Improving CO₂ Absorption in PVDF Membrane with Cross-Linked Polymer Coatings

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ABSTRACT

This study aims to enhance the absorption of CO₂ in polyvinylidene fluoride (PVDF) membranes through surface modification using various polymers, including chitosan, nylon, dopamine, and ethylenediamine (EDA). The main challenge addressed is achieving effective crosslinking and robust adhesion between the membrane surface and the coated polymer layer to improve CO₂ capture efficiency. Surface modifications were examined using SEM and FTIR analyses. SEM imaging confirmed the preservation of membrane porosity post-modification, indicating successful polymer integration without pore obstruction. Nylon coatings altered surface morphology, with enlarged pore apertures and roughening surfaces due to formic acid exposure during dissolution. FTIR spectroscopy confirmed the presence of the respective polymers, exhibiting characteristic peaks for each. Membranes coated with EDA exhibited enhanced CO₂ absorption flux, attributed to their hydrophilic nature and larger pore dimensions. Optimization of EDA coating parameters, including deposition time and concentration, revealed a direct correlation between increased EDA deposition and enhanced CO₂ absorption flux. This highlights the significant impact of these parameters on membrane performance in gas absorption. Consequently, tailored surface modifications offer a promising approach for enhancing membrane functionality in gas separation applications and advancing membrane-based CO₂ capture technologies.

Keywords: Cross-linking, surface modification, CO₂ selective permeability, CO₂-polymer interaction, membrane gas absorption

1.0 INTRODUCTION

Researchers have elucidated the significant role of CO₂, a predominant greenhouse gas, in driving the greenhouse effect. In response, various methodologies have been devised to mitigate CO₂ emissions into the atmosphere. Membrane gas absorption (MGA) technology is chosen over other conventional technologies due to its lower energy consumption and potential for compact design [1, 2]. It facilitates contact between a liquid absorbent and mixed gas, leading to efficient separation and capture of CO₂ from industrial emissions. Nevertheless, the membrane in this process poses limitations on CO₂ absorption by the absorbent. Its presence introduces resistance to the mass transfer of gas into the liquid phase [3], thereby impeding the diffusion of CO₂ into the membrane pores. Furthermore, challenges arise from membrane wetting, which can diminish CO₂ absorption performance over prolonged operation periods. The inherent properties of the membrane utilized in MGA processes are

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susceptible to deterioration, particularly when membrane pores become wetted by liquid absorbents. Despite the hydrophobic characteristics of the membrane, there remains a possibility of absorbent penetration into its pores during extended operation. Therefore, enhancing the surface properties of the membrane becomes imperative to prevent degradation over prolonged operational periods, thereby ensuring sustained CO$_2$ absorption efficiency and mitigating operational costs.

In this work, the main innovation is the use of crosslinker polymers to modify the surface properties of PVDF membranes, thereby improving CO$_2$ capture in MGA. This study specifically explores the impact of various polymers and optimization of coating parameters, which have not been extensively addressed in previous research. Research gaps in existing studies include the lack of focus on the detailed adhesion between the membrane and the crosslinked polymer and how these modified layers aid in CO$_2$ absorption. Addressing these gaps is necessary to enhance the efficiency and stability of membrane-based CO$_2$ capture technologies.

Surface modification of the membrane offers a strategic approach to improve the adhesion between the membrane and the crosslinked polymer [4]. One effective technique involves coating the membrane surface with CO$_2$ affinity nanofillers combined with a crosslinker polymer. This requires exploring various polymer types to determine their potential for effective crosslinking with the membrane. The specific polymers chosen in this work include chitosan, nylon, dopamine, and EDA. These polymers were selected for their high hydrophilicity [5–7], which enhances CO$_2$ affinity and capture in MGA processes. The mechanism of CO$_2$ absorption in the modified membrane involves the interaction of CO$_2$ molecules with the modified surface, where the enhanced hydrophilicity and pore structure facilitate greater CO$_2$ flux. The crosslinked polymer layer acts as a selective barrier, optimizing the separation process.

