An Experimental Study PVDF and PSF Hollow Fiber Membranes for Chemical Absorption Carbon Dioxide

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Abstract: Poly (vinylidene fluoride) (PVDF) and poly-sulfone (PSF) polymer solutions were made at a concentration of 18% by weight of the polymer as a non-soluble additive of polymer solution in 1-methyl-2-pyrrolidone (NMP) solvent. PVDF and PSF hollow fiber membranes were fabricated via the wet phase-inversion process. Fabricated membranes were characterized in terms of gas permeability, wetting resistance, water contact angle and overall porosity. In order to study the structure of the membranes made, the scanning electron microscopy images of the model (TM3000, HITACHI, Japan) were used. The morphology study indicates that the PSF membrane shows an open cross-section structure with smaller pore sizes. However, the PVDF membrane illustrates a thick sponge-like structure. The fabricated PVDF membrane shows higher wetting resistance, surface porosity, water contact angle, and N_2 permeability. The performance of the produced membranes was examined for the Absorption of carbon dioxide in a gas-liquid contactor membrane through the solution of mono-ethanolamine (MEA). The results show that CO_2 absorption flux of the PVDF hollow fiber membrane is higher than PSF hollow fiber membrane. The maximum CO_2 absorption flux of 8.10×10^{-3} (mole/m^2 s) at the liquid phase flow rate of 300 ml/min for PVDF hollow fiber membrane was achieved and also the maximum CO_2 absorption flux of 6.50×10^{-3} (mole/m^2 s) at the liquid phase flow rate of 300 ml/min for PSF hollow fiber membrane was obtained. It can be concluded that a porous hydrophobic hollow fiber membrane with high surface porosity and high gas permeability can be a productive alternative for CO_2 absorption through gas-liquid membrane contactors.
Keywords: hollow fiber membrane, gas-liquid contracting process, chemical absorption, PVDF, PSF

1. Introduction

Global warming is mainly due to greenhouse gas emissions, the major part of which is carbon dioxide gas[1-3]. Carbon capture and storage is one of several solutions recommended by the International Energy Agency to reduce the impact of human activities on the global climate. Using this technology may reduce carbon dioxide emissions by 14% to 17%[4]. The technologies currently used in the gas confectionery industry to absorb carbon dioxide gas are dependent on the absorption of carbon dioxide by amine-based chemical solvents. Monoethanolamide (MEA) is currently the most important industry-standard solvent for the carbon dioxide capture process[5-6]. Upon absorption of carbon dioxide gas, the carbon dioxide gas released. The minimum energy required to absorption 90% of carbon dioxide gas from a coal-fired power plant is about 4-5% of the pure electricity produced by the same plant. Carbon dioxide gas absorption by monoethanolamide without compression is about 5 times the minimum energy required. The release of this gas in the air has increased the temperature of the planet. According to all the reasons for the improvement and economization of gas refining equipment, the removal of carbon dioxide from industrial streams and domestic use, and especially natural gas (down to mole%), is essential because of the huge reserves of this critical substance in the country[7-9]. Extensive methods for removing carbon dioxide by Absorption in alkane amine ammonium solutions are available with conventional equipment, tray towers, bubble towers, filled towers, and spray towers. The use of alkane amines allows us to rehydrate the liquid solvent by simply heating. Therefore, a carbon dioxide capture process involves two major absorption and stripping units[10]. This process has operational problems such as overcrowding, channelization, persistence, and fatigue[11-13]. Today, these processes are known as a suitable alternative to the traditional gas absorption processes with an amine solution. Membrane processes have major benefits to absorption processes. Lower power consumption, lower operating costs, less initial installation and investment, no risk of fire and explosion, being very suitable and compatible with environmental laws, etc.[14-17]. The

nerve fiber membrane collision system is one of the preferred methods to be considered by researchers[18-20]. In this system, two-phase fluids collide with an appropriate membrane structure. For example, in a hollow fiber membrane, a common gas-liquid interface occurs at the mouth of the membrane pores[21-23]. Current developments in the chemical industry and similar industries have led to increased process speed and reduced energy consumption throughout the process[24-26]. One of the most important processes in such industries is the separation of different materials. To perform industrial processes, raw material components must often be separated and the product obtained from these processes must be separated and purified. On the other hand, in most industries, taking into account environmental laws, the need for separation processes is more than ever before[27]. In fact, as the separating processes and the related equipment are so large that in most industries, a large part of the cost of a product is related to the costs of separating and purifying the product[28]. For this reason, finding a simpler separation method at a lower cost can be considered. In choosing an appropriate separation method, the efficiency of those methods, access to equipment, separation costs, cost of construction and energy costs should be fully evaluated, taking into account environmental issues and policy issues[29]. Also, the separation targets must be specified in the process. In a separation process, different goals such as concentration, purification, separation, and displacement of the reaction balance can be considered. In this regard, membranes have been developed for the separation of various types of materials in solid, liquid, and gas states[30]. One of the most important factors is the type of polymer used in membrane fabrication. Typically the polymer used to make the membrane is for use in the hydrophobic gas-liquid membrane contactor system to prevent the penetration of the Absorption liquid into the membrane pores. The penetration of the Absorption liquid into the pores of the membrane will block the pores and reduce the level of contact between the gas and the liquid. This increases the mass transfer resistance and reduces the gas absorption flux[31-36].

