

Research Paper

Improvement of the Performance of PDMS Top Layer of Mixed Matrix Membrane Incorporated with Treated ZIF-8 for Gas Separation

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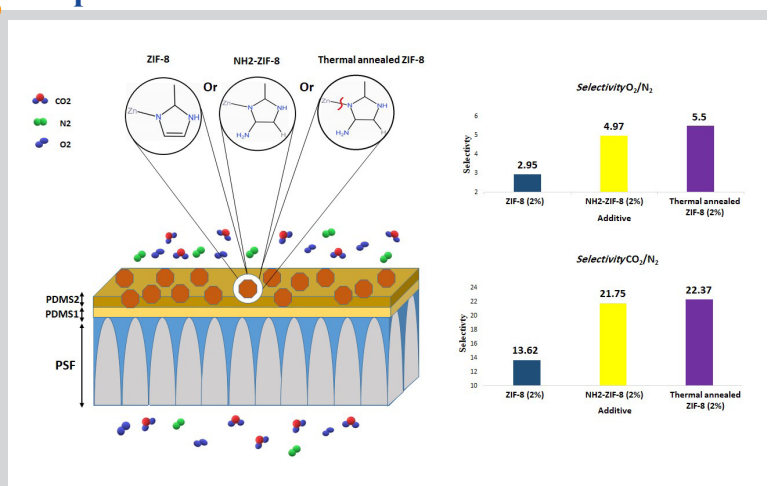
Keywords

ZIF-8
 Gas separation
 Mixed matrix membrane (MMM)
 PDMS membrane

Highlights

- MMMs contain two thin selective layer of PDMS on porous PSF membrane.
- Different types of ZIF-8 nanoparticles were dispersed in the structure of PDMS layer.
- CO_2/N_2 and O_2/N_2 selectivity of the prepared MMMs was improved.
- The intrinsic selectivity of ZIF-8 played an important role to enhance the gas separation.

Graphical abstract



Abstract

Selectivity and permeability are two significant parameters in the gas separation process. Hence, nowadays, modification of membrane to improve the parameters mentioned above, have highly gained attention. In this study, to increase the performance of the polymeric membrane, bare ZIF-8 nanoparticle (NP), as well as annealed and NH_2 -functionalized ones (Medium-sized particles less than 100 nm), were introduced into the structure of polydimethylsiloxane (PDMS) top layer at different concentrations. The high porosity and gas adsorption characteristics of the ZIF-8 made it a proper nanofiller to modify and improve the efficiency of polymeric membranes. The CO_2/N_2 and O_2/N_2 selectivity of the membranes improved regarding the loading ZIF-8. In addition, NH_2 -functionalized and thermal annealed ZIF-8s employed to compare the result of the treated NPs on the efficiency of the fabricated MMMs. Consequently, the selectivity of both mentioned pair gases improved. At 2 wt% of annealed ZIF-8s, the mixed matrix membrane (MMM) presents a desired separation selectivity over 5.5 and 22.37 for O_2/N_2 and CO_2/N_2 , respectively.

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1. Introduction

Nowadays, the drawbacks of global warming and energy consumption have attracted a unique general consideration to the case of CO_2 emission [1,2]. Compared to other energy resources, natural gas is commonly used to produce energy, and CO_2 is the major impurity in natural gas streams, and also known as a significant factor in rising global warming [3,4]. Conventional methods for capturing or separation CO_2 , like pressure-swing adsorption, amine-based absorption, and cryogenic distillation, are not Eco-friendly [5,6]. Recently, membrane-based separation processes because of their operational simplicity, low environmental footprint, and low energy consumption that overcome the disadvantages of the traditional methods have attracted increasing attention and considered as a prospective alternative

process [7-10]. The membrane materials are the main factors for gas separation efficiency [11]. Gas separation operations owing to their better processability, commercial, and operational properties through polymeric membranes have been promoted [12]. Innumerable polymers, in rubbery or glassy states, as the primary membrane materials applied in the membrane separation process, have investigated [13]. Compared to all membrane materials, the (polydimethylsiloxane) $-\text{Si}(\text{CH}_3)_2\text{O}-$ (PDMS) membrane is considered as a promising polymeric membrane to be used for separation of liquids and gases for its hydrophobic nature, high permeability to gases and organic molecules, sizeable free volume, low cost, and excellent chemical stability [7,10,11,14,15]. Nevertheless, membranes made of polymeric

