



Amine Based CO₂ Absorption in Membrane Contactor Using Polyvinyl Pyrrolidone-modified Polysulfone Flat Sheet Membrane: Experimental Study and Mass Transfer Resistance Analysis

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ABSTRACT

Membrane contactor using amine based absorbents is an efficient technology for CO₂ separation from gaseous mixtures. A novel porous polysulfone (PSF) flat membrane was prepared via non-solvent phase inversion method. The PSF membrane was modified by adding polyvinyl pyrrolidone (PVP) to the dope solution. The fabricated membrane was used in the serpentine flow field contactor module for CO₂ absorption. The membranes were characterized through scanning electron microscopy (SEM), atomic force microscopy (AFM) and contact angle analyses. The SEM results revealed that PVP-modified PSF membrane had a finger-like structure while the PSF membrane showed a sponge-like structure. AFM data and contact angle analysis demonstrated that the membrane porosity, surface roughness and hydrophobicity enhanced when PVP was added to the dope solution. These favorite specifications resulted in better CO₂ absorption flux of PVP-modified membrane which was 133% higher than that of unmodified PSF membrane. Different gas and liquid flow rates and absorbent concentration employed during CO₂ absorption experiments, demonstrated that increasing these parameters caused a great improvement in mass transfer rates of carbon dioxide. Investigation on mass transfer resistances presented an each individual phase, indicating that by increasing the flow rate of gas phase its contribution to overall mass transfer resistance significantly reduced which indicated that the predominant resistance was in the gas phase. In comparison, the mass transfer coefficient achieved using the PVP-modified PSF membrane was remarkably greater than that of PSF membrane.

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1. INTRODUCTION

Global warming as the consequence of greenhouse gases emission to the atmosphere will result in some environmental hazards such as less ice, more drought and more extreme weather incidents. Among greenhouse gases, CO₂ is regarded as the most hazardous gas with respect to its high concentration in the atmosphere and its greater role in greenhouse effect [1]. Hence, finding an efficient approach to solve the CO₂ problem existing in industrial off gas mixtures is an important issue in separation processes.

Nowadays, molecular sieve based adsorption, cryogenic distillation systems and physical and chemical absorption are conventional approaches applied for CO₂ removal [2]. Among those approaches, packed towers, bubble columns, venturi scrubbers and tray columns are extensively used as conventional gas/liquid contacting devices for CO₂ capturing by absorption into aqueous solutions [3]. However, the most commercial one is packed column using alkanolamines as absorbent solutions. There are some problems in operation of these contacting devices that restrict their applications. These limitations can be numbered as flooding, channeling, entrainment, foaming and also some drawbacks such as large size, low specific gas-liquid interfacial area, high capital and operating cost [4].

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An interesting alternative for the above mentioned conventional approaches is membrane-based gas separation. Although the application of this system was developed by decreasing the thickness and increasing the selectivity of membranes used in the system, the commercial application of this method has been limited due to low permeability and low mass transfer rate across gas separation membranes [5]. Thus, it is favorable to combine the advantages of membrane separation and gas-liquid absorption processes in a single unit. In this way, a novel approach has recently been emerged as membrane contactor to overcome the aforementioned problems. In this technique, the membrane is not a selective part of the system and just acts as a stationary barrier which offers effective contact between gas and liquid phases [6]. Hence, a membrane contactor serves as a modular system with high specific interfacial area, simple scale-up, separate control of gas and liquid streams and high selectivity with high mass transfer flux provided by liquid absorbent [7]. A major drawback in the performance of the membrane contactor module which reduces its removal efficiency is the additional mass transfer resistance, in addition to extra gas and liquid phase resistances, imposed by using the membrane. It is well understood that the diffusivity of gas phase is greater than the liquid phase, therefore, completely gas-filled membrane pores ensured by hydrophobic membranes with optimized pore size can diminish the membrane resistance [8].