Crosslinking represents a versatile method for surface modification, encompassing UV, physical, chemical, and thermal crosslinking techniques [8, 9]. These methods may involve grafting, blocking, or oxidative mechanisms [10], each offering unique advantages in enhancing membrane performance for CO$_2$ capture applications. Chemical crosslinking stands out as the predominant method due to its widespread application and reliability in membrane modification. This approach involves the reaction between the membrane and a crosslinking polymer in the presence of a catalyst, facilitating the crosslinking process [10]. Compared to physical crosslinking, chemical crosslinking offers greater stability [11], thereby augmenting membrane performance and hydrophilicity [10]. The effectiveness of chemical crosslinking hinges on both the functional groups presents in the polymer and the desired properties of the modified membrane. By judiciously selecting the appropriate crosslinking method based on these factors, researchers can tailor the membrane to achieve specific separation characteristics and enhance its suitability for diverse industrial applications.

Crosslinker polymers can be applied to the membrane surface using the dip-coating method, which represents a straightforward approach for surface modification [12, 13]. Classified as a physical modification technique, dip-coating involves immersing a polyvinylidene fluoride (PVDF) membrane into a solution of
monomers, whereupon crosslinking or polymerization reactions immobilize the monomers onto the membrane surface [14, 15]. This modification strategy not only enhances the hydrophobicity of the membrane surface but also induces superhydrophobic surface features. The deposition of monomers increases the surface area of the membrane, consequently influencing its morphology, including hydrophobicity, thickness, and pore structure [16]. For example, studies by Yang et al. [17] demonstrate that coating PVDF membranes with nano-silica alters their microstructure, resulting in a lotus-like surface morphology exhibiting exceptional superhydrophobic properties [14, 18]. This effect is attributed to the roughening of the membrane surface induced by nano-silica coating [19]. Notably, the degree of superhydrophobicity, as indicated by the contact angle, is influenced by the concentration of nano-silica, with angles exceeding 165° achieved at optimal concentrations but diminishing below 145° at higher concentrations [17]. Thus, the concentration of the coating material emerges as a critical parameter governing membrane surface properties and must be carefully controlled to achieve desired performance characteristics.

Several parameters associated with the coating polymer profoundly influence CO₂ absorption flux, including coating temperature, duration, and concentration. Modulating these parameters can result in a denser membrane surface, thereby impacting pore size and porosity [20, 21]. Consequently, these parameters play a pivotal role in determining the CO₂ absorption flux of the coated membrane. However, achieving effective crosslinking of the polymer on the membrane surface presents a challenge, primarily due to the risk of inadequate adhesion resulting from weak chemical interactions between the membrane and the coated layer [22]. Therefore, optimizing the coating of the crosslinker polymer at specific parameters is essential to ensure its role as a robust bridge between the membrane surface and the CO₂ affinity nanofiller, enhancing the efficiency and stability of the CO₂ capture process. The main objective of this work is to investigate the influence of various coating parameters on CO₂ absorption flux and address the challenge of achieving robust adhesion between the membrane and the crosslinked polymer, thereby contributing to the advancement of membrane-based CO₂ capture technologies.

2.0 METHODS

2.1 Materials

PVDF with an average molecular weight of 530,000 pellets (Aldrich) used as the polymer for fabricating the support membrane, dissolved in 1-Methyl-2-pyrrolidinone (NMP) (Sigma-Aldrich). Ethanol was used as one of the non-solvents in the coagulation bath during the immersion phase. Diethanolamine (DEA) (Sigma-Aldrich) was used as the absorbent for the MGA operation. Modification of the fabricated PVDF membranes was achieved through dip-coating with chitosan (low molecular weight, Aldrich), nylon 6 (Aldrich), dopamine (Sigma-Aldrich) and ethylenediamine (EDA, Sigma-Aldrich) polymers. The solvents used to dissolve chitosan, nylon and dopamine were acetic acid (Merck), formic acid (Fisher Scientific) and hydrochloric acid (R&M Chemicals), respectively. Tris hydroxymethyl]aminomethane (USB) was incorporated to adjust the pH of
the dopamine coating solution, as self-polymerization of dopamine to polydopamine occurs optimally under slightly alkaline condition. All materials were used as received without further purification.

