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Zeolite-incorporated PVDF Hollow Fiber Membrane Contactor for Carbon Dioxide Stripping from Water

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ABSTRACT

Polyvinylidene fluoride (PVDF) hollow fiber mixed matrix membranes (HFMMMs) were prepared by incorporating hydrophobic Zeolite Socony Mobil–5 (ZSM-5) particles into the spinning dope. These membranes were then applied for CO_2 stripping from a diethanolamine (DEA) solution. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) analyses were carried out to examine the membrane morphology and surface roughness. The cross-sectional SEM images showed that adding ZSM-5 changed the membrane structure from a sponge-like form to a finger-like configuration. AFM results indicated that surface roughness increased when ZSM-5 was introduced into the dope solution. In CO_2 stripping tests, both stripping flux and efficiency improved as the liquid-phase velocity increased, whereas changes in gas velocity had only a minor effect on the flux. For the HFMMM, the maximum CO_2 stripping flux reached 2.30×10^{-3} mol/m²·s, and the highest stripping efficiency was 83.3% at a liquid velocity of 0.7 m/s. When the liquid temperature was raised from 80 to 90 °C at the same velocity, the CO_2 flux further increased from 2.30×10^{-3} to 6.30×10^{-3} mol/m²·s. In long-term operation, the HFMMM exhibited better resistance to wetting and showed a smaller decline in flux. Over 120 h, the plain PVDF membrane experienced a flux reduction of 73.5%, while the HFMMM showed only a 24.2% decrease.

Keywords: ZSM-5 particles; hollow fiber mixed matrix membrane; membrane contactor; CO2 stripping

1.0 INTRODUCTION

Hydrogen sulfide (H_2S), sulfur dioxide (SO_2) and specially carbon dioxide (CO_2) are known as the main greenhouse gases that elimination of them from post-combustion gases is a global concern [1]. Packed columns, bubble columns and spray towers are the traditional equipments which commonly are applied for this purpose, particularly in oil, gas and petrochemical industries [2]. In regeneration towers CO_2 is separated from solvent at partly over normal pressure and high temperature. This type of towers has several process limitations for instance flooding, loading, entrainment and channeling which participate in decreasing of mass transfer. In addition, high energy expenditure of these towers is one of the most important deficiencies that resulted in high cost of operation [3, 4]. Therefore, the development of alternative techniques for minimizing both environmental and economical unfavorable effects has attracted consideration of researchers.

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Gas-liquid membrane contacting process (MC) for CO_2 absorption and stripping through polymeric hollow fiber membranes (HFM) is one of the technologies which has been widely developed for this purpose [5]. One of the most advantages of MC is high surface area per unit volume ratio which can reduce the process cost and energy utilization. Also, the above-mentioned process problems do not happen as the liquid and gas flow, separately.

Incorporation of inorganic materials in polymeric membrane which is known as mixed matrix membranes (MMMs) can be used as an alternative instead of polymeric membranes. Available information about hollow fiber MMMs in literatures presented proper characteristics such as gas permeability, hydrophobicity and mechanical stability of MMMs [6-8]. Polymeric membranes have been widely used for CO_2 stripping processes due to their attractive advantages, including low cost, ease of fabrication, good mechanical flexibility, and straightforward scalability for industrial applications. However, these membranes often suffer from inherent limitations such as hydrophobicity (which restricts effective contact with aqueous solutions), relatively low thermal and chemical stability under harsh operating conditions, and a trade-off between permeability and selectivity that limits overall performance. To overcome these drawbacks, the incorporation of inorganic fillers to form mixed matrix membranes (MMMs) has emerged as a promising strategy, although the application of MMMs specifically for CO_2 stripping processes has been investigated only rarely to date. For instance, montmorillonite (MMT) nanoclay has been incorporated at various loadings into a PVDF spinning dope to produce hollow fiber mixed matrix membranes for CO_2 stripping from water. The resulting membranes exhibited elongated finger-like channels and higher surface porosity. They also showed increased contact angles and improved resistance to wetting relative to unmodified PVDF fibers. When 5 wt.% MMT was added, the CO_2 stripping flux increased by about 38% compared with the plain PVDF membrane under identical operating conditions [9].

As noted earlier, adding inorganic nanoparticles to polymer matrices is a well-known strategy for enhancing membrane surface hydrophobicity. ZSM-5, an aluminosilicate zeolite with high silica and low aluminum content, has been widely used as a filler, adsorbent, and catalyst in membrane-related applications. ZSM-5 zeolite was selected as the inorganic filler in this study due to its distinct advantages over many other zeolites commonly used in gas separation applications. Its well-defined medium-pore structure, consisting of intersecting 10-membered ring channels (approximately 0.51–0.56 nm in diameter), provides effective molecular sieving and diffusion pathways for CO_2 while restricting larger or less desirable molecules, contributing to good selectivity [10]. High-silica ZSM-5 exhibits pronounced hydrophobic characteristics compared to low-silica zeolites, which reduces competitive water adsorption in humid environments and preserves CO_2 uptake under realistic operating conditions. Additionally, ZSM-5 offers superior thermal and chemical stability, often stable up to temperatures exceeding 1000 °C in high-silica forms, outperforming more hydrophilic frameworks that are prone to structural degradation or dealumination under harsh conditions [11]. While low-silica zeolites may display higher absolute CO_2 adsorption capacities in dry, low-pressure scenarios due to stronger electrostatic interactions with extra-framework cations, ZSM-5's balanced CO_2 affinity—driven by physisorption and moderate quadrupolar interactions—combined with its hydrophobicity and stability, makes it particularly suitable for incorporation into mixed matrix membranes for CO_2 stripping processes[8]. Han *et al.* [10] modified ZSM-5 using

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alkyltrichlorosilanes with different chain lengths, including Octyltrichlorosilane (OTS), decyltrichlorosilane (DTS), dodecyltrichlorosilane (DDTS) and hexadecyltrichlorosilane (HDTS). Their results showed that longer alkyl chains produced more hydrophobic ZSM-5 surfaces, forming a hydrophobic layer around the particles. When ZSM-5 was treated with HDTS, the contact angle increased dramatically from 12.5° for the unmodified particles to 160° at 25 °C for the modified ones.