Both membrane material and membrane contactor structure affects its separation performance. Although PTFE is considered as a membrane displaying high hydrophobicity and good absorption performance, it is an expensive material which restricts its application. Simons et al. [9] investigated the $\text{CO}_2 / \text{CH}_4$ separation in two hollow fiber membrane contactors using PP and poly phenylene oxide (PPO) membranes using amine as the absorbent. They concluded that the PP membrane demonstrated higher CO_2 absorption in a membrane contactor using the PP hollow fiber membrane and amino-acid salt solution as the absorbent. Their results demonstrated that the overall mass transfer coefficient was evidently higher, once a composite solution was applied compared to the single solution. Yan et al. [10] used PP hollow fiber membrane in a contactor for absorption of CO_2 from flue gas using potassium glycinate (PG) and monoethanolamine (MEA) solutions as absorbents. According to obtained data, the aqueous PG solution showed lower potential for membrane wetting after nearly 40 hours of continuous operation compared to MEA solution. In addition to the membrane material, its structure is an important factor in the success of membrane contactor performance. Thus, some researchers have attempted to modify hollow fiber membranes employing a variety of additives in the dope solution of membrane materials [11]. The synthesis of polyethersulfone hollow fiber

membranes using o-xylene as an additive of dope solution was investigated [12]. It was found that a significant reduction was resulted in water permeability and membrane pore size by applying this additive. Polysulfone based membranes have been applied in different membrane separation processes. Strong hydrophobicity, high resistnace against chemicals and heat renders them as good candidates for membrane gas absorption purpose. Rahbari et al. [13] investigated the influence of employing glycerol as the additive to the spinning dope of polysulfone membranes and showed that the membrane permeability increased using this additive leading to reduction of mass transfer resistance. Unlike hollow fiber membrane contactors, a few number of investigations can be found in the literature with focus on flat sheet membrane contactor [14] in which parallel or once-through flow pattern was used for directing fluid in the module. Zhang et al. [15] assessed the efficiency of PTFE and PP membranes with different porosities in flat-plate membrane contactors for CO_2 absorption with NaOH solution and indicated that the mass transfer rate was remarkably affected by the membrane porosity.

To our best knowledge, no research has been conducted for adsorption of CO_2 in a membrane contactor using polysulfone (PSF) with the serpentine flow field. Also, addition of polyvinyl pyrrolidone (PVP) to the dope solution of polysulfone membrane for CO_2 capturing has not been reported in the literature yet. This offers higher porosity which provides higher contacting surface between gas and liquid associated with higher CO_2 adsorption capacity. The effects of liquid and gas flow rates and concentration of MEA on CO_2 absorption fluxes and mass transfer resistances during the experiments are determined. The contribution of mass transfer resistance of separate phases to overall mass transfer resistance is also analyzed.

2. THEORY

2. 1. Governing Equations for Mass Transfer

According to the film theory, overall mass transfer in membrane contactor module can be considered as resistance in series model which takes place in three steps; i) mass transfer from the bulk gas phase into the membrane surface, ii) mass transfer through the membrane pores and iii) mass transfer from the membrane-liquid interface into bulk liquid phase [13]. Different resistances against CO_2 transprt across the gas absorption mambrane is schematically depicted in Figure 1. The flux of CO_2 ($\text{mol}/\text{m}^2.\text{s}$) through a flat sheet membrane is described by the following equation [16]:

$$J_i = K_i(C_i^{id} - C_{il}) = k_{ig}(C_{ig} - C_{img}) = k_{im}(C_{img} - C_{ieg}) = k_{il}E(C_{ie} - C_{il}) \quad (1)$$

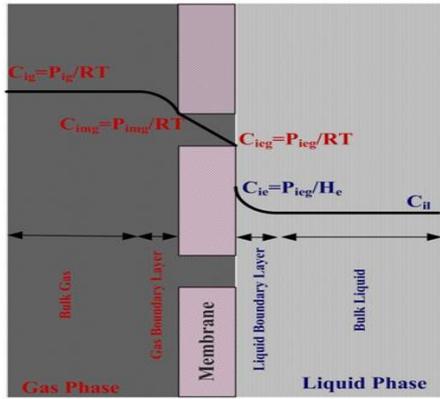


Figure 1. Different resistances across the hydrophobic microporous membrane

where K_l is an overall mass transfer coefficient defined based on the liquid phase (m/s); k_{ig} , k_{im} and k_{il} are the individual mass transfer coefficients (m/s) in the gas, membrane and liquid phases for the species CO_2 (represented by the subscript i), respectively; C_{il} and C_{ig} are CO_2 concentrations (mol/m^3) in the liquid and gas phases, respectively; C_{img} , C_{ieg} and C_{ie} are CO_2 concentrations at the gas-membrane, gas-liquid and the liquid-gas interfaces, respectively; C_i^{id} is CO_2 concentration in the liquid phase which is assumed to be ideally in equilibrium with its concentration in the gas phase and E is an enhancement factor applied accounting for the chemical reaction occurring in the liquid phase. For the fast reaction assumption, this term can be calculated using Equation (2) [16]:

$$E = \frac{\sqrt{k_2 D_{il} C_{amine}}}{k_{il}} \quad (2)$$

$$\log(k_2) = 10.99 - \frac{2152}{T(K)} \quad (3)$$

where C_{amine} is the absorbent bulk concentration (mol/m^3); k_2 is the rate constant defined based on the second-order reaction ($\text{m}^3/\text{mol}\cdot\text{s}$) calculated from Equation (3); [17] D_{il} denotes the binary diffusivity of CO_2 in liquid phase (m^2/s) and is defined through Equation (4) [18]:

$$D_{il} = D_{i,water} (\mu_{water} / \mu_l)^{0.8} \quad (4)$$

$$D_{i,water} = 2.35 \times 10^{-6} \exp(-2119/T) \quad (5)$$

where $D_{i,water}$ is the CO_2 -water binary diffusion coefficient (m^2/s) defined by Equation (5); μ_{water} and μ_l are viscosity of water and the liquid phase, respectively; and T is the temperature (K).

Getting back to Equation (1), by using $C_i = P_i/RT$ for gas phase concentrations and $C_i = P_i/H_e$ for equilibrium concentrations at the gas-liquid interface and also assuming $C_{il} = 0$ based on fast chemical reaction between

CO_2 and amine, we can rewrite Equation (1) as follows [19]:

$$J_i = K_l (P_{ig} / H_e) = (k_{ig} / RT) (P_{ig} - P_{img}) = (k_{im} / RT) (P_{mg} - P_{ieg}) = k_{il} E (P_{ieg} / H_e) \quad (6)$$

where P_{ig} , P_{img} and P_{ieg} are CO_2 partial pressures in the bulk gas phase, gas-membrane interfacial and membrane-liquid interface (Pa), respectively; H_e is Henry's law constant for solution of CO_2 in the liquid phase ($\text{m}^3\cdot\text{Pa}/\text{mol}$) [16-18] and R is the universal gas constant ($\text{J}/\text{mol}\cdot\text{K}$).

Based on the resistance in series model, the overall mass transfer coefficient defined based on the liquid phase (K_l) can be described by the Equation (7) [20, 21]:

$$1/K_l = 1/Ek_{il} + RT/(k_{im}H_e) + RT/(k_{ig}H_e) \quad (7)$$

2. 2. Determination of Mass Transfer Coefficient

The following equation gives a rough estimation for determining mass transfer coefficient in the liquid phase in laminar flow [22]:

$$k_{il} = 1.62(D_{il}^2 u_l) / (L d_{hyd})^{0.33} \quad (8)$$

where d_{hyd} is the module hydraulic diameter (m), u_l is the velocity of liquid stream (m/s) and L represents the length of channel (m). Estimation of the gas phase mass transfer coefficient is provided by Equation (9) [23]:

$$k_{ig} = 0.023(D_{ig} / d_{hyd})(\rho_g u_g d_{hyd}) / \mu_g^{0.8} (\mu_g / (\rho_g D_{ig}))^{0.33} \quad (9)$$

where D_{ig} is the binary diffusivity of CO_2 in the gas phase (m^2/s); ρ_g , μ_g and u_g are density (kg/m^3), viscosity (Pa.s) and gas phase velocity (m/s), respectively. Furthermore, the membrane mass transfer coefficient without wetting can be calculated using Equation (10) [24]:

$$k_{im} = \frac{\varepsilon_m D_{ie}}{\tau_m t_m} \quad (10)$$

where ε_m denotes the porosity of membrane, D_{ie} is the effective diffusivity (m^2/s), τ_m and t_m are membrane tortuosity and membrane thickness (m), respectively.

2. 3. Application of Wilson Plot Method

According to Equation (7), if liquid flow rate is kept constant, the term $1/(Ek_{il} + RT/(k_{im}H_e))$ will be independent of the gas flow rate. Therefore, the overall mass transfer coefficient (K_l), calculated based on liquid phase, would be dependent on the mass transfer coefficient of gas phase (k_{ig}) which is only proportional to the gas velocity (u_g) according to Equation (9). That is because the other physiochemical parameters of the system would be constant. Thus, a graph of $1/K_l$ versus $\lambda = RT/((H_e u_g^{0.83}))$, known as Wilson plot, yields a straight line that the membrane mass transfer coefficient

is obtained from its intercept [11]. Consequently, this alternative technique can be applied for evaluating the membrane resistance [25].