The penetration of water into the membrane pores reduces the contact surface between the gas and liquid and reduces the mass transfer rate. For this reason, in liquid-gas membrane contact systems, water-based polymers, such as poly (vinylidene fluoride), are commonly used. On the other hand, the structure and physical properties of the membrane, such as the diameter of the pores, total porosity, the critical pressure of water entering the pores, the angle of water contact with the membrane, also affect the membrane function . Therefore, it is necessary to study the performance of various polymers in the gas-liquid membrane contact system[37-42]. The mechanism of CO_2 absorption is shown in Figure 1. Table 1 summarizes several findings of absorption performances that have been reported by various researchers for the past 10 years. Research objectives include the following:

1-Making a membrane of fiber between poly-sulfone and poly (vinylidene fluoride) in a phase separation method.

2-Determine the profile and structure of the membranes made.

3-Using membranes made to Absorption carbon dioxide gas by a 1 molar monoethanolamide aqueous solution in a gas and liquid membrane contact system.
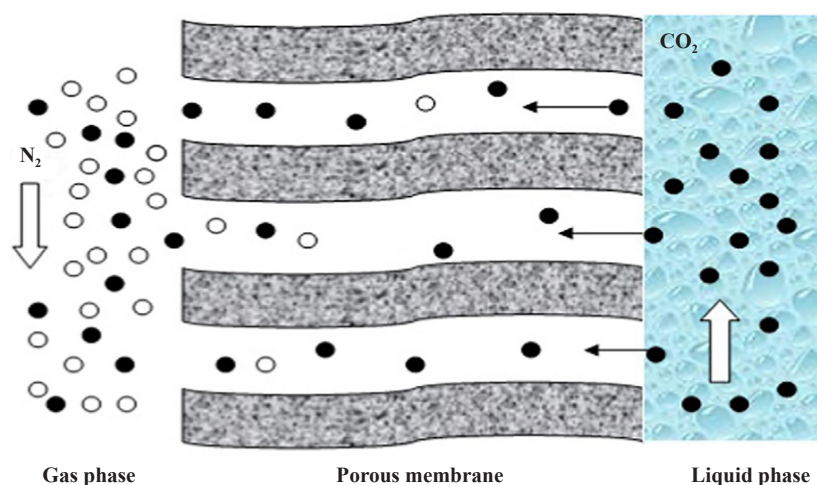

Figure 1. CO_2 absorption phase gas-liquid membrane contactors system[27]

Table 1. Research findings on CO_2 absorption flux by other researchers

Membrane type	Liquid absorbent	CO_2 absorption flux (mole m^{-2} s^{-1})	Reference
HF PVDF	1 M MEA	$8.0 * 10^{-3}$	[61]
PTFE	5 M MEA	$2.03 * 10^{-3}$	[62]
PTFE	0.03 AMP	$1.08 * 10^{-4}$	[63]
pp	0.5 M MEA	$4.4 * 10^{4}$	[64]
PVDF/triacetin	0.5 M NaOH	$(1-3.2) * 10^{-3}$	[65]
PVDF, PTFE	2 M MEA	$1.08 * 10^{-2}$	[66]
PVDF	1 M MEA	$7.2 * 10^{-4}$	[67]
PSF	1 M MEA	$3.9 * 10^{-3}$	[27]

2. Materials and methods

2.1 Materials

Poly-sulfone polymer Udel P-1700 (Solvay Advanced Polymers) and poly (vinylidene fluoride) Polymer Commercial (Kynar® 740, Mn = 156,000) from Arkema Inc. The USA were used to make the nylon fiber membrane. 1-methyl-2-pyrrolidine (NMP > 99.5%) was purchased from Merck, which was used as a non-purified solvent. Monoethanolamide (99%) supplied by Sigma-Aldrich was used as a gas absorbent. Water was used as a coagulation bath in the process of making membranes[1,43-45].