In our previous work [7], ZSM-5 particles were similarly modified with HDTS following the approach of Han *et al*., after which PVDF/ZSM-5 hollow fiber mixed matrix membranes were produced with varying particle loadings. These membranes were used in a gas–liquid contactor for CO_2 absorption, and an optimal ZSM-5 content of 0.5 wt.% in the PVDF spinning solution was identified.

Diethanolamine (DEA), a secondary alkanolamine, serves as the CO_2 absorbent in this work. We selected DEA because it offers a practical compromise in amine scrubbing systems. Its heat of reaction with CO_2 is lower than that of primary amines such as monoethanolamine (MEA) – roughly 70 kJ/mol versus 85 kJ/mol – leading to reduced energy demands during thermal stripping [12]. DEA is also less corrosive than MEA, shows lower reactivity toward sulfur species, and maintains reasonable stability. While its CO_2 absorption kinetics are slower than MEA's, this makes DEA suitable for applications prioritizing efficient regeneration over maximum initial uptake rates, unlike tertiary amines such as methyldiethanolamine (MDEA) which exhibit even poorer CO_2 reactivity [13]. Despite these attributes, research on mixed matrix membranes for CO_2 stripping from DEA solutions remains sparse, with few studies examining the impact of inorganic fillers like ZSM-5 on mass transfer, membrane-amine compatibility, or long-term performance in such systems. The present study addresses this gap by investigating ZSM-5-based MMMs specifically for DEA-mediated CO_2 stripping.

In this study, a mixed matrix membrane containing 0.5 wt.% of surface-modified ZSM-5 was used in a gas–liquid membrane contactor to strip CO_2 from aqueous DEA solutions. The effects of key operating parameters including liquid-phase velocity, gas-phase velocity, and liquid temperature on CO_2 stripping flux and efficiency were examined. In addition, the long-term performance of the membrane was assessed over 120 hours of continuous operation.

2.0 EXPERIMENTAL

2.1 Fabrication and Characterization of HFMs

ZSM-5 zeolite (Tianjin Hutong Global Trade Co., Ltd., China) was first modified prior to membrane preparation. A total of 5 g of ZSM-5 was mixed with 25 g of toluene (Merck) and stirred at 500 rpm for 1 h at room temperature to ensure uniform dispersion. Subsequently, 4 g of HDTS (Alfa Aesar) was added, and the mixture was refluxed at 70 °C for 12 h. The resulting product was filtered and rinsed with toluene to remove any unreacted HDTS, followed by drying at 110 °C for 5 h to eliminate residual solvent.

The modified ZSM-5 was dispersed in 1-methyl-2-pyrrolidone (NMP, >99.5%, Merck), and the suspension was sonicated for 45 min at 45 °C to break up particle agglomerates. PVDF polymer (Kynar® 740, Arkema Inc., USA) was pre-dried at 70 °C for 24 h to remove moisture and then gradually introduced into the ZSM-5/NMP suspension under vigorous

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stirring (600 rpm) until a uniform dope solution was obtained. Before spinning, the dope was ultrasonicated and allowed to degas at room temperature for 24 h to remove entrapped air. The compositions of the spinning solutions are listed in Table 1.

Hollow fibers were fabricated using a wet phase inversion spinning process, described in detail in a previous study[14]. The hollow fiber membranes were prepared using a dope extrusion rate of 4.50 mL/min, while the internal coagulant consisted of an NMP–water mixture containing 80 wt% NMP and 20 wt% water, delivered at a flow rate of 1.55 mL/min. Tap water was used as the external coagulation bath, maintained at approximately 25 °C. Spinning was carried out without an air gap, and the spinneret used had an outer diameter of 1.20 mm and an inner diameter of 0.55 mm. After spinning, the fibers were immersed in water for three days to wash out residual solvent, then air-dried under ambient conditions.

Table 1. The relative composition of the solutions

Solution name	NMP (wt.%)	ZSM-5 (wt.%)	PVDF (wt.%)	Solution viscosity (centipoises)
2815.3	18	0.0	82	PVDF
2785.2	18	0.50	81.5	PVDF/ZMS-5

The properties of the fabricated PVDF hollow fiber membranes including average pore size, effective surface porosity, total porosity, water contact angle, collapsing pressure, critical entry pressure of water (CEPw), and nitrogen gas permeation were evaluated following the methods described in earlier publications [15]. The average pore size and effective surface porosity were determined through nitrogen permeation tests following the procedure of Li *et al.* [16], as detailed in our previous work [15]. Water contact angle measurements were carried out to assess the hydrophobicity of the membrane outer surface. The wetting resistance of the fibers was examined using CEPw, while overall porosity was obtained via a gravimetric technique. The mechanical strength of the membranes was assessed by measuring their collapsing pressure. Morphological features including cross-sections and inner and outer surfaces were observed using a tabletop SEM (TM3000). Surface roughness (Ra) of the outer membrane surface was quantified with an AFM instrument (SPA 300 HV, Japan). The viscosity of the polymer dope solutions was measured using a viscometer (model EW-98965-40, Cole Parmer, USA). The characterization results of the hollow fiber membranes are summarized in Table 2, while a detailed discussion of these findings can be found in our previous publication [7].