3. EXPERIMENTAL

3. 1. Materials Polysulfone beads (PS Mn: 22,000 Da, Sigma-Aldrich), N,N-dimethylformamide (DMF 99.5%, Dae Jung, Korea) and Polyvinyl pyrrolidone (PVP, with Mw=25,000 g/mol, Merck) were used for preparation of the casting solution as the membrane substrates polymer, the solvent and pore former additive, respectively [26]. Besides, Sodium dodecyl sulfate (SDS, Merck) was used to precipitate bath of phase inversion method.

3. 2. Membrane Fabrication The non-solvent phase inversion method was used to synthesize flat sheet PSF membranes. Two different dope solutions were prepared containing 18 wt% PSF beads with and without 1 wt% PVP (hereafter named as PSF and PVP-modified samples) dissolved in DMF. The solutions were allowed to mix for at least 8 h at 298 K until the homogeneous polymer dope solutions were completely formed and then degassed at room temperature for 12 h. After attaching a 100 micron thick polyester fabric to a polished glass plate, the dope solution was poured onto the polyester fabric. The precipitation bath for initiating the phase inversion contained distilled water, 0.1 wt% SDS and 2 wt% DMF [27]. The prepared membranes were immediately immersed in the precipitation bath for 30 min and then washed. For complete removal of residual solvents and additives, the membranes were remained into the water bath for at least 24 h. Finally, in order to dry the membranes, two sheets of filter papers were placed on both sides of the fabricated membranes for 24 h at room temperature.

3. 3. Membrane Characterization Tests

3. 3. 1. SEM and AFM Observation Surface and cross-section observation of fabricated flat membranes was performed using scanning electron microscopy (SEM model: KYKY-EM3200) operating at 24 kV. Before running surface scanning, physical vapor deposition method was used for coating the samples with a gold layer. Also, the membranes were fractured in liquid nitrogen to make ready them for the cross-section microscopy.

The surface morphology and roughness of the PSF membranes were investigated using atomic force microscopy (AFM model: Easyscan 2 Flex). The scan size of 5 μm \times 5 μm was selected for imaging the membrane surfaces at atmospheric pressure. Surface scanning was repeated three times for each membrane and the arithmetic average of three roughness values

was reported. The mean roughness value (S_a) measured by an AFM is defined as [28]:

$$S_a = \frac{1}{LW} \int_0^L \int_0^W |f(x, y)| dx dy \quad (11)$$

where $f(x, y)$ represent the surface relative to the center plane and L and W denote surface dimensions. Based on the pore size distribution function (Fr) obtained by AFM data, it is possible to estimate the mean pore size of membranes (r_{ave}) by Equation (12) [28]:

$$r_{ave} = \frac{\int_{r_{min}}^{r_{max}} r F_r dr}{\int_{r_{min}}^{r_{max}} F_r dr} \quad (12)$$

3. 3. 2. Measurement of Membrane Porosity and Contact Angle

Based on definition, membrane porosity (ϵ) is the volume of pores divided to the total volume of the membrane which is estimated by measuring the dry mass (m_{dry}) and wet mass (m_{wet}) of membranes and using Equation (13) [26]:

$$\epsilon = \frac{\frac{m_{wet} - m_{dry}}{\rho_w}}{\frac{m_{wet} - m_{dry}}{\rho_w} + \frac{m_{dry}}{\rho_p}} \quad (13)$$

where ρ_p is the polymer density (1.25 g/cm³ for polysulfone) and ρ_w is the water density.

To analyze the membrane ability for preventing the liquid phase penetration into membrane pores, the contact angles of distilled water on the fabricated membranes were determined by a contact angle goniometer (Dataphysics OCA 15, Germany) using sessile drop method. For each sample, the volume of a single water drop created on the membrane surface was 4 μl . Contact angle measurements were repeated for three times and the average value was calculated and reported.

3. 4. Construction of PSF Membrane Module

The membrane contactor module consisted of two flow field plates and a membrane interposed between them. In this study, the serpentine type of channels was formed on the 10 cm \times 10 cm flow field plates for directing gas and liquid streams. The main advantage of this kind of module is that it can be easily stacked for scale up purpose. Figure 2 shows the serpentine flow field used in this study and a parallel one usually used in the literature. The width, wall thickness and the depth of the channels were 1.0 mm.

3. 5. CO₂ Absorption Experiment The experimental setup employed to capture CO₂ in membrane contactor, is schematically represented in Figure 3. The feed gas

containing a mixture of CO₂ and nitrogen (15% CO₂ and 85% N₂) was introduced to one side of the membrane module. To get the best performance, a counter current flow mode was established in all experiments by passing monoethanolamine (MEA) solution on the other side of the membrane at different concentrations.