2.2 Membrane Fabrication
The PVDF membrane was fabricated using the Non-Solvent Induced Phase Separation (NIPS) method [23]. Firstly, PVDF powder underwent drying in an oven at 60°C, while the NMP solvent was heated up to the same temperature in an oil bath. Subsequently, 15 wt.% of the PVDF powder was gradually introduced into the heated solvent, and the resulting solution was stirred overnight at 60°C. Following this, the solution was allowed to cool to room temperature before degassing for 1 hour to eliminate any air bubbles. The casting blade thickness was adjusted to 400 µm prior to casting the dope solution onto a glass plate. The cast polymer was then immersed in a coagulation bath comprising 20 wt.% ethanol and 80 wt.% water for a duration of 24 hours. Finally, the fabricated PVDF membrane was removed from the coagulation bath and dried at room temperature for 3 days before subsequent modification could commence.

2.3 Membrane Modification
The PVDF membrane modification was accomplished through the dip-coating method, using chitosan, nylon, dopamine, and EDA polymers. Coating solutions of chitosan, nylon, and dopamine were prepared at a concentration of 1 wt.% while the EDA solution was prepared at a concentration of 1.7 M. 1 wt.% Chitosan was dissolved in acetic acid glacial, and 1 wt.% nylon 6 pellets were dissolved in formic acid. Both solutions were stirred at 25°C until homogeneous. Meanwhile, 1 wt.% dopamine polymer was dissolved in a Tris-buffer, with HCl solution gradually added to adjust the pH to 8.5, and then stirred in a dark environment at 25°C. The self-polymerization of dopamine to polydopamine occurs only in a slightly alkaline state [24]. As for EDA coating solution, the reagent was diluted with distilled water to yield a 1.7 M EDA concentration and stirred at 80°C.

The dip-coating process for membranes modification with various polymers was conducted by immersing the membrane samples into the coating solution for 1 hour. After immersion, the membranes were rinsed with water to remove any excess coating solution. Finally, the membranes were dried overnight at room temperature. Upon identifying the polymer with the most promising MGA performance, further dip-coating experiments were conducted by varying coating time (0 to 120 mins) and polymer concentration (0.5 to 3 M) to optimize membrane’s CO₂ absorption capability.

2.4 Membrane Characterization
The PVDF membranes, both unmodified and modified, underwent comprehensive characterization to assess their physical and chemical properties. The surface morphology of the membranes was examined using a field emission scanning electron microscope. Fourier transform infrared spectroscopy (FTIR) was used to determine the chemical composition of the membranes. Additionally, membrane porosity was determined via the gravimetric method. Membrane samples measuring 2 cm x 1 cm were first dried in an oven at 40°C and weighed to obtain initial dry weight. Subsequently, the samples were immersed in 2-butanol for 2 hours, and the weight of the wetted membrane
Improving CO₂ Selectivity in PVDF Membrane

was recorded. Porosity (ε) was then calculated using the following equation:

$$\varepsilon = \left( \frac{m_w - m_d}{\rho_b} \right) \times 100\%$$  \hspace{1cm} (1)

where ε represents the porosity of the membrane (%), $m_w$ and $m_d$ denote the weights of the wet and dry membrane, respectively (in g), while $\rho_b$ and $\rho_m$ represent the densities of butanol and PVDF membrane, respectively (in g/cm³). The static water contact angle was measured to assess membrane surface hydrophilicity. Using a surface meter and the sessile drop method, a 10 μL water droplet was placed onto a 1 cm x 3 cm membrane sample affixed to a glass slide. A high-speed camera captured the droplet image, and the WCA was calculated using the Young-Laplace equation. This analysis was repeated at least three times on different spots of the membrane to determine the average WCA.

2.5 MGA Performance

The MGA process was conducted under atmospheric pressure and room temperature, using the MGA setup depicted in Figure 1. Pure CO₂ served as the feed gas, while DEA was used as the liquid absorbent. Throughout the 3-hour MGA operation, gas and liquid flow rates were maintained at 120 mL/min and 100 mL/min, respectively. Prior to evaluating CO₂ absorption flux, a 15-min system stabilization period was implemented.