2.2 Polymer solution preparation

18% by weight solutions of poly-sulfone and poly (vinylidene fluoride) polymers were prepared in the diethylamide solvent. To make any kind of polymer solution, the specified amount of solvent was weighed and poured into a glass bottle. Then, the specific amount of each weighted polymer was gradually added to the solvent so that the polymer beads did not clump together[46-50]. The solutions were stirred using a mechanical stirrer to dissolve all the polymer grains in the solvent. After the polymer grains were completely dissolved in the solvent, the solutions were placed in ultrasonic for 1 hour to remove air bubbles in the polymer solutions. If there is an air bubble in the polymer solution, the bubble is formed on the surface of the bubble and the membrane is torn. The viscosity of the polymer solutions was also measured using a Cole Parmer viscometer, EW-98965-40, USA. The composition of the materials used to make the polymer solutions and the viscosity of the solutions are shown in Table (2).

Table 2. Composition of the materials polymer solutions and the viscosity of the solutions

polymer solutions	Polymer (Wt. %)	NMP (Wt. %)
PSF	18	82
PVDF	18	82

2.3 CO_2 Absorption experiment

The carbon dioxide gas uptake flux was measured with a 1 M monoethanolamide solution in a gas-liquid membrane contact system. For this purpose, a set of mid-hollow fiber membranes containing 10 membranes was inserted in a stainless steel module as described in Table (3). Pure carbon dioxide gas using the pressure of the gas tank in the membrane conduit and the 1 M monoethanolamide solution as a liquid adsorbent by pumping into the module shell and discordantly. The gas flow rate was constant at 200 ml/min and the fluid flow intensity varied in the range of 50-300 ml/min. The gas-phase pressure was set at 1 bar and the liquid phase pressure was 0.2 times higher than the gas phase pressure to prevent bubble formation in the liquid[51-53]. Carbon dioxide concentration was measured in the output fluid of the module by the titration method. To titrate 10 ml of the output fluid from the module that absorbed carbon dioxide gas was poured into an Erlenmeyer and added 12 ml of 1 M sodium hydroxide (NaOH) solution to dissolve the dissolved carbon dioxide gas. Not in the solution, there is completely ionized. Then 5 ml of barium chloride solution (BaCl$_2$) was added to the solution. Then the obtained solution was shaken well until all the carbon dioxide dissolved in the solution (physically or chemically) deposit as barium carbonate (BaCO$_3$). The residual amount of sodium hydroxide in the solution was titrated with HCl and phenolphthalein was used as the reagent. The amount of hydrochloric acid used in this step is used to calculate the amount

of carbon dioxide absorbed as a mole of carbon dioxide per mole of monoethanolamide. Before sampling for titration, the gas uptake test was performed in the gas-liquid membrane contactor system for 30 min to standardize the test conditions. The amount of hydrogen chloride (HCl) is used in this stage to calculate the amount of carbon dioxide Absorption by the moles of carbon dioxide (CO_2) to the number of moles of Mono-ethanol amine (MEA). Before taking samples, all tests were performed for 30 minutes to achieve a steady state.

$$M_{CO_2}\left(\frac{moL}{L}\right) = \frac{(N.V)_{HCL}}{V_{sample}}$$
(1)

The total area of the membrane was considered as the surface liquid-gas contact deal for mass transfer, so the empirical amount of carbon dioxide flux J_{CO_2} ($\frac{mol}{V_{sample}}$) is calculated from the following relation:

$$J_{CO_2} = \frac{Q_L.M_{CO_2}}{V_{sample}} * 1000$$
(2)

Where Q_L is Absorption flow rate (m^3s^{-1}), M_{CO_2} is the concentration of carbon dioxide in the Absorption solution (mol/L) and A_i is the collision surface between air-liquid (m^2). Absorption membrane contactor-module output flow rate was measured by a liquid flow meter. Gas-liquid contact surface is measured based on Absorption flow on the pipe or the surface contact module. When the liquid Absorption flows on the shell side, the surface area is calculated using the following relation:

$$A_0 = n\pi d_i L$$
(3)