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Table 2. Properties of HFMs

Membrane name	Average pore size (nm)	Effective surface porosity ε/Lp ($\times 10^2 m^{-1}$)	CEPw ($\times 10^5$ Pa)	Overall porosity (%)	Collapsing pressure ($\times 10^5$ Pa)	Water contact angle (°)	Roughness (Ra)	N_2 permeance at 4 bar (10^{-6} mol/m^2 Pa s)
PVDF	25.18	1250	4.00	72.21	8.50	81.23	4.23	4.83
PVDF/ZMS-5	36.23	2983	3.50	75.64	6.00	87.23	7.14	9.2

2.2 Carbon Dioxide Stripping Test

The CO_2 stripping test was conducted using a MC system. Twenty hollow fibers were assembled into a stainless-steel membrane contactor module. The gas–liquid membrane contactor was constructed using a module with an internal diameter of about 15 mm and an overall length of 250 mm. The hollow fibers installed inside the module had outer diameters ranging from roughly 0.9 to 1.0 mm, while their inner diameters varied between 0.45 and 0.50 mm. Only a portion of each fiber contributed to mass transfer, giving an effective length of around 150 mm. In total, twenty fibers were packed into the module.

A 1 M aqueous diethanolamine (DEA, >99%, Merck) solution was prepared, saturated with pure CO_2 in a gas–liquid membrane contactor, and then used as the liquid feed for the CO_2 stripping experiments. Pure N_2 served as the sweep gas on the shell side of the module, while the CO_2-loaded DEA solution was introduced into the lumen side of the hollow fibers in a counter-current configuration. To minimize membrane wetting, the gas stream was always initiated before introducing the liquid.

Unless otherwise specified, the liquid phase temperature and pressure were maintained at 80 °C and 0.7×10^5 Pa, respectively. The temperature of the DEA solution was controlled using an external electric heater installed in the feed tank, as illustrated in Figure 1. The heater was equipped with a digital temperature controller to regulate the solution temperature within ±0.5 °C of the set value. Continuous magnetic stirring was applied in the feed reservoir to ensure uniform temperature distribution and to prevent thermal gradients within the solution. The liquid lines were insulated to minimize heat loss before entering the membrane module. The solution temperature was continuously monitored using a calibrated thermocouple immersed in the feed tank, and the heater output was automatically adjusted to maintain the desired operating temperature (80–90 °C) throughout the stripping experiments. The liquid pressure was kept 0.2×10^5 Pa higher than the gas pressure to avoid bubble formation in the liquid stream. CO_2 concentrations at the module inlet and outlet were determined using a double titration method [17], which was then used to calculate the stripping flux and efficiency. The experimental setup for the stripping membrane contactor system has been described in previous studies [18]. The CO_2 stripping efficiency (η) was determined using the following expression:

$$\eta(\%) = \left(1 - \frac{C_{l,o}}{C_{l,i}}\right) \times 100 \tag{1}$$

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where $C_{l,o}$ and $C_{l,i}$ represent the CO_2 concentrations in the liquid phase ($mol \cdot m^{-3}$) at the outlet and inlet of the membrane module, respectively. The CO_2 stripping flux was determined using the following equation:

$$J_{CO_2} = \frac{\left(C_{l,i} - C_{l,o}\right) \times Q_l}{A_i} \quad (2)$$

where J_{CO_2} is the CO_2 stripping flux ($mol \cdot m^{-2} \cdot s^{-1}$), Q_l is the liquid flow rate ($m^3 \cdot s^{-1}$), and A_i is the effective inner surface area of the hollow fiber membranes. The flow diagram of the experimental system has been described in previous studies [19]. A schematic representation of the setup is shown in Figure 1.

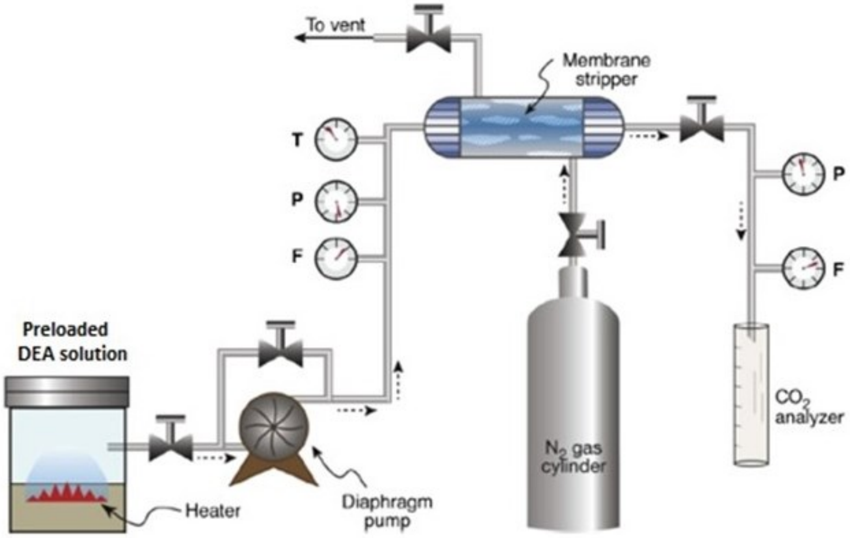

Figure 1. Schematic representation of the experimental system [18]

3.0 RESULTS AND DISCUSSION

3.1 SEM Images Analysis

The membrane structure is influenced by both the phase inversion rate and the composition of the casting solution. Previous studies have shown that a rapid phase inversion process typically leads to the formation of asymmetric membranes with more porous morphologies[20]. Figure 2 presents SEM images of the cross-sections and inner and outer surfaces of the unmodified PVDF hollow fiber and the membrane containing 0.5 wt.% ZSM-5.