The absorption flux of CO₂ was determined using the following equation, where the inlet and retentate gas flow rates were measured using a bubble flowmeter.

$$J_{CO_2} = \frac{(Q_{g, in} - Q_{g, r}) \times \rho_g}{MW_g A}$$  \hspace{1cm} (2)

where $J_{CO_2}$ represents the mass transfer rate of CO₂ in mol m⁻² s⁻¹, $Q_{g, in}$ and $Q_{g, r}$ denote the inlet and retentate gas flow rates, respectively, in mL/s, $\rho_g$ signifies the density of CO₂ gas in g/mL, $MW_g$ denotes the molecular weight of CO₂ (g/mol) and $A$ represents the membrane contact area in m².

Figure 1 MGA process setup

3.0 RESULTS AND DISCUSSION

SEM images depicting the modified PVDF membranes are presented in Figure 2. Notably, all the modified membranes retained their porous structure on the membrane surface following surface modification with a thin-film polymer layer. This observation indicates the successful
coating of the thin-film polymer without obstructing membrane pores. Under SEM analysis, the PVDF/Chitosan membrane exhibited minimal alterations in surface morphology compared to the neat PVDF membrane. The smoother coating surfaces observed can be attributed to the amorphous structure of the polymer molecules [25], which offer enhanced dimensional stability and even distribution, thereby minimizing shrinkage. This finding aligns with the observations of Silitonga et al. [26], who reported that chitosan crosslinking on PVDF membrane surfaces yielded minimal changes in surface roughness.

The PVDF/Nylon membrane exhibited an observable increase in pore size and surface roughness (Figure 2c) compared to the other modified membranes. This morphological alteration is likely attributed to the presence of the nylon coating solution, which influences the overall structure of the PVDF membrane. The use of concentrated formic acid for dissolving nylon 6 pellets before membrane coating may have contributed to the structural changes observed in the PVDF membrane during the coating process. A study by Poletto et al. [27] demonstrated that nylon membrane fabricated using formic acid as a solvent exhibited increased porosity compared to those prepared using hydrochloric acid. Consequently, the Nylon-coated PVDF membrane in this investigation displayed enlarged pore structures and a rougher surface morphology, consistent with these findings.

Interestingly, a discernible color change was observed on the PVDF membrane upon coating with dopamine, manifesting as a darker brownish hue. This alteration in coloration signifies the oxidation of dopamine molecules to polydopamine [28], resulting in the formation of an adhesive layer on the membrane surface during the coating process. Subsequent SEM analysis of the membrane surface (Figure 2d) revealed smoother surfaces compared to PVDF/Nylon membranes. Nonetheless, the membrane retained a noticeably rougher surface texture compared to the neat PVDF membrane, featuring small and uniformly distributed pores. In contrast, SEM imaging of the PVDF/EDA membrane (Figure 2e) depicted small and evenly distributed pores with a slightly rougher surface. The presence of the EDA layer on the PVDF membrane surface induced a morphology characterized by relatively larger pore sizes and a modestly rougher surface texture compared to the neat PVDF membrane. EDA is a hydrophilic compound whose amino groups can interact with CO₂ molecules. This interaction facilitates the formation of carbamate intermediates [29], thereby enhancing the CO₂ capture capability of the membrane.
To analyze the chemical structure and confirm the presence of surface modifications, FTIR spectroscopy was carried out. In Figure 3, the strong absorption peaks observed at 1213 cm⁻¹ and 1168 cm⁻¹ correspond to the stretching vibrations of C-F and CF₂, respectively, which are indicative of the repeating -CF₂- units in the crystalline structure. Additionally, the band at 760 cm⁻¹ and 875 cm⁻¹ are characteristic features of the PVDF polymer [30]. A comparison between the neat PVDF membrane and membranes coated with chitosan revealed distinct spectral features, as illustrated in Figure 3, which highlighting the modifications introduced by the chitosan coating. The adsorption peak in the range of 3100 cm⁻¹ to 3600 cm⁻¹ signifies the presence of -OH and -NH₂ stretching attributed to the hydroxyl and amino groups inherent in chitosan [26]. Additionally, peaks corresponding to the deformations of -N-H stretching of the amino group and the C=O stretching of the N-acetyl group are evident at 1650 cm⁻¹ and 1580 cm⁻¹, respectively. Conversely, analysis of the PVDF membrane coated with nylon polymer reveals a notable band
at 1636 cm\(^{-1}\), indicative of the presence of amide functional group and carbonyl group stretching, characteristic of nylon 6 polymer [31]. Another prominent peak observed at 1540 cm\(^{-1}\) corresponds to the C-N stretching attributed to the amide group within the nylon 6 polymer.