Where n is the number of fibers (in this study, 10), d_i is inner diameter of fibers, and (m) and L are effective fiber length. In this system, two-phase fluid system uses a membrane structure appropriate to collide. For example, the shared level of gas-liquid is created in the opening of membrane pore. Gas-liquid hollow fiber membrane contactor can be a promising alternative for the CO_2 absorption processes. In this system, the porous membrane acts as a fixed interface between the gas and liquid phases without dispersing one phase into another. The form of the pilot reactor is shown in Figure 2.
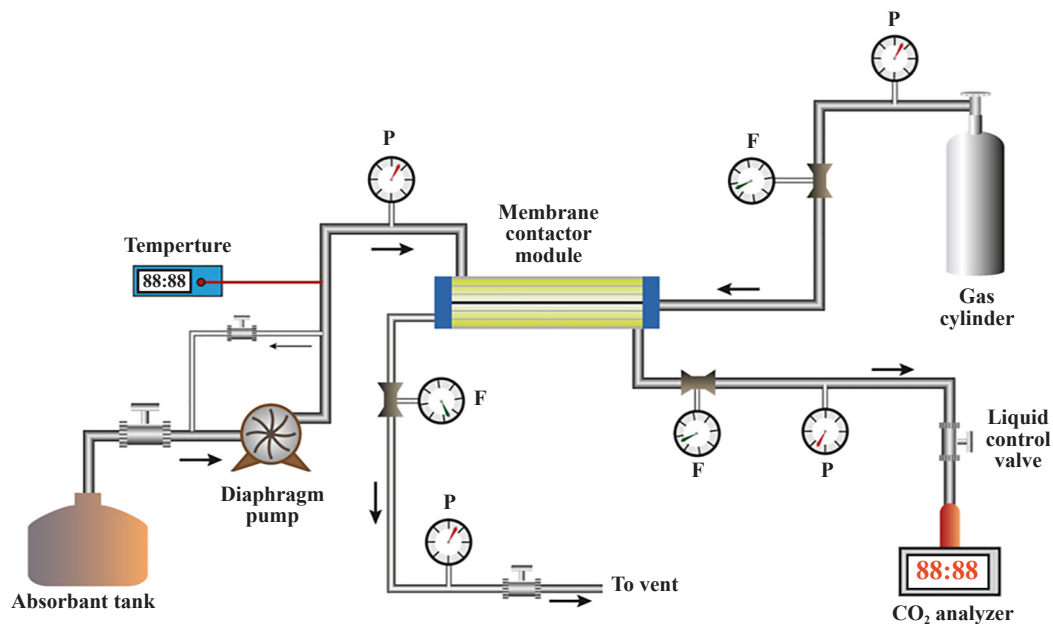

Figure 2. Absorption carbon dioxide system[27]

Table 3. Properties of fabricated PSF and PVDF hollow fiber membranes

Dope extrusion rate (ml/min)	4.5
Bore composition (wt. %)	80/200 NMP/Water
Bore flow rate (ml/min)	1.55
external coagulant	Tap water
Air gap distance (cm)	0.0
the outer diameter of the inner spinner (mm)	0.55-1.2
Spinning dope temperature (°C)	25
External coagulant temperature (°C)	25
The inner diameter of the module (mm)	14
Length of the module (mm)	270
Output diameter fiber (mm)	0.70-0.90
Input diameter of fibers (mm)	0.45-0.50
The effective length of fiber (mm)	150
The number of fibers	10
Contact area	4521 in

2.4 Fabrication and characterization of porous hollow fiber membranes

PVDF and PSF Polymer (PSF and PVDF Udel P-1700-Solvay Advance Polymer) for the building hollow fiber membranes: 1-methyl, 2-pyrrolidone (NMP > 99.5%) as a gross solvent and ethanol as non-solvent additives were purchased from Merck Company Germany. In all cases tap water was used as coagulation bath (spinning process). Mono-ethanol amine (MEA > 98%) was purchased from Sigma-Aldrich Co and used as the absorbent liquid. Table 2 and table 3 shows the Properties of fabricated PVDF and PSF hollow fiber membranes. dope was applied as an external coagulant for solidification of polymer solution resulting in formation of hollow fiber. After that the Spinneret hollow fiber was drowned into the water for three days to remove the ethanol and remaining NMP. Then it was naturally hung to be dried in environment temperature for one to two days.

3. Results and Discussion

The cross-sectional and internal surface structure of the membranes made by scanning electron microscopy was investigated. Figures 3 and 4 show the cross-sectional and internal surfaces of the nylon fibers. The membranes have an external diameter of from 0.70 to 0, 90 mm, the inner diameter is from 0, 45 to 0, 50 mm and the wall thickness is from 0,225 to 0,250 mm. Because all the membranes were made at the same rate of discharge of the polymer solution and the diffusion fluid flow rate, they were approximately equal in size. In general, the structure of the membrane depends on the rate of change in the phase of the polymer solution in the phase separation process. The change in the phase of the polymer solution depends on the viscosity of the polymer solution. A polymer solution with a viscosity has a faster phase change. The viscosity of the polymer solution affects the penetration rate of the coagulant to the membrane structure, so the less viscosity of the polymer solution results in a finger-shaped structure. The viscosity of polymer solutions is presented in Table 4. The cross-sectional images of the poly (vinylidene fluoride) membrane indicate that a thick sponge layer is formed in the middle of the membrane that is surrounded by a low thickness finger structure on the inner and outer surfaces of the membrane. Due to the hydrophobicity of the polymer of poly (vinylidene fluoride), the phase separation process is slow during the construction of this membrane, which can be attributed to the formation of a thick sponge layer in this membrane. As shown in Figures 3 (A) and (B), the poly-sulfone membrane cross-section has a thick thumb structure near the outer surface of the membrane, with a low thickness foam structure near the inner surface of the membrane. According to Table 4, the viscosity of the solution of poly-sulfone is determined from the viscosity of the solution the less poly(vinylidene fluoride) is due to the formation of the thickening of the fingers of this membrane. Due to the use of water (non-solvent) in the coagulation bath, the fingertip is formed at the outer surface of the poly-sulfone membrane because water as a non-solvent polymer separation rate accelerates the phase. From Figures 3 and 4 (C), it is understood that the use of high solvent concentration as Figures 3 and 4 (C) disintegrate slows down the phase separation process and forms