As seen in Figure 2(A1), the neat PVDF fiber contains a central sponge-like layer surrounded by thin finger-like regions adjacent to the inner and outer surfaces. This sponge-like structure results from the slow penetration of water into the middle of the fiber during phase inversion. In contrast, Figure 2(B1) shows that incorporating ZSM-5 into the spinning solution reduces the thickness of the sponge-like core and promotes the development of longer, thicker finger-like channels. This change is attributed to the lower viscosity of the ZSM-5-containing dope, which accelerates solvent–nonsolvent exchange and thus speeds up phase inversion [21]. Furthermore, adding hydrophobic particles to the

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polymer solution narrows the miscibility gap in the ternary phase diagram, enhancing demixing and favoring the formation of finger-like structures.

The inner surfaces of the hollow fibers are essentially free of a dense skin layer because a bore fluid with a high concentration of NMP was employed (see Figures 2(A2) and 2(B2)). Previous studies have shown that using a solvent-rich bore solution suppresses skin layer formation on the lumen side of the membrane [22, 23]. The outer surface morphologies of the membranes are presented in Figures 2(A3) and 2(B3). Compared with the inner surfaces, the outer surfaces appear significantly smoother, indicating the presence of a skin layer formed as a result of using water as the external coagulant, which induces a faster phase inversion process.

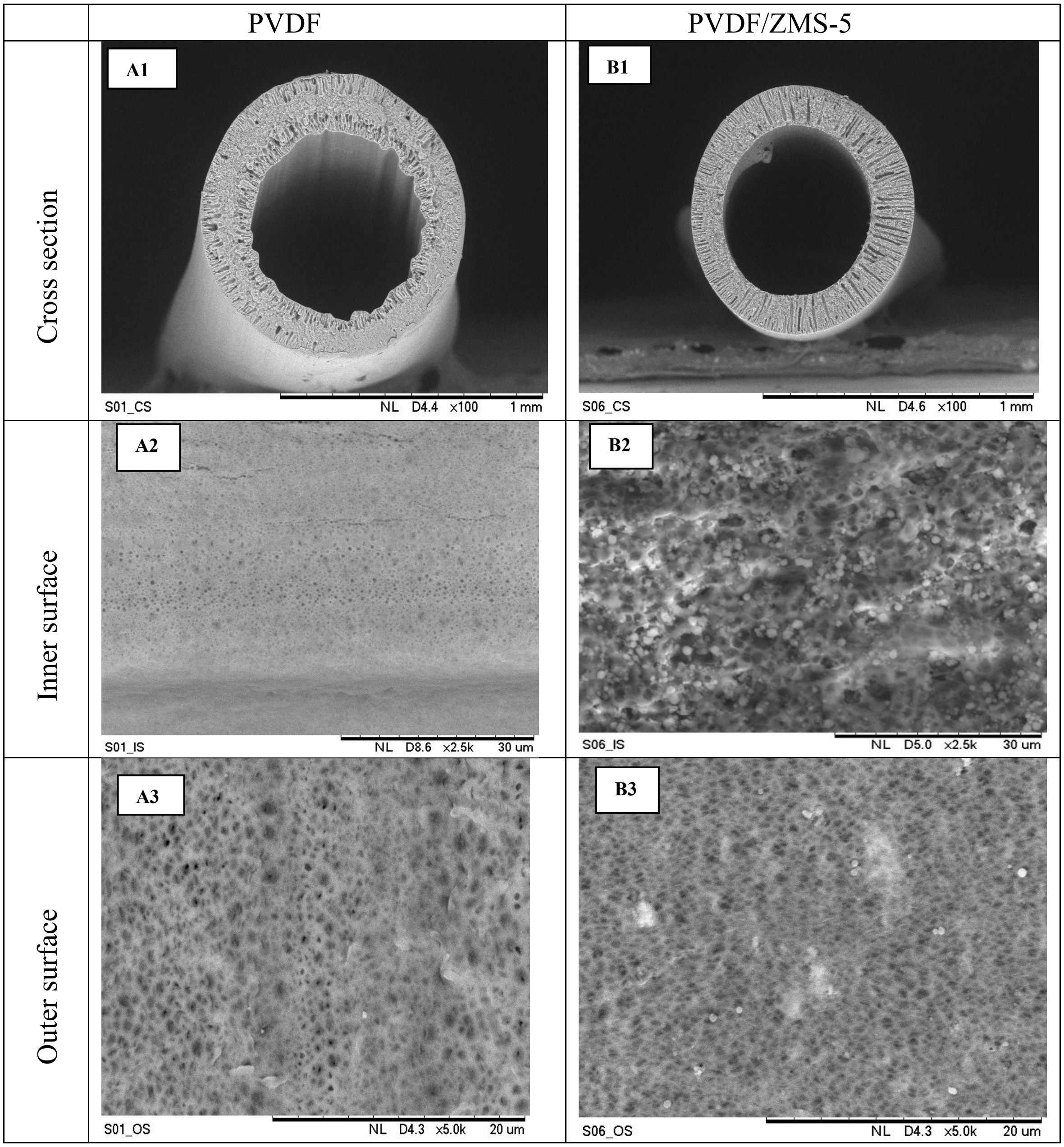

Figure 2. SEM image of fabricated PVDF HFMs

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For membrane PVDF/ZMS-5, small white spots can be observed on the outer surface. These features are attributed to localized agglomeration of ZSM-5 particles, which may occur during dope preparation when particle–particle interactions exceed polymer–particle interactions. In mixed-matrix membranes, such localized agglomeration can potentially influence membrane performance by creating non-uniform regions that may affect mass-transfer pathways or interfacial compatibility. However, in the present study, the agglomerated regions were limited and sparsely distributed, while the overall particle dispersion remained adequate. As a result, no significant deterioration in membrane integrity or separation performance was observed, indicating that the level of agglomeration was not sufficient to adversely affect the overall membrane behavior.