Furthermore, the FTIR spectroscopy analysis of the PVDF/EDA membrane presented in Figure 3 shows a significant alteration in the chemical structure of PVDF after EDA coating. The broad and strong band spanning the range of 1540 cm\(^{-1}\) and 1700 cm\(^{-1}\) indicates the N-H deformation of the primary amine group and N=O stretching. Additionally, a minor band observed at 3400 cm\(^{-1}\) indicates the presence of O-H stretching or N-H stretching attributable to the amino group in EDA. This observation suggests that EDA may directly crosslink with the PVDF membrane through a dehydrofluorination reaction, facilitating linkage between polymer chains [32]. However, the absence of peaks corresponding to NH\(_2\) and C=C group vibrations of dopamine at 1580 cm\(^{-1}\) and 1650 cm\(^{-1}\), respectively, suggests a low concentration of dopamine coating. This may be attributed to the simpler chemical structure of dopamine compared to other cross-linking agents, such as nylon and EDA, which possess longer chains or bulky structures. Overall, the presence of distinctive polymer peaks on the membrane surfaces depicted in Figure 3 indicates the successful deposition of the respective polymer coating onto the PVDF substrate.

![Figure 3 FTIR spectra for the neat and modified PVDF membranes with different polymers](image)

Changes in membrane porosity play a crucial role in determining the CO\(_2\) absorption flux performance. In this work, the porosities of modified membranes were observed to range between 77% to 81%, a marginally modest deviation from the neat membrane porosity of 78%. High porosity is inherently advantageous for membranes as it minimizes mass transfer resistance, facilitating efficient gas transport through the membrane [33]. The remain of high porosity in polymer-coated PVDF membranes
Improving CO\textsubscript{2} Selectivity in PVDF Membrane

suggests that the CO\textsubscript{2} absorption flux is unlikely to be significantly hindered by alterations in membrane structure. Rather, any discrepancies in CO\textsubscript{2} absorption flux performance among these membranes are likely attributable to variations in the functional groups of the polymers, influencing their interaction with CO\textsubscript{2}.

The gas separation performances of both neat and modified membranes were evaluated by assessing their CO\textsubscript{2} absorption flux, as depicted in Figure 4. Over a 3-hour MGA test period, the CO\textsubscript{2} absorption flux of the neat PVDF remained consistently at 0.007 mol/m\textsuperscript{2}.s, attributed to its inherent high porosity. While the polymer-modified membrane also exhibited high porosity, the deposition of thin-film polymers created an additional surface barrier. Therefore, this introduced an additional mass transfer resistance for gas molecules traversing the membrane pores, resulting in a reduced quantity of CO\textsubscript{2} absorbed by the liquid absorbent.

The performance of membranes coated with chitosan and nylon exhibited notable decrements, as depicted in Figure 4. Both modified membranes demonstrated a CO\textsubscript{2} absorption flux of 0.0034 mol/m\textsuperscript{2}.s. The diminished performance of the PVDF/Chitosan membrane can be attributed to its altered morphology. Analysis revealed that the pore size of the chitosan-modified membrane was the smallest, as discussed in Figure 2. This reduced pore size likely impedes CO\textsubscript{2} gas penetration through the coating layer. Similarly, the reduced porosity of the PVDF/Nylon membrane may hinder CO\textsubscript{2} absorption flux. Notably, the porosity of the nylon-modified PVDF membrane was the lowest at 78%, whereas other modified membranes exhibited porosities above 80% (80.5% for EDA-modified, 81.3% for chitosan-modified and 81.8% for dopamine-modified membranes). During the surface coating process, the nylon solution may infiltrate the inner structures of the membrane, leading to

![Figure 4](image-url) CO\textsubscript{2} absorption flux of PVDF membrane modified with different coating polymers

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decreased CO₂ absorption flux. Furthermore, the absence of hydroxyl and amine units in the PVDF/Nylon membrane (Figure 3) renders it relatively less hydrophilic than other membranes, resulting in reduced interaction with CO₂ gas and increased difficulty in CO₂ absorption by the liquid absorbent [34, 35].