Using two ball valves embedded at the module inlet and outlet, samples were taken from the gas phase and CO₂ concentration was analyzed by TCD gas chromatography (GC) (Agilent, USA). A mass flow controller (Dwyer GFC-1107, USA) in the range of 50-250 ml/min was used to control gas flow rates at 298 K and atmospheric pressure. A peristaltic pump (Thomas SR25, Germany) with variable flow rates of 2-12 ml/min was applied for directing the absorbent solution in the liquid line. A pressure difference of 2-4 psig was applied between two sides of the membrane. This was carried out using a pressure gauge and a needle valve in the liquid stream which was necessary to avoid the dispersion of gas bubbles into the liquid. For each run, after at least 20 min when steady state condition was reached, three CO₂ loaded samples were taken under the same operating conditions and the average value of mass transfer fluxes were calculated. The double end point chemical titrimetric method was used for measuring CO₂ content in the outlet absorbent liquid which was essential to calculate the overall absorption flux of CO₂. In this method, hydrochloric acid solution as a titrant, phenolphthalein and methyl orange as indicators were used [29]. Due to using fresh MEA solution for each run, CO₂ concentration in the inlet liquid absorbent was equal to zero and hence based on the mass balance for the liquid phase and CO₂ logarithmic mean concentration difference (LMCD) across the membrane, the overall mass transfer coefficient based on liquid phase was determined using Equation (14) [30]:

$$K_L = \frac{Q_L C_{il,out}}{A_m \Delta C_{LMCD}} \quad (14)$$

where Q_L is the volumetric flow rate of liquid phase (m³/s); A_m represents membrane mass transfer surface area (m²) and $C_{il,out}$ is CO₂ concentration in the outlet liquid (mol/m³). ΔC_{LMCD} is calculated using Henry's constant by Equation (15) [31]:

$$\Delta C_{LMCD} = \frac{(HC_{ig,in} - C_{il,out}) - HC_{ig,out}}{\ln\left(\frac{HC_{ig,in} - C_{il,out}}{HC_{ig,out}}\right)} \quad (15)$$

4. RESULTS AND DISCUSSIONS

4. 1. Characterization of Synthetized Membranes

Specifications of PSF and PVP-modified fabricated membranes are listed in Table 1.

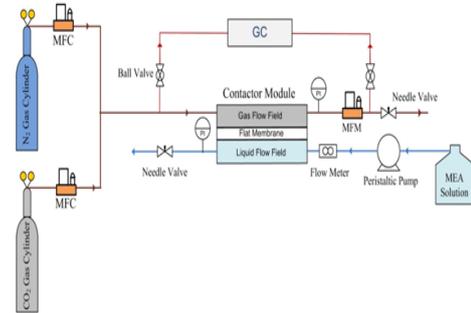


Figure 2. Different flow fields for directing fluids: a) two channel serpentine, b) four channel serpentine and c) parallel flow field

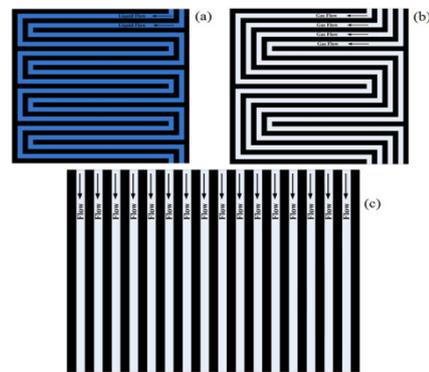


Figure 3. Experimental setup of CO₂ absorption using membrane contactor module

The surface and cross-section SEM images of PSF and PVP-modified flat sheet membranes are shown in Figure 4. As it is clear in Figures 4a and 4c, there is a significance difference in the morphology of two samples: a finger-like structure for the PVP-modified PSF membrane and a sponge-like one for the PSF membrane. In fact, the properties of dope solution changed by addition of PVP; the viscosity increased and the miscibility decreased. The change in the viscosity of dope solution reduced the solvent-non-solvent mutual diffusion. Faster precipitation of dope solution in non-solvent phase due to the decrease in the miscibility of dope solution was the other main reason for changing the morphology of PSF membrane from a sponge-like (for slow phase inversion) to a finger-like structure. This would result in a higher CO₂ flux.

By comparing Figures 4b and 4d, a change in surface properties of the membranes by addition of PVP can be observed. The PVP-modified membrane showed higher porosity and surface roughness compared to nonmodified PSF membrane which is also confirmed by the data reported in Table 1.