3.2 Carbon Dioxide Stripping Results

CO_2 stripping experiments using a 1 mol/L DEA solution were performed with the hollow fiber membranes. Figures 3 and 4 present the effects of liquid velocity on CO_2 stripping flux and stripping efficiency, respectively. In all tests, the CO_2 concentration at the liquid inlet was kept at 5×10^{-3}(mol/L).

Both flux and efficiency increased as the liquid velocity rose. This improvement is attributed to the reduction of the liquid-side boundary-layer resistance at higher velocities, which enhances mass transfer. A similar behavior has been reported for CO_2 absorption in hollow fiber membrane contactors [24], and other studies have also shown that increasing the liquid velocity lowers mass transfer resistance [25, 26]. Moreover, higher flow rates shift the flow regime from laminar toward turbulent, which further promotes CO_2 desorption. For example, increased turbulence achieved by installing a stirrer was found to boost gas stripping flux in PTFE and PES flat-sheet membranes [27].

For membrane PVDF/ZMS-5, the maximum stripping flux of 2.30×10^{-3} (mol/m^2 s) and the highest stripping efficiency of 83.3% were obtained at a liquid velocity of 0.7 m/s. The superior performance of the mixed matrix membrane (PVDF/ZMS-5) over the plain PVDF membrane is attributed to its higher surface porosity, greater hydrophobicity, and increased N_2 permeance (Table 3). The enhanced surface porosity in particular provides more accessible pathways for CO_2 to diffuse through the membrane pores.

Although increasing the liquid velocity enhances CO_2 stripping flux and efficiency by reducing the thickness of the liquid boundary layer and improving turbulence, further increases beyond the investigated range are not expected to produce proportional improvements. At sufficiently high velocities, the liquid-side mass transfer coefficient approaches a practical maximum, and the resistance of other steps (membrane pores and gas phase) becomes comparatively more significant. Moreover, excessively high liquid flow rates shorten the residence time of the solution within the membrane module, which may limit the overall extent of CO_2 desorption despite improved local mass transfer coefficients. From a practical standpoint, higher liquid velocities also increase pumping energy requirements and may raise the risk of membrane pore wetting due to elevated hydraulic pressure. Therefore, an optimal liquid velocity exists where mass transfer enhancement and energy efficiency are properly balanced.

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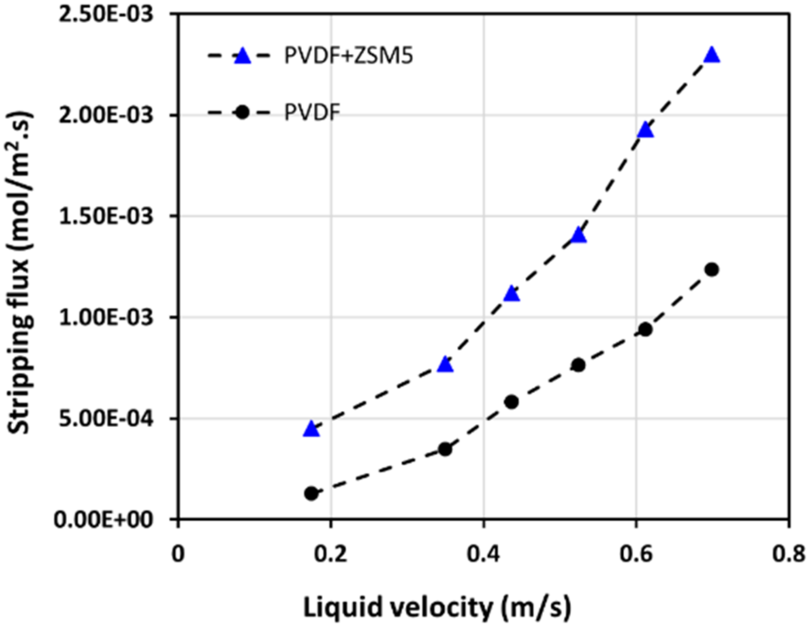

Figure 3 CO_2 stripping flux *vs.* liquid velocity. (M_{DEA}=1 mol/l, T=80 ºC, Q_l =50-200 mL/min, Q_g=100 mL/min)