Interestingly, the CO₂ absorption performance of the PVDF/EDA membrane surpasses that of other coated membranes and exhibits a higher CO₂ absorption flux compared to the neat PVDF membrane. The heightened performance can be associated with the hydrophilic nature of EDA, which facilitates gas absorption through the membrane pores. The presence of amino groups at each end of EDA molecules enhances its affinity towards CO₂ owing to its acidic nature [36, 37], thereby augmenting CO₂ absorption flux by the PVDF/EDA membrane. Consequently, a greater quantity of CO₂ is drawn closer to the membrane, facilitating easier absorption by the liquid phase, and resulting in an increased CO₂ absorption flux. Furthermore, the surface of the EDA-modified PVDF membrane exhibits larger pore size, facilitating the facile penetration of CO₂ gas through the coating layer for absorption by the liquid absorbent. Despite the additional barrier created by the EDA coating layer on the membrane surface, the CO₂ absorption flux of this modified membrane remains highly tolerable.

Following the identification of EDA-modified PVDF membrane as exhibiting the highest CO₂ absorption flux, further optimization was pursued through variation of coating parameters, namely coating time and EDA solution concentration. In this work, PVDF/EDA membranes were coated at 80°C, with coating times of 30, 60 and 120 mins. As illustrated in Figure 5, membrane thickness increased proportionally with longer coating times. This phenomenon can be attributed to the heightened capillary force of the solution, facilitating greater adherence to the membrane surface over prolonged exposure [38]. Moreover, extended coating times promote stronger bonding between functional groups of the PVDF membrane and the EDA coating solution. Enhanced adsorption of polymer chains from the coating solution onto the membrane surface results in a thicker EDA coating layer [39]. Consistent with the model proposed by Naik et al. [39], surface thickness of porous materials demonstrates a linear increase with dipping time of the coating solution. Improved chemical interaction between the membrane and the coating solution correlates with higher deposition of the coating solution on the membrane surface, further enhancing membrane performance.

Over a 3-hour CO₂ absorption operation, the flux of CO₂ absorbed increased for all three PVDF/EDA membranes, coated for 30, 60, and 120 mins. This trend suggests that the modified PVDF membranes effectively attracted more CO₂ gas, facilitating its travel through the membranes and subsequent capture by the liquid absorbent. The PVDF/EDA membrane coated for 30 mins exhibited the lowest CO₂ absorption flux, attributed to insufficient EDA polymer deposition on the membrane surface. Shorter coating times resulted in less EDA polymer crosslinking on the PVDF membrane surface and a thinner modified membrane, as depicted in Figure 5. Furthermore, the hydrophilicity of the modified membrane plays a crucial role in attracting CO₂ gas [40]. Membranes prepared with shorter coating times had reduced hydrophilicity,
Improving CO₂ Selectivity in PVDF Membrane

diminishing their ability to attract CO₂ gas to the membrane surface. Consequently, fewer CO₂ gas molecules were able to travel through the membrane pores and be absorbed by the liquid absorbent. In contrast, the PVDF/EDA membrane prepared with a coating time of 120 mins exhibited the highest CO₂ absorption flux. This suggests that extended coating time enhances the membrane's ability to attract and absorb CO₂ gas molecules. As previously mentioned, a greater deposition of EDA polymer on the PVDF membrane surface increases its hydrophilicity, which in turn enhances the attraction of CO₂ gas. Consequently, this facilitates more efficient absorption of CO₂ by the liquid absorbent through the membrane.

**Figure 5** CO₂ absorption flux and membrane thicknesses of PVDF/EDA membranes prepared at different coating time

For the modified membrane, a higher amount of EDA polymer deposition is desirable due to its enhanced hydrophilicity. However, increased polymer deposition can impede CO₂ flux, as a thicker polymer layer creates a barrier for CO₂ gas passage [39]. Typically, longer coating times result in decreased flux for modified membranes. Surprisingly, in this study, PVDF/EDA membranes prepared with longer coating times exhibited higher CO₂ absorption flux despite the thicker EDA layer. This finding suggests that a greater amount of EDA polymer, with its enhanced hydrophilicity and CO₂-attractive functional groups, can significantly improve CO₂ absorption performance. However, excessive deposition of EDA is not advisable, as it increases mass transfer resistance and reduces CO₂ passage through the membrane.

