Tung, K.L., Chang, H.W. and Lee, K.R. "Influence of fluorocarbon flat-membrane hydrophobicity on carbon dioxide recovery", Chemosphere, 75(10), 1410, (2009).

[26] Franco, J.A., Kentish, S.E., Perera, J.M. and Stevens, G.W., "Poly (tetrafluoroethylene) sputtered polypropylene membranes for carbon dioxide separation in membrane gas absorption", Ind. Eng. Chem. Res., 50(7), 4011, (2011).

[27] Paul, S., Ghoshal, A.K. and Mand, B., "Theoretical studies on separation of CO_2 by single and blended aqueous alkanolamine solvents in flat sheet membrane contactor (FSMC)", Chem. Eng. J., 144(3), 352, (2008).

[28] Khaisri, S., de Montigny, D., Tontiwachwuthikul, P., and Jiraratananon, R., "Comparing membrane resistance and absorption performance of three different membranes in a gas absorption membrane contactor", Sep. Purif. Technol.,65(3), 290, (2009).

[29] Lu, J.G., Zheng, Y.F. and Cheng, M.D., "Membrane contactor for CO_2 absorption applying amino-acid salt solutions", Desalination, 249(2), 498, (2009).

[30] Lv, Y., Yu, X., Jia, J., Tu, S.T., Yan, J. and Dahlquist, E., "Fabrication and characterization of superhydrophobic polypropylene hollow fiber membranes for carbon dioxide absorption", Appl. Energy., 90(1), 167, (2012).

[31] Mansourizadeh, A. and Ismail, A.F., "Effect of additives on the structure and performance of polysulfone hollow fiber membranes for CO_2 absorption", J. Membr. Sci., 348(1-2), 260 ,(2010).

[32] Bakeri, Gh., Matsuura, T., Ismail, A.F. and Rana, D., "A novel surface modified polyetherimide hollow fiber membrane for gas-liquid contacting processes", Sep. Purif. Technol., 89, 160, (2012).

[33] Simons, K., Nijmeijer, K. and Wessling, M., "Gas–liquid membrane contactors for CO_2 removal", J. Membr. Sci., 340(1-2), 214, (2009).

[34] Ghasem, N., Al-Marzouqi, M. and Zhu, L., "Preparation and properties of polyethersulfone hollow fiber membranes with o-xylene as an additive used in membrane contactors for CO_2 absorption", Sep. Purif. Technol., 92, 1, (2012).

[35] Rahbari-Sisakht, M., Ismail, A.F. and Matsuura, T., "Development of asymmetric polysulfone hollow fiber membrane contactor for CO_2 absorption", Sep. Purif. Technol., 86, 215, (2012).

[36] Drioli, E., Criscuoli, A. and Curcio, E., Membrane contactors: Fundamentals, applications and potentialities, Elsevier, p. 516, (2006).

[37] Rangwala, H.A., "Absorption of carbon dioxide into aqueous solutions using hollow fiber membrane contactors", J. Membr. Sci.,112(2), 229, (1996).

[38] Gilliland, E.R. and Sherwood, T.K., "Diffusion of vapors into air streams", Ind. Eng. Chem., 26(5), 516, (1934).

[39] Mavroudi, M., Kaldis, S.P. and Sakellaropoulos, G.P., "A study of

mass transfer resistance in membrane gas–liquid contacting processes", J. Membr. Sci., 272(1-2), 103, (2006).

[40] Wilson, E.E., "A basis for rational design of heat transfer apparatus", Trans. Am. Soc. Mech. Eng., 37, 47, (1915).

[41] Singh, S., Khulbe, K.C., Matsuura, T. and Ramamurthy, P., "Membrane characterization by solute transport and atomic force microscopy", J. Membr. Sci.,142(1), 111, (1998).

[42] Amini, M., Jahanshahi, M. and Rahimpour, A., "Synthesis of novel thin film nanocomposite (TFN) forward osmosis membranes using functionalized multi-walled carbon nanotubes", J. Membr. Sci., 435, 233, (2013).

[43] Li, N.N., Fane, A.G., Ho, W.S.W. and Matsuura, T., (Eds.), Advanced membrane technology and applications, John Wiley & Sons Inc., New York, NY, (2008).

[44] Dindore, V.Y., Brilman, D.W., F., Feron, P.H.M. and Versteeg, G.F., "CO_2 absorption at elevated pressures using a hollow fiber membrane contactor", J. Membr. Sci., 235(1-2), 99, (2004).

[45] Fontananovaa, E., Jansen, J.C., Cristiano, A., Curcio, E. and Drioli, E., "Effect of additives in the casting solution on the formation of PVDF membranes", Desalination, 192 (1-3), 190, (2006).

[46] Kimmerle, K. and Strathmann, H., "Analysis of the structure-determining process of phase inversion membranes", Desalination, 79(2-3), 283, (1990).

[47] Mansourpanah, Y., Alizadeh, K., Madaeni, S., Rahimpour, A. and Soltani Afarani, H., "Using different surfactants for changing the properties of poly(piperazineamide) TFC nanofiltration membranes", Desalination, 271(1-3), 169, (2011).

[48] Xu, A., Yang, A., Young, S., de Montigny, D. and Tontiwachwuthikul, P., "Effect of internal coagulant on effectiveness of polyvinylidene fluoride membrane for carbon dioxide separation and absorption", J. Membr. Sci., 311 (1-2), 153, (2008).

[49] Mansourizadeh, A. and Ismail, A.F., "A developed asymmetric PVDF hollow fiber membrane structure for CO_2 absorption", Int. J. Greenh. Gas. Con., 5 (2), 374, (2011).

[50] Yang, M.C. and Cussler, E.L., "Designing hollow-fiber contactors", AIChE J., 32(11), 1910, (1986).

[51] Lin, S.H., Hsieh, C.F., Li, M.H. and Tung, K.L., "Determination of mass transfer resistance during absorption of carbon dioxide by mixed absorbents in PVDF and PP membrane contactor", Desalination, 249(2), 647, (2009).