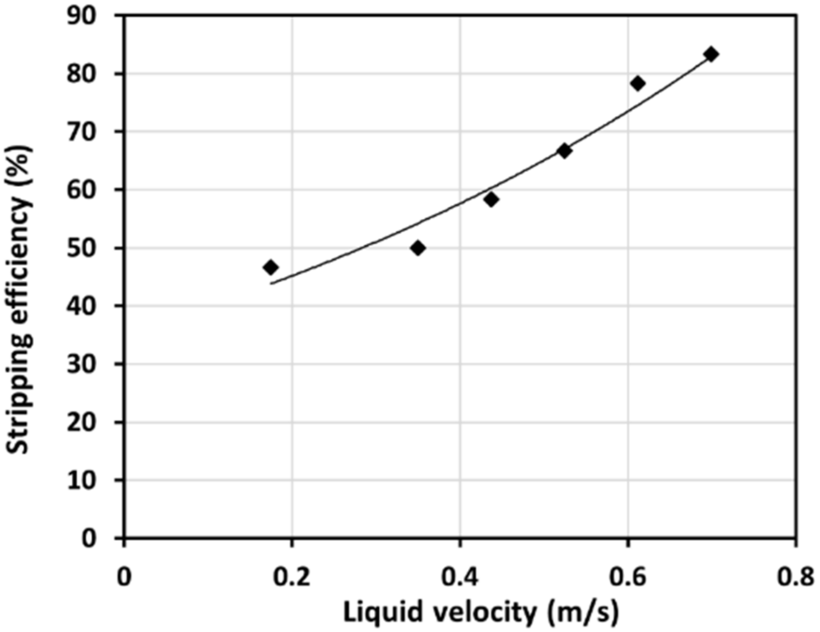

Figure 4. Stripping efficiency of membrane PVDF/ZMS-5 *vs.* liquid velocity (M_{DEA}=1 mol/l, T=80 ºC, Q_l =50-200 mL/min, Q_g=100 mL/min)

The influence of gas velocity on the CO_2 stripping flux was examined at a DEA solution temperature of 80 °C. As shown in Figure 5, increasing the gas velocity results in only a slight improvement in stripping flux. Similar observations were reported by Rahbari-Sisakht *et al.* [28], who found that gas-phase mass transfer resistance had minimal impact on CO_2 stripping when using surface-modified PVDF hollow fiber modules. Another study calculated the mass transfer coefficients for the liquid phase, gas phase, and membrane

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when using polysulfone (PSf) hollow fibers. Their analysis showed that the liquid-phase mass transfer coefficient (k_L) was the smallest, indicating that the liquid film contributes the most resistance.

Overall, previous research consistently demonstrates that CO_2 stripping in membrane contactors is largely governed by the liquid-side mass transfer resistance. The trends observed in Figure 5 confirm this conclusion; the limited impact of gas velocity indicates that the liquid-phase resistance dominates the overall mass transfer process.

The relatively minor influence of gas velocity on CO_2 stripping flux indicates that gas-phase mass transfer resistance is not the controlling step under the present operating conditions. Once a sufficient sweep gas flow is provided to maintain a low CO_2 partial pressure on the shell side, further increases in gas velocity only slightly reduce the already small gas-side boundary-layer resistance. Consequently, increasing gas velocity beyond 0.02 m/s is not expected to significantly enhance overall performance. In addition, higher gas flow rates would increase pressure drop and energy consumption without substantial improvement in stripping efficiency. These observations confirm that the overall process is predominantly controlled by liquid-phase mass transfer resistance rather than gas-phase limitations.

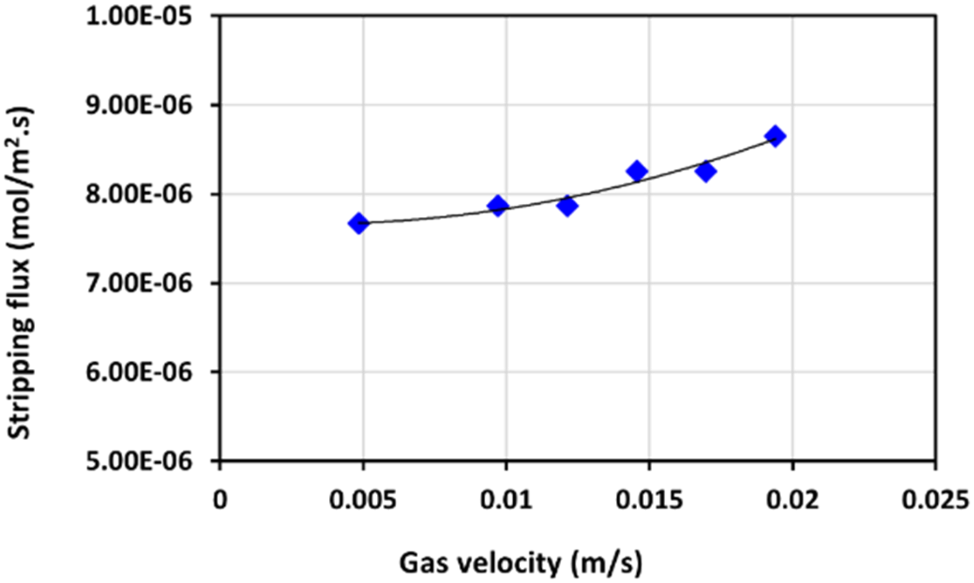

Figure 5. CO_2 stripping flux of membrane PVDF/ZMS-5 *vs.* gas flow rate. (M_{DEA}=1 mol/l, T=80 °C, Q_l=100 mL/min, Q_g=50-200 mL/min)

The influence of DEA solution temperature on the CO_2 stripping flux was evaluated, and the results are shown in Figure 6. The data indicate that temperature has a strong effect on the stripping performance. This enhancement is primarily due to the decrease in CO_2 solubility as the liquid temperature increases [29]. Temperature also directly affects both the equilibrium constant of the chemical reaction and the diffusion coefficient, further promoting CO_2 release from the solution [26].

Weiland *et al*. [30] reported that raising the solution temperature by 10 °C increased the equilibrium partial pressure of CO_2 by a factor of 5–8. Consistent with this, the stripping flux in our study rose from 2.30×10^{-3} to 6.30×10^{-3} $mol\cdot m^{-2}\cdot s^{-1}$ at a liquid velocity of 0.7

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m/s when the DEA solution temperature was elevated from 80 to 90 °C. This clearly demonstrates the strong positive influence of temperature on the CO_2 desorption rate.