an unclosed inner surface with an open structure with a finer porosity and is the same structure of the study for Polyvinyl dine Fluoride membranes using 90% by weight of solvent as a fluid[54-56]. Removal of the inner shell of the membrane could reduce the membrane's resistance to mass transfer in the gas absorption process.
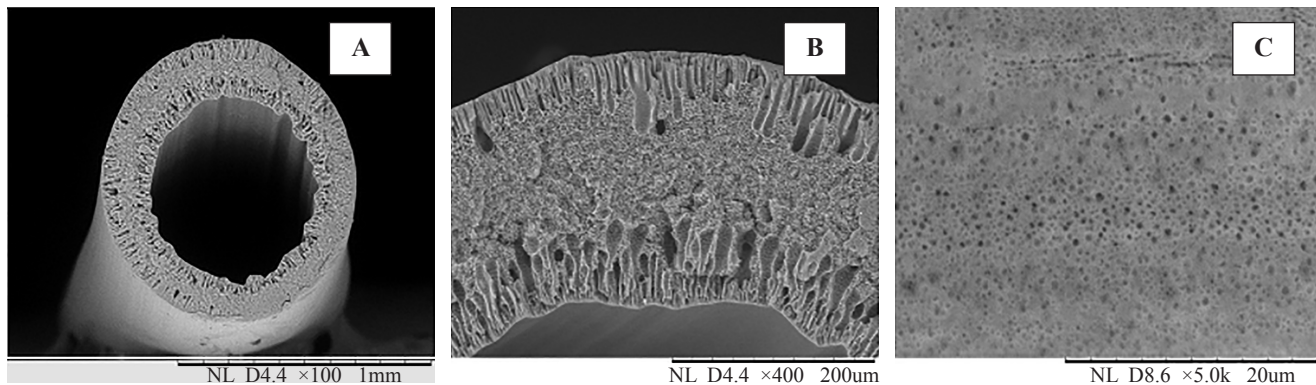

Figure 3. SEM cross-sectional images (A), cross-sectional area (B) and internal surface (C) of the fibers of the poly(vinylidene fluoride) (M1)
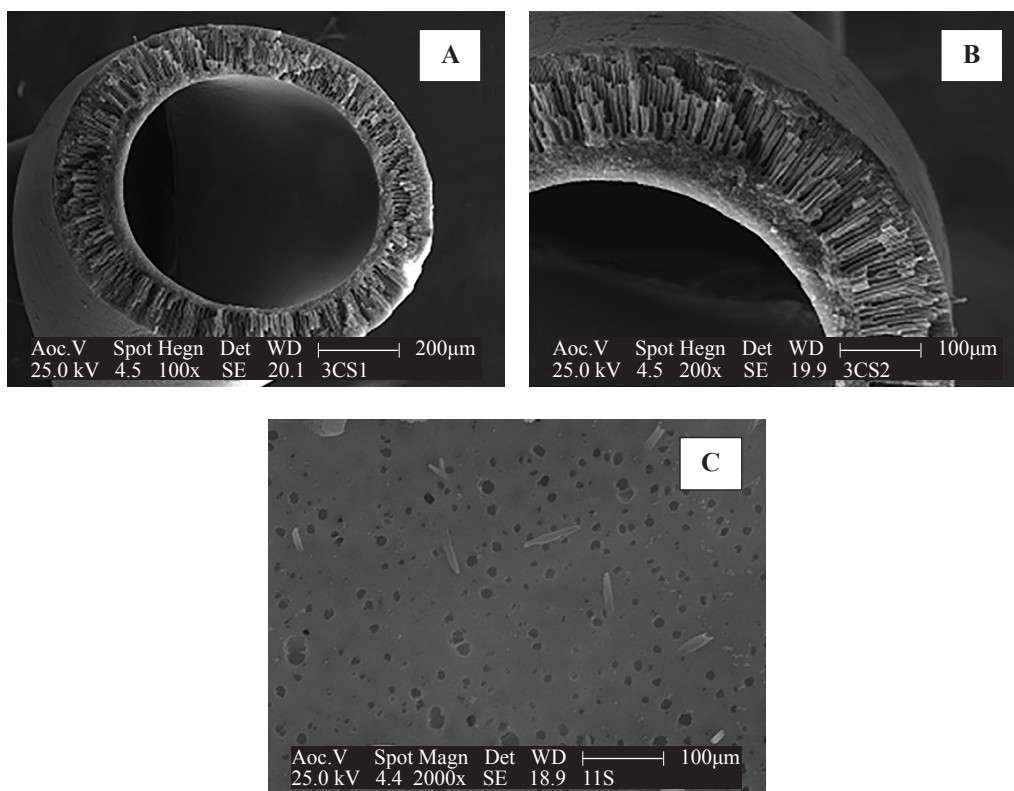

