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Investigation of the Structure and Performance of PVC/SiO_2 Nanocomposite Hollow Fibers as a Membrane Contactor

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1. ABSTRACT

The use of membrane contactors for the removal of acidic gases is one of the significant advancements in engineering processes and environmental protection. Despite the numerous advantages of membrane contactors, the wetting of polymeric membranes by liquid absorbents remains the most critical challenge in the development of this technology. In fact, the polymer membrane wetting by liquid absorbents increases the mass transfer resistance of the membrane and reduces gas absorption. In this study, to reduce the issue of wetting, hydrophobic PVC hollow fiber membranes containing silica nanoparticles at different weight percentages (0, 1, 1.5, and 2%) were prepared. The fabricated membranes were evaluated using XRD, SEM, TEM, AFM, contact angle measurement, tensile strength testing, and pure CO_2 absorption tests. SEM images confirmed the presence of nanoparticles on the surface and internal structure of the nanocomposite membranes. Contact angle measurements showed that the addition of nanoparticles increased the contact angle of the membranes. Specifically, the contact angle in nanocomposite membranes with 1.5% weight of nanoparticles increased from approximately 77° to around 94°. Additionally, tensile strength measurements indicated that the presence of nanoparticles in the membrane structure enhanced the tensile strength by about 10 MPa. Finally, the performance of both pure and nanocomposite membranes in CO_2 gas absorption within the membrane contactor system was evaluated. The results showed that after 20 days of gas absorption, the permeation flux of pure membranes significantly decreased, whereas the gas absorption flux in nanocomposite membranes containing 1.5% weight of nanoparticles remained almost constant during this period.

Keywords: Polyvinyl Chloride, Nanocomposite, Hydrophobic Nanoparticles, Membrane Contactor, CO_2.

2. INTRODUCTION

In recent decades, the emission of greenhouse gases—particularly carbon dioxide (CO_2)—has become one of the major global environmental challenges. In addition to its destructive environmental effects, this gas also contributes to the acidification of seawater and oceans [1–4]. Therefore, finding effective and economical solutions for the separation and capture of CO_2 from the environment is essential. Membrane contactors, with their high specific surface area and operational flexibility, can significantly reduce issues such as flooding and channeling while consuming less energy compared to conventional methods. Studies have shown that absorbent solutions, especially aqueous solutions of organic compounds such as alkanolamines, can penetrate the pores of polymeric membranes [5]. As a result, these membrane

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pores gradually undergo wetting during long-term operation. Partial wetting increases the overall mass transfer resistance and negatively affects the stability of the membrane during prolonged use. Thus, addressing the wetting problem in gas–liquid membrane contactors would greatly enhance their functional performance. The obtained results indicated that modified membranes exhibited longer operational stability compared to unmodified (pure) membranes. Investigations reveal that despite the significant importance of PVC in the fabrication of membrane contactors for CO_2 removal, very few studies have focused on this type of membrane. Accordingly, in this study, PVC hollow fiber membranes were selected as the base material due to their favorable thermal, mechanical, and chemical properties. To improve the performance of these membranes in CO_2 absorption and enhance their resistance to wetting, hydrophobic silica nanoparticles were employed.

The main objective of this research is to examine the effect of varying concentrations of silica nanoparticles on the structural, mechanical, and functional properties of the membranes, as well as to improve hydrophobicity in the membrane contactor system. This was assessed through various tests, including X-ray diffraction (XRD), scanning electron microscopy (SEM), contact angle measurement, and tensile strength testing. In addition, efforts were made to identify the optimal conditions for fabricating high-performance nanocomposite hollow fiber membranes by investigating different structural and operational parameters.

3. MATERIALS AND METHODS

3.1. Material

PVC (specific gravity: 1.4000 g/cm^3), used as the membrane material, was obtained from Ghadir Petrochemical Company. Dimethylformamide (DMF) (molecular weight: 73.09 g/mol, density: 0.944 g/cm^3) was purchased from Merck as the solvent, and diethanolamine (DEA) (molecular weight: 105.14 g/mol, density: 1.097 g/cm^3) was purchased as the chemical absorbent. Additionally, hydrophobic silica nanoparticles (SiO_2) (size: 20 nm, density: 200 g/L, purity: 99.5%), made in Germany, were obtained from Artin Tejarat Exir Company.

3.2. Fabrication of flat membranes

To prepare flat membrane samples, a three-component polymer solution was prepared. For producing the flat membranes, the desired solution was poured onto a glass plate and cast using a special blade with a specified thickness. Then, to carry out the phase separation process, the cast solution was immersed in a water bath.

3.3. X-ray Diffraction

To determine the effect of the presence of SiO_2 nanoparticles on the structure of the membranes, X-ray diffraction analysis was used. The structural analysis of pure and nanocomposite membranes was performed using an X-ray diffraction device (XRD, D8 Advance, Bruker, Germany).

3.4. Contact Angle Test

For this purpose, a contact angle goniometer device (model CAG-20, Jikan, Iran) was used. In this test, flat membrane samples with the same formulation as the hollow fiber membranes were prepared, and their contact angles were measured. To increase the accuracy of the results and reduce errors, the test was repeated three times for each sample, and finally, the average values were reported.