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 ($^\circ$)
PSF	129.29	64.22	7.38	69.6
PVP-modified	117.91	67.63	13.92	77.2

3D AFM images of PSF and PVP-modified fabricated membranes are displayed in Figure 5. In these pictures, the dark sections represent the depressions (membrane pores) and the bright ones are representatives of nodules. Furthermore, the height of the surface's lumps is the criteria to determine the roughness of the substrate [32]. Based on the values reported in Table 1, it is clear that by addition of PVP to the dope solution, the membrane surface morphology changed and the surface roughness increased.

According to the data reported in Table 1, the effect of PVP on membrane surface contact angle can be evaluated. From the table, it is clear that the contact angle of PSF sample increased when PVP was added to the dope solution and hence hydrophobicity of the fabricated membrane increased. As the hydrophobicity of the membrane increased, the probability of membrane wetting tended to decrease which is a positive sign for CO₂ removal efficiency.

4. 2. The Effect of Gas/Liquid Phase Flow Rates

To assess the CO₂ absorption performance, both fabricated membranes, i.e. PSF and PVP-modified membranes, were employed in the membrane contactor module. Figure 6 shows the absorption flux of CO₂ across the fabricated membranes. It can be concluded that by increasing the liquid velocity, the CO₂ absorption flux also increased. This can be attributed to the decrease in thickness of liquid boundary layer at high flow rates which increased mass transfer coefficients [33].

Moreover, in order to evaluate the impact of gas phase velocity on the overall mass transfer resistance, CO₂ absorption flux was measured in different gas flow rates from 50 to 250 ml/min. As it is obvious from the presented data in Figure 7, CO₂ mass transfer flux enhanced when gas flow rate was increased which can be as result of a decrease in the thickness of stagnant diffusion layer, too. Hence, both liquid and gas phase mass transfer resistances play prominent rules and should not be neglected in the overall mass transfer resistance for design and scale-up purposes. Similar observations was also reported by Lv et al. concerning the dependence of CO₂ mass transfer flux on the liquid and gas flow rates [34].

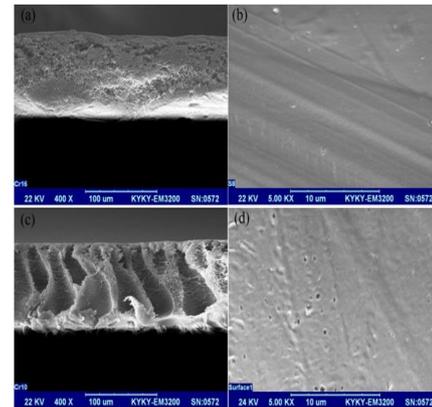


Figure 4. SEM images of fabricated PSF flat membranes: (a) cross section of PSF, (b) surface of PSF, (c) cross section of PVP-modified and (d) surface of PVP-modified membranes

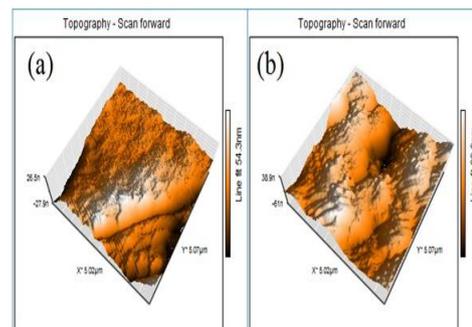


Figure 5. AFM images of fabricated PSF flat membranes: (a) PSF and (b) PVP-modified membranes

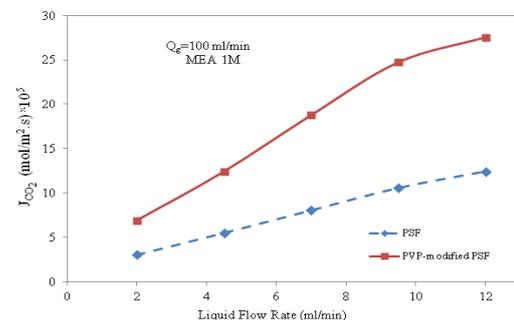


Figure 6. CO₂ absorption fluxes at various liquid flow rates using PSF and PVP-modified membranes (constant gas flow rate of 100 ml/min)