Figure 4. SEM cross-sectional images (A), cross-sectional area (B) and internal surface (C) of the fibers of the PSF (M1)

Table 4. Viscosity polymer solutions

polymer solutions	Viscosity polymer solutions (cp at 25 °C)
PVDF	2815.3
PSF	930.6

3.1 Characteristics of membrane

The results of measuring the average pore size, effective porosity, critical pressure input, total porosity and contact angle of the membrane surface with the water of poly (vinylidene fluoride) and poly-sulfone membranes are presented in Table 5. In the process of making asymmetric membranes, the overall porosity of the membrane can be controlled using

the relative composition of the material in the polymer solution. As shown in Table 5, the porosities of poly (vinylidene fluoride) and poly-sulfone membranes are 72.21% and 71.41%, respectively. The high porosity of the membranes produced is due to the low concentration of polymer in the polymer solution. To assess the resistance of the membranes to wetting, a critical pressure input test (CEPw) was performed. In the gas-liquid membrane contact, the membrane holes must be filled with gas and prevent the introduction of liquid into the membrane pores. The introduction of absorbent liquid into the membrane pores reduces the contact between the gas and liquid and increases the resistance of the membrane mass transfer. Therefore, the use of high-resistance wetting membranes against wetting is preferred for gas-gas applications in liquid-gas membrane contactor. As can be seen from Table 3, the membrane of the poly (vinylidene fluoride) fiber has a greater CEPw value than the nylon fiber membrane of the poly-sulfone. As already mentioned, poly (vinylidene fluoride) polymer is more hydrophobic than poly-sulfone polymer. Therefore, further hydrophobicity of the poly (vinylidene fluoride) membrane increases the contact angle with this membrane water and also increases the CEPw of this membrane. Figure 5 shows the penetration of nitrogen gas (N_2) for average pressure values. According to the data of Table 5 and Figure 5, the nitrogen gas permeability in the membrane of the poly (vinylidene fluoride) fiber membrane is higher than the poly-sulfone membrane. The higher the gas permeability in this membrane the average pore size of the membrane is larger. The chemical carbon dioxide gas test was carried out using a 1 molar monoethanolamide solution in a gas-liquid membrane contactor. Liquid adsorbent flows in the shell of the module and contact with the skin layer of the membranes, and pure carbon dioxide gas flows in the direction of the membrane cavity in the opposite direction to the liquid flow. The amount of carbon dioxide gas absorption of membranes was measured and compared with the change in the intensity of the adsorbent fluid flow. The results of the experiments on carbon dioxide gas adsorption in terms of fluid flow intensity are shown in Figure 6. Based on Figure 6, the flux absorption of carbon dioxide in both membranes increases with increasing absorption fluid flow due to the reduction in the thickness of the boundary layer of the liquid around the fibers by increasing the liquid velocity, which leads to a decrease in the fluid transfer mass transfer resistance. Also, with increasing fluid velocity, the flow regime changes from relaxed to turbulent, which results in the absorption of more carbon dioxide gas. As shown in Figure 6, in low currents from absorbing fluid, the carbon dioxide gas absorption flux increases both slowly and with gentle gradients, and the liquid flow rate is about 150 (ml/min) the slope of the gas absorption flux significantly increases, indicating a decrease in the thickness of the boundary layer around the fibers. It is also seen from Figure 6 that the adsorption rate of the poly (vinylidene fluoride) membrane gas is higher than that of the poly-sulfone membrane. As seen from the results of the specification of the membrane, the contact angle of the Polyvinyl dine Fluoride fiber membrane is greater than the polysulfone membrane, so the penetration of water into the pores of the poly-sulfone membrane is easier than the poly (vinylidene fluoride) membrane, and as this membrane is in the early stages of the process absorption gets wet. In this case, the membrane resistance controls the mass transfer process. The wetting of the membrane can increase the total transfer mass resistance and greatly affects the absorption flux[57-61]. Also, the effective porosity of the poly (vinylidene fluoride) membrane surface is much higher than that of the poly-sulfone membrane, resulting in a higher level of liquid and gas contact in the membrane than the poly-sulfone membrane, which increases the mass transfer rate. At the intrinsic intensity of the adsorbent flow of 300 ml/min[-1], the maximum flux of carbon dioxide gas is 8.10×10^{-3} (mole/m^{2}s) and $6.50.10 \times 10^{-3}$ (mole/m^2 s) to an arrangement was made for the poly (vinylidene fluoride) and poly-sulfone naphthenic membrane.