Figure 6 presents optical images of PVDF/EDA membranes prepared at varying EDA coating concentrations. It is evident that the appearance of the PVDF/EDA membranes changes noticeably with increasing EDA concentration. Specifically, the membranes exhibit a yellowish hue as the EDA concentration is increased.
from 0.5 M to 3.0 M. This color change is attributed to the stronger interaction between the EDA polymer and the PVDF membrane surface at higher coating concentrations. A study by Eum et al. [36] reported similar findings, noting that the color of PVDF/EDA membranes transitioned from white to dark brown as the EDA concentration was increased from 1.7 M to 3.0 M.

![Figure 6 CO₂ absorption flux and images of PVDF/EDA membranes prepared at different EDA concentration](image)

The CO₂ absorption flux of the PVDF/EDA membranes increases with higher EDA coating concentrations, as evidenced by the trends observed during the absorption operation (Figure 6). This suggests that as the EDA coating concentration on the PVDF membranes increases, the membranes become more effective at attracting CO₂ gas through the coating layer. Consequently, a greater amount of CO₂ gas is absorbed by the liquid absorbent, resulting in higher CO₂ absorption flux. Notably, the flux of the PVDF/EDA membrane prepared at an EDA concentration of 0.5 M is the lowest among the tested concentrations. This is due to the lower hydrophilicity of the modified PVDF membrane at this concentration, which diminishes its ability to attract CO₂ gas. The initial WCA of the PVDF membrane surface was 85.33±2.35°. After the addition of EDA, the WCA decreased to 78.61±1.93°, 73.51±2.15° and 68.93±1.51° for membranes modified with 0.5 M, 1.7 M and 3.0 M of EDA, respectively. This outcome was expected due to the presence of EDA’s amine functional groups on the membrane surface, which introduce hydrophilic functionalities. The presence of these amine groups increases the membrane’s water-attracting properties.
thereby resulting in a lower WCA. Therefore, low hydrophilicity in the coating layer is undesirable as it reduces the effectiveness of CO\textsubscript{2} removal.

From Figure 6, it is apparent that the flux of the PVDF/EDA membrane prepared at 3.0 M surpasses that of the PVDF/EDA membrane prepared at 1.7 M after the first hour of MGA operation and remains the highest throughout the 3-hour operation period. This indicates that membranes prepared with higher EDA coating concentrations can attract and absorb larger amounts of CO\textsubscript{2} gas over extended periods of operation. These findings underscore the importance of optimizing EDA coating parameters to enhance the hydrophilicity and CO\textsubscript{2} absorption capacity of PVDF membranes. The study contributes valuable insights into the design and fabrication of high-performance membranes for CO\textsubscript{2} capture, highlighting the potential for improved operational efficiency through tailored surface modifications.

4.0 CONCLUSION

This study successfully modified PVDF membrane using a dip-coating method with various polymers, including chitosan, nylon, dopamine, and EDA, to enhance CO\textsubscript{2} absorption in MGA. Among the modified membranes, the PVDF/EDA membrane exhibited the highest CO\textsubscript{2} absorption flux, surpassing the neat PVDF membrane. The better performance of the PVDF/EDA membrane was attributed to its increased hydrophilicity, which facilitated enhanced interaction with CO\textsubscript{2} molecules. Further optimization of the PVDF/EDA membrane by adjusting the coating time and EDA concentration revealed that a membrane coated for 120 mins with an EDA concentration of 3.0 M demonstrated the best CO\textsubscript{2} absorption performance. This improvement is linked to the enhanced hydrophilicity of the PVDF/EDA membrane at higher concentrations and longer coating durations, which facilitates closer interaction of CO\textsubscript{2} molecules with the membrane surface, thus enhancing absorption efficiency. The findings highlight the significant impact of coating parameters on the membrane's CO\textsubscript{2} capture capability. This study demonstrates that tailored surface modifications using EDA can substantially improve membrane functionality for gas separation applications, advancing membrane-based CO\textsubscript{2} capture technologies.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.
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Improving CO$_2$ Selectivity in PVDF Membrane