Although 90 °C may appear relatively high for polymeric membranes, PVDF is well known for its good thermal stability compared with many other common membrane polymers. PVDF typically exhibits a melting temperature in the range of 160–170 °C and maintains structural integrity at temperatures well above 100 °C under non-oxidative conditions. Therefore, short-term operation at 90 °C during the stripping experiments is not expected to cause thermal degradation of the polymer matrix.

However, prolonged exposure to elevated temperatures may gradually influence certain membrane properties, including mechanical strength, crystallinity, and pore structure stability. In membrane contactor applications, sustained high-temperature operation may also increase the likelihood of pore wetting due to changes in surface tension and polymer relaxation effects over time. Although no visible structural deformation or performance instability was observed during the duration of the present experiments, these potential long-term thermal effects should be considered in extended industrial operation and warrant further durability studies.

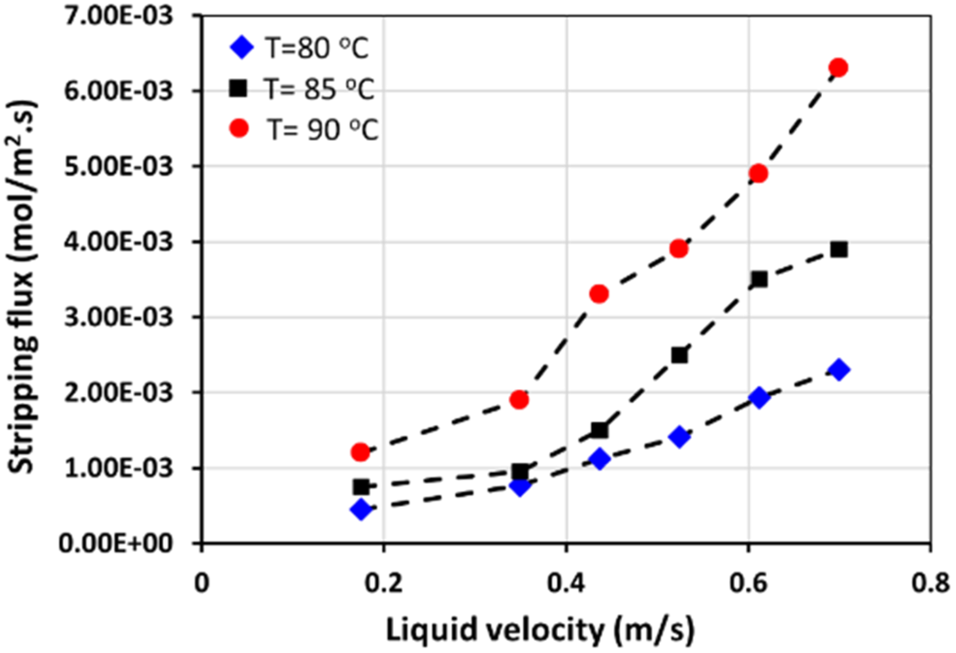

Figure 6. CO_2 stripping flux of membrane PVDF/ZMS-5 *vs.* liquid phase temperature. (M_{DEA}=1 mol/l, Q_l=100 mL/min, Q_g=100 mL/min)

A long-term CO_2 stripping experiment was conducted to evaluate the stability of membrane performance over 120 hours of continuous operation (Figure 7). For the unmodified membrane, the stripping flux gradually declined, resulting in a total reduction of 73.5% by the end of the test. In contrast, the PVDF/ZMS-5 membrane exhibited only a 22% drop during the first 20 hours, after which the flux stabilized and remained nearly constant for the remainder of the experiment. This initial decline in PVDF/ZMS-5 flux is likely due to minor wetting of the membrane pores and partial saturation of the CO_2 absorbent, while the overall structural integrity and particle dispersion limited further

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deterioration. The total flux reduction for PVDF/ZMS-5 membrane was approximately 24.2%, significantly lower than that of PVDF, demonstrating the enhanced operational stability imparted by the incorporation of ZSM-5.

These results indicate that the PVDF/ZSM-5 mixed matrix membrane possesses superior resistance to wetting compared with the control membrane. The observed decrease in flux is likely linked to capillary condensation of water vapor within the membrane pores. When the gas- and liquid-phase pressures are similar, partial pore wetting can occur through this mechanism, which typically leads to a short initial period of stable flux before further changes are seen[31]. Because the flux became steady after a brief operating period, it can be inferred that the DEA solution did not significantly alter the membrane structure or surface properties, and that capillary condensation was the dominant factor governing partial wetting.