Table 5. Specifications of hollow fiber membranes made of PSF and PVDF

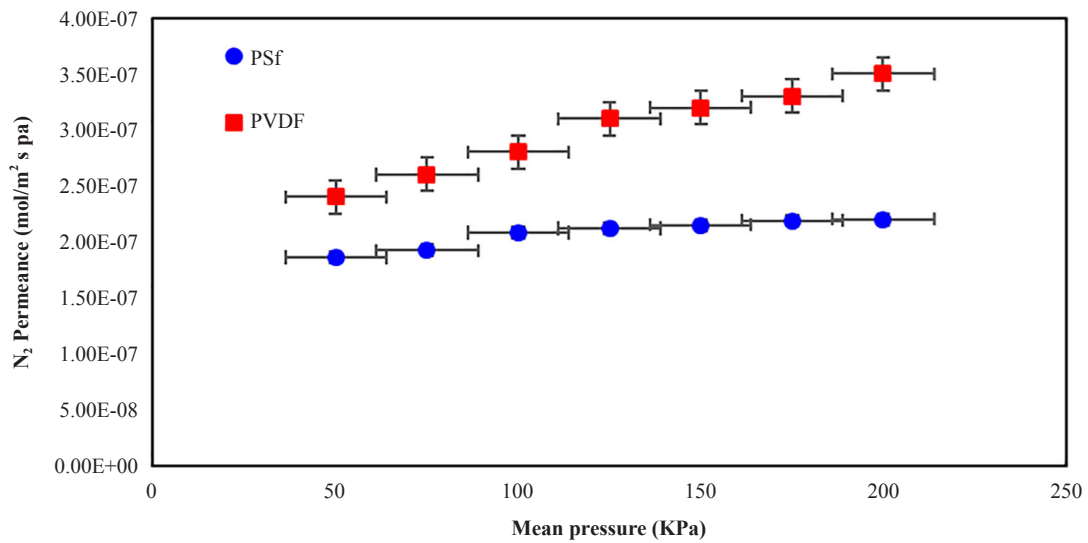| membranes	PSF	PVDF
The average pore size (nm)	13.42	21.18
Effective surface porosity (ε/Lp ($10m^{-1}$))	546	1250
Critical pressure of water entry ($\times 10^5$ Pa)	5.50	7.00
Total porosity (%)	71.41	72.21
Membrane braking pressure ($\times 10^5$ Pa)	8.50	9.50
Contact ratio with water	64.32	81.23

Figure 5. The amount of permeability Absorption of N_2 as a function of the average pressure of the hollow fiber membranes
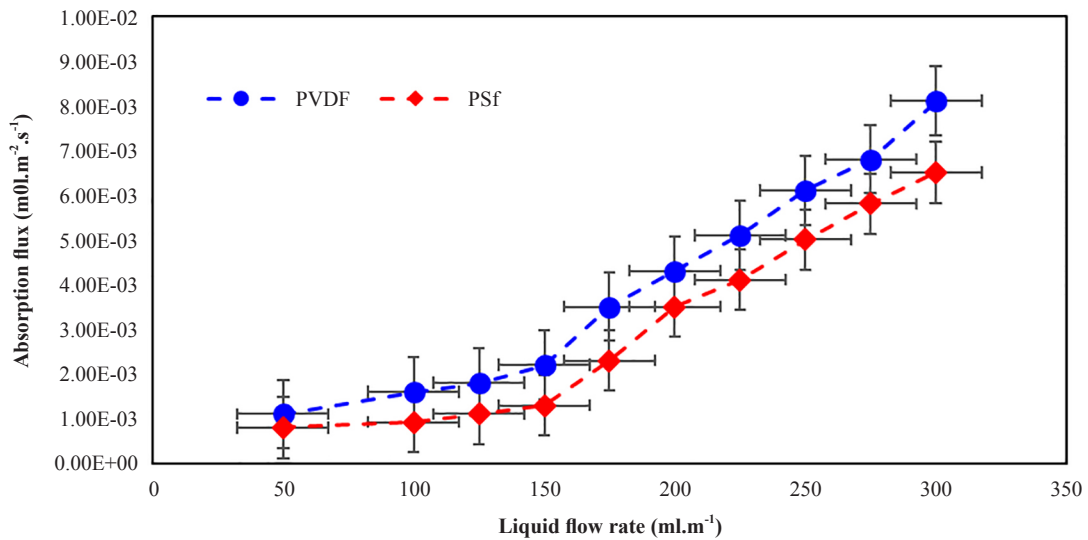