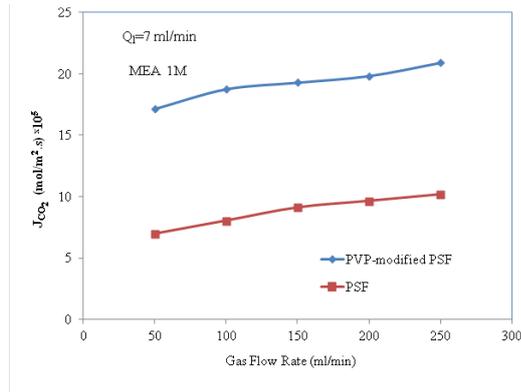


Figure 7. CO₂ absorption fluxes at various gas flow rates using PSF and PVP-modified membranes (constant liquid flow rate of 7 ml/min)

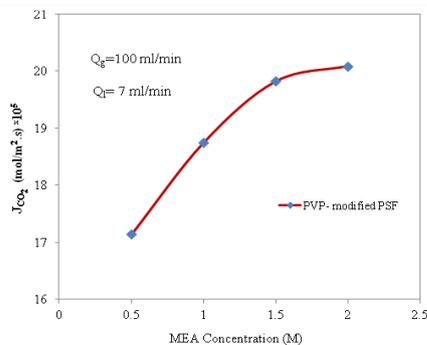


Figure 8. CO₂ absorption fluxes at various MEA concentrations using PVP-modified membrane

4. 3. Comparing the Performance of Different Membranes

According to the data of mass transfer flux plotted in Figure 6, the capability of PSF and PVP-modified PSF membranes for CO₂ absorption can be compared. It is clear that the absorption flux of PVP-modified PSF membrane was remarkably enhanced by addition of PVP as an additive. For example, the CO₂ absorption flux of PVP-modified PSF membrane was 2.33 times higher than that of the PSF membrane at the liquid flow rate of 7 ml/min. This can be considered as the consequence of the modification made in the structure of PSF membrane by addition of PVP. This modification increased the membrane porosity leading to an improvement in its permeability and therefore the gas-liquid contacting area. Also, increase of the membrane hydrophobicity improved its wettability resistance. Indeed, both factors were accounted for enhancement of CO₂ absorption flux using PVP-modified PSF membrane.

4. 4. The Impact of the Absorbent Concentration

As shown in Figure 8, absorption rate of CO₂ increased when MEA concentration increased from 0.5 to 1.5M and then remained almost constant at higher

concentrations, i.e. 2 M. This phenomenon can be explained by knowing that CO₂ diffused into the membrane pores at the gas-liquid interface will disappear more rapidly at higher MEA concentration leading to higher concentration gradient in the gas phase which is responsible for the improvement in CO₂ absorption flux. However, at the concentration higher than 1.5 M, it seems that enhancement of absorption flux is stopped by thermodynamic limitation imposed by solubility of CO₂ into MEA solution.

4. 5. Determination of Membrane Mass Transfer Coefficient

Wilson plot of $1/K_1$ vs. λ for two fabricated PSF flat membranes using 1M MEA solution as the absorbent is shown in Figure 9. Having in hand the enhancement factor and liquid phase mass transfer coefficient from Equations (2) and (6), respectively, k_{im} was determined from the intercept of Wilson plot, as mentioned before, membrane mass transfer coefficients for PSF and PVP-modified PSF membranes were 2.53×10^5 and 7.91×10^5 , respectively. This shows a remarkable increase in membrane mass transfer coefficient with addition of PVP to the dope solution. The reliability of this method can be confirmed by high R-squared value. Yang et al. [35] used the Wilson plot and reported a relationship of $1/K_1$ with reciprocal of fluid velocity to evaluate the liquid phase mass transfer coefficient in designing hollow fiber membrane contactors.

4. 6. Evaluation of Individual Mass Transfer Resistances to the Overall Transport

Referring to Equation (7), the resistance corresponding to each step in the abovementioned three-resistances mass transfer model can be estimated. The left side in this equation is known as the overall mass transfer resistance defined based on liquid phase and three terms in the right side represent mass transfer resistances of liquid ($1/EK_{il}$), membrane ($RT/(k_{im}H_e)$) and gas ($RT/(k_{ig}He)$) phases, respectively. The contribution of individual mass transfer resistance to the overall mass transfer resistance, called the fractional resistance (f), was estimated. Figure 10 shows the calculated data related to individual resistances, f_l , f_m and f_g , at different gas flow rates for PVP-modified PSF membrane.

Figure 10 indicates a reduction in percentage of the gas phase resistance to the overall mass transfer resistance with an increase in the gas flow rate. Rising gas flow rate from 50 to 250 ml/min reduced its contribution to the overall mass resistance by 28%. This reduction can be attributed to the decrease of the gas boundary layer thickness. This occurred in expense of an increase in the membrane phase resistance by 41%. The liquid phase resistance remained substantially constant as a result of fast chemical reaction occurring in the gas-liquid interface.