3.5. Mechanical Strength Test

The mechanical strength of pure and nanocomposite membranes was determined using a tensile testing machine (Universal Testing Machine, STM-5 model, capacity 5 kN, Sentam). The length of each sample was 10 centimeters. The stretching speed in all cases was 10 mm/s. The test was repeated three times for each sample, and the average results were reported.

3.6. Atomic Force Microscope (AFM)

The morphology and surface roughness of the membranes were studied using an AFM device (Nanosurf Mobile S model, Switzerland). Scanning was performed at a speed of 5 µm/s (1 Hz), with a force of 0.15 nN and a scan size of 1000 nm.

3.7. Pure CO2 Absorption Test

To evaluate the performance of pure and nanocomposite membranes, a pure CO2 absorption test was conducted in a membrane contactor module. In this test, an aqueous solution containing 30 wt.% DEA was used as the liquid absorbent. During the test, the absorbent liquid flowed counter-currently in the shell side, while the CO2 gas flowed inside the membranes. It is worth mentioning that a peristaltic pump was used to control the mass flow rate of the liquid absorbent and to pump it into the shell side. Additionally, the feed gas was injected from a tank containing compressed pure CO2 gas into the hollow fiber membranes.

4. RESULTS AND DISCUSSION

4.1. Investigation of the mechanical strength of flat membranes

The presence of nanoparticles in the structure of nanocomposite membranes has significantly improved the tensile strength compared to pure PVC membranes. This enhancement can be attributed to the reinforcing and modifying effects of SiO_2 nanoparticles in the PVC polymer. The nanoparticle network may fill the interstitial spaces within the PVC matrix and enhance its structural integrity. Good interactions (such as weak van der Waals forces and hydrogen bonding) between the SiO_2 nanoparticles and the PVC membrane can improve load transfer efficiency and stress distribution, thereby enhancing the mechanical properties of the membrane.

4.2. Contact angle test and atomic force microscopy

The hydrophobicity of PVC membranes has been improved by adding varying weight percentages of SiO_2 nanoparticles. One of the main reasons for the increased contact angle in nanocomposite membranes is their enhanced surface roughness compared to pure PVC membranes, as examined by AFM. The presence of nanoparticles on the surface of the nanocomposite membranes has led to an increase in both surface roughness and hydrophobicity, which is also confirmed by the AFM images. It is worth noting that the contact angle of the membranes increased with the addition of hydrophobic nanoparticles.

4.3. Investigation of the XRD pattern of flat membranes

In nanocomposite membranes, the addition of SiO_2 nanoparticles has no significant effect on the XRD pattern of the pure PVC membrane, indicating that the original membrane has been well modified by the addition of SiO_2 nanoparticles without any observable structural changes. It is worth noting that the change in the intensity of the semi-crystalline phase diffraction peak in the nanocomposite membrane compared to the pure membrane can be attributed to the presence of the nanoparticles. The presence of SiO_2 nanoparticles in the polymer matrix acts as a nucleating agent, leading to the crystallization of the chains around these nanoparticles.

4.4. Effect of Operating Pressure

The effect of pressure on the CO_2 absorption flux was investigated in this study. The feed gas was injected into PVC hollow fiber membranes, and the results are presented in Figure 9. The findings indicate that increasing the operating pressure leads to a rise in the partial pressure and concentration of CO_2 at the gas-liquid interface. As a result, a greater amount of CO_2 gas comes into contact with the absorbent liquid and can be absorbed by it. Moreover, as the operating pressure increases, the gas becomes more compressed.

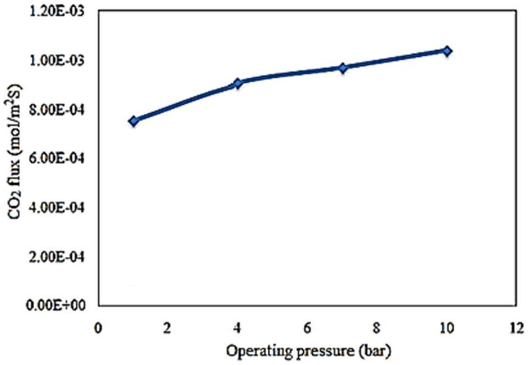

Figure 1. CO_2 absorption flux versus operating pressure for the nanocomposite membrane containing 2 wt% hydrophobic SiO_2 nanoparticles.

5. CONCLUSION

In this study, pure and nanocomposite PVC membranes containing SiO_2 nanoparticles were fabricated and investigated in a membrane contactor system for CO_2 gas absorption. SEM images revealed the presence of nanoparticles on the surface and within the internal structure of the nanocomposite membranes. Contact angle measurements indicated that the nanocomposite membrane containing 2.5 wt% of SiO_2 nanoparticles exhibited the highest contact angle compared to the other membranes. Mechanical property evaluations of various membranes showed that the incorporation of nanoparticles significantly improved the tensile strength of the nanocomposite membranes compared to pure PVC membranes. The results of the long-term CO_2 absorption test in the membrane contactor system demonstrated a considerable improvement in the performance of the PVC membrane after modification with SiO_2 nanoparticles. Therefore, it can be claimed that the surface modification of PVC membranes with SiO_2 nanoparticles can be an important step toward enhancing the performance of gas–liquid membrane contactors.

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