Figure 6. The effect of absorption flow rate (MEA) on the absorption of CO_2 in gas-liquid membrane contactors

3.2 Comparison of long-term carbon dioxide absorption gas hollow fiber membranes

To investigate the applicability of the membrane made in long-term carbon dioxide absorption gas hollow fiber membranes with distilled water, the long-term carbon dioxide absorption gas hollow fiber membranes experiment was carried out for 170 h (approximately 1 week) at ambient temperature, with the results shown in Figure 7. The results of long term CO_2 absorption experiment showed that the CO_2 absorption flux of the PVDF membrane decreased about 76% and reached to 6.88×10^{-3} (mol m^{-2} s^{-1}), 20 h after the beginning of the process. The CO_2 absorption flux of the PSF membrane decreased by about 24% and reached 9.75×10^{-3} (mol m^{-2} s^{-1}), 70 h after the beginning of the process. The hollow fiber membrane made with poly (vinylidene fluoride) polymer withstands moisture for up to 20 hours from the start of the process and exhibits an almost constant gas absorption flux, while the membrane made with polysulfide has withstood moisture for 70 hours. These factors make the polysulfone membrane more resistant to the penetration of the adsorbent liquid and therefore have a longer resistance to moisture. Also, the drop in absorption flux of the polysulfone membrane is significantly lower than that of the other membrane, indicating higher resistance to moisture.
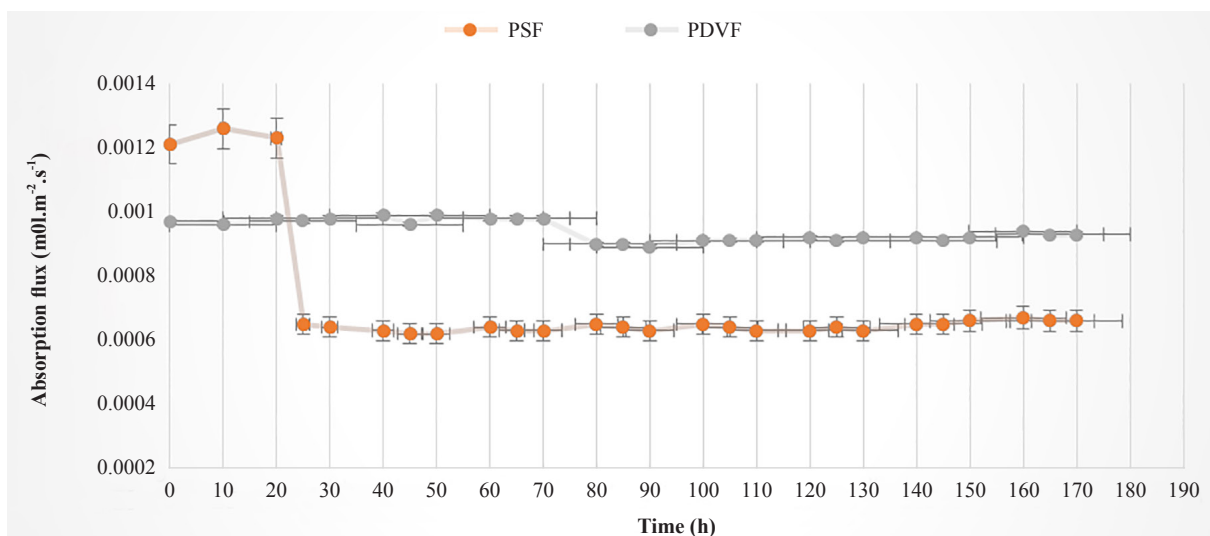
Figure 7. The carbon dioxide absorption flux over time

4. Conclusion

In this study, fiber membranes were made between poly (vinylidene fluoride) and poly-sulfone in a wet phase separation method. They were used for chemical absorption of carbon dioxide gas by 1 molar monoethanolamide solution in the gas-liquid membrane contact system. The results show that the total porosity of membranes is 72.71% and 71.41%, which is a high amount of porosity of the membranes because of the low concentration of polymer in the polymer solution. The critical pressure of the water inlet of the poly (vinylidene fluoride) membrane is significantly higher than the poly-sulfone membrane, which is due to the greater hydrophobicity of the membrane. Nitrogen gas permeability has increased for both membranes with increasing gas pressure, and this increase is higher for poly (vinylidene fluoride) membranes. The carbon dioxide gas absorption flux of both membranes increases with increasing absorption liquid velocity. Using a membrane made of Polyvinyl dine Fluoride polymer, the maximum flux absorption of $8.10 * 10^{-3}$ molar/m^2 in 300 ml /min was obtained from the adsorbent flow rate.

Conflict of interest

The author declares no competing financial interest.

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