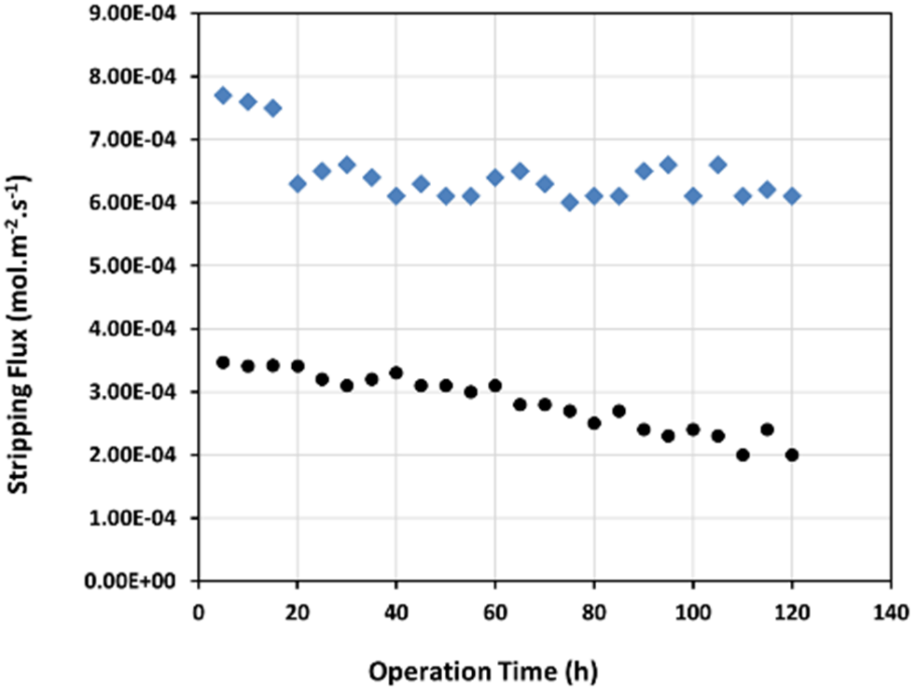

Figure 7. Long-term study of CO_2 stripping process over 120 h. (● plain PVDF, ♦ PVDF+ ZSM-5) (Q_l=100 mL/min, Q_g=100 mL/min, $P_l = 0.7\times10^5\ Pa$, $P_g = 0.5\times10^5\ Pa$, T=80 °C).

Table 3 summarizes and compares the performance of the best membrane developed in this study (PVDF/ZSM-5, 0.5 wt.%) with representative membranes reported in the literature for CO_2 stripping via membrane contactors. The comparison includes membrane material, absorbent type, operating conditions, and reported stripping performance.

Although some membranes (e.g., PVDF-PEG and PEI systems) demonstrate higher instantaneous stripping fluxes, many studies report significant long-term flux decline due to membrane wetting. In contrast, the PVDF/ZSM-5 mixed matrix membrane developed in the present work exhibits a balanced performance, combining competitive stripping flux (6.30×10^{-3} mol·m^{-2}·s^{-1} at 90 °C) with substantially improved operational stability, showing only 24.2% flux reduction over 120 h of continuous operation.

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Table 3. Comparison of CO_2 Stripping Performance of the Present PVDF/ZSM-5 Membrane with Reported Membrane Contactors

Membrane Material	**Absorbent**	**Key Operating Conditions**	**Maximum Stripping Flux ($mol\cdot m^{-2}\cdot s^{-1}$)**	**Key Findings / Limitations**	**Reference**
PTFE hollow fiber	MEA	Effect of gas & liquid velocity, temperature	Not explicitly stated	Flux enhanced by temperature & liquid velocity; long-term performance limited by wetting	[26]
PVDF hollow fiber	Water	60 °C, 60 mL/min	32% efficiency (flux not reported)	Efficiency improved with temperature; flux decreased with higher liquid flow rate	[32]
PEI hollow fiber (14 wt.%)	DEA	Membrane contactor system	2.7×10^{-2}	Highest flux at 14 wt.% PEI; improved wetting resistance with higher polymer content	[33]
Dense PTMSP	RTILs	$\Delta p = 10$ bar, $\Delta T = 20$ °C	Overall mass transfer coefficient: $(1.6–3.8) \times 10^{-3}$ cm/s	Stable long-term performance; membrane resistance ~8% of total	[34]
PVDF-PEG / PEI-PEG	DEA	Liquid velocity 0.7–0.85 m/s	4.0×10^{-2} (PVDF-PEG)	High flux but severe long-term flux reduction due to wetting	[35]
PP + 1.5 wt.% silica NPs	Not specified	Liquid velocity 2.5 m/s	Higher than many hydrophobic membranes (exact value not specified)	Flux improved with NP loading; enhanced hydrophobicity	[36]
PVDF + 0.5 wt.% ZSM-5 (HFMMM)	DEA (1 M)	80–90 °C, 0.7 m/s liquid velocity	6.30×10^{-3} (at 90 °C)	Improved wetting resistance; only 24.2% flux decline over 120 h	Present Study

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Furthermore, unlike dense membranes such as PTMSP, where membrane resistance can contribute noticeably to mass transfer limitations, the porous PVDF/ZSM-5 hollow fiber membrane maintains high surface porosity and hydrophobicity, minimizing membrane resistance while improving wetting resistance.

Overall, the comparison highlights that the main advantage of the present membrane lies not only in its stripping performance but also in its enhanced long-term stability, which is a critical factor for practical industrial applications.

4.0 CONCLUSIONS

Modified ZSM-5 zeolite was incorporated into the PVDF dope solution to produce hollow-fiber mixed matrix membranes (HFMMMs) for CO_2 stripping from DEA solutions. SEM cross-section images revealed that adding ZSM-5 shifted the membrane morphology from a sponge-like structure to a more pronounced finger-like configuration. The inclusion of ZSM-5 also increased the surface roughness of the outer layer because the zeolite particles were partially exposed on the membrane surface, which in turn raised the outer-surface contact angle. The stripping flux and removal efficiency improved with an increase in liquid flow rate, and the HFMMM consistently exhibited higher fluxes than the neat PVDF fibers due to its greater surface porosity and higher N_2 permeance. Changes in gas flow rate, however, had little influence on CO_2 stripping performance. A substantial rise in CO_2 flux was observed when the DEA solution temperature was increased from 80 °C to 90 °C. During long-term operation, the HFMMM demonstrated superior resistance to wetting and showed a much smaller decline in flux compared with the unmodified PVDF membrane. This enhanced stability is attributed to the hydrophobic nature of the ZSM-5 particles embedded in both the membrane matrix and surface.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no conflict of interest.

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