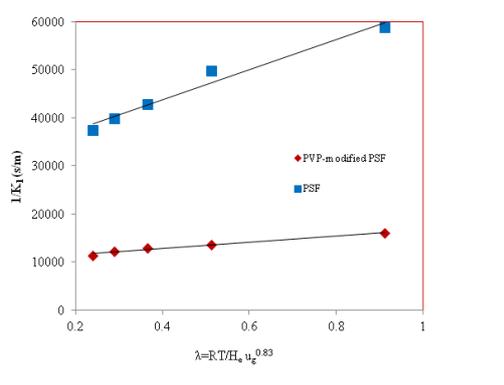


Figure 9. Wilson plot at various gas velocities

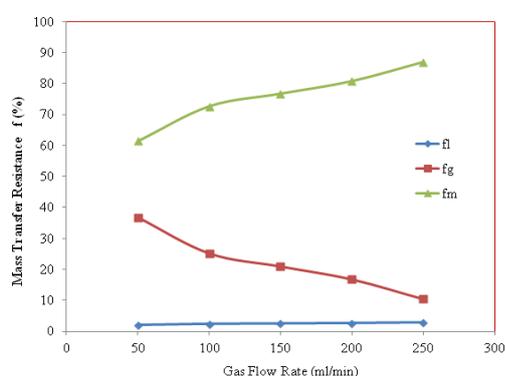


Figure 10. Contribution of mass transfer resistance of each step at various gas flow rates

5. CONCLUSION

The performance of flat sheet membrane contactors for CO₂ absorption by MEA was investigated using a new porous PSF membrane fabricated via phase inversion method. PVP was added to the dope solution of PSF membrane and hence the morphology of polysulfone membrane changed from a sponge-like to finger-like with the addition of PVP to the dope solution. CO₂ absorption flux of the PVP-modified PSF membrane was considerably higher than that of PSF membrane which was attributed to its higher surface area, porosity and hydrophobicity. Results indicated that an increase in the both liquid and gas flow rates enhanced CO₂ absorption flux due to the disturbance of stagnant film adjacent to membrane interface. The MEA concentration had a positive impact on the mass transfer flux of CO₂, too. It was concluded that addition of PVP to PSF membrane remarkably enhanced the mass transfer coefficient of the membrane. Mass transfer resistance analysis displayed that the overall mass transfer through the membrane is controlled by the gas phase. The results of the current study are promising from two points of view; first, it can enhance the CO₂ capture efficiency using the novel membrane developed

in this study. Second, the economy of the process can be also improved using a contactor with the lower surface area and smaller size for the same task.

6. REFERENCES

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Amine Based CO₂ Absorption in Membrane Contactor Using Polyvinyl Pyrrolidone-modified Polysulfone Flat Sheet Membrane: Experimental Study and Mass Transfer Resistance Analysis

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تماس دهنده غشایی بر پایه جاذب‌های آمینی، یک تکنولوژی موثر در جداسازی CO₂ از مخلوط‌های گازی می باشد. غشای نوین تخت متخلخل از جنس پلی‌سولفون به طریق روش تغییر فاز غیر حلال آماده شد. غشای PSF با اضافه کردن PVP به محلول افزودنی اصلاح گردید. غشای ساخته شده در ماژول مارپیچی غشایی به منظور جذب CO₂ مورد استفاده قرار گرفت. غشا مورد استفاده توسط آنالیزهای SEM، AFM و اندازه‌گیرنده زاویه تماس مورد ارزیابی قرار گرفت. نتیجه حاصل از آنالیزها نشان داد که شار جذب CO₂ با غشای اصلاح شده توسط PVP، ۱۳۳٪ بیشتر از غشای اصلاح شده PSF بوده است. دبی‌های متفاوتی از گاز و مایع و غلظت جاذب در حین فرایند جذب CO₂ نشان داد که افزایش این پارامترها، انتقال جرم CO₂ را به طور چشمگیری بهبود بخشید. مطالعات بر روی مقاومت انتقال جرم در هر فاز، نشان داد با افزایش نرخ جریان فاز گاز، اثر آن در مقاومت انتقال جرم کلبه طور قابل توجهی کاهش یافت که این موضوع نشان داد که مقاومت اصلی در فاز گاز بوده است. در مقام مقایسه، ضریب انتقال جرم بدست آمده با استفاده از غشای PSF اصلاح شده با PVP به طور چشمگیری بیشتر از غشای PSF بوده است.

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