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substances, which included PDMS, are mostly limited by the poor ability to sieve molecules in response to size, and swelling of chains, which eventuates considerable reduction of separation efficiency. High permeability and selectivity features are hard to obtain simultaneously. Generally, polymeric membranes are restricted by tradeoff behavior among permeability and selectivity [16].

Several studies have evaluated the efficiency of the fabricated membranes for gas separation. The efficacy of coating conditions like concentration, coating procedure, curing temperature, and the number of sequential coatings on the efficiency of the PDMS composite membranes were studied via Madaeni et al. [10]. Also, Peng et al. [17], Liu et al. [18], Achalpurkar et al. [19], Shieh and Chung [20], and Shamsabadi et al. [21] investigated the polymer concentration, coating temperature and other vital parameters on their resulting thin-film composites membranes performances. Conversely, inorganic membranes offer superb gas flux and selectivity, with excellent chemical and thermal stability; nevertheless, extensive usage is limited due to the high manufacture prices. A proven effective method to elevate the membrane efficiency is embedding nanofillers with various natures into the polymer structures to create MMMs [22,23]. Among all categories of fillers, a family of porous crystalline structures, named metal-organic frameworks (MOFs), formed by inorganic moieties and organic ligands is known as the most significant interesting contenders due to premier intrinsic separation properties and high compatibility with polymers. ZIF, a well-known subset of MOFs, have metal nodes (generally Co, Fe and, or Zn) and ligands as organic linkers (imidazolate or their derivative), in this case, ZIF-8 a sodalite structure by a pore size about 11.6 Å, connected by six small flexible ring apertures of about 3.4 Å is obtained by bridging center of Zn(II) metal into 2-methyl imidazole [23-27]. Strong coordination bond among the anionic nitrogen atom and the center metal ions in the organic (imidazolate) linkers lead to high chemical and thermal stabilities (up to 450 °C). Furthermore, unique molecular sieving structural pores, large surface area (1300–1700 m²/g), specific adsorption properties made ZIF-8 as an ideal filler with superlative features [28].

Several papers have reported the benefits of adding various inorganic NPs, particularly ZIF-8, to the polymeric membranes to enhance their performance. It has been inserted into polymers like Matrimid [7], PPEES [29], PIM-1 [13], and PSF [30]. Also, Zhang et al. concluded that, additional primary sites within the pores and even an increase in CO₂ uptake related to pure ZIF-8 starved of any changes in the crystal integrity were obtained by introducing ammonia impregnated ZIF-8 [6].

Thus, this work set out to study the effects of ZIF-8 nanofillers on the ideal efficiency of composite membranes, containing two thin selective layers of PDMS on porous Polysulfone (PSF) membrane. It is the first time, based on our knowledge, that on the top of the PSF membrane, ZIF-8 added to a double thin layer of PDMS. To determine the thermal stability, functional group, crystal structure, and morphology of the membranes before and after adding ZIF-8, thermal gravimetric analysis (TGA), attenuated total reflectance-infrared spectroscopy (ATR-IR), X-ray diffraction (XRD), and Field Emission-Scanning electron microscope (FE-SEM) applied. However, ZIF-8 can be altered with various functional groups as a strategy to surge its dependence with CO₂ gas, and diffusion path for CO₂ transport by thermal annealing process and also breaking the weak bond Zn-N to expand unpaired electrons on the N atoms for CO₂ adsorb described in the literature [31]. Thus, ZIF-8 modification, including the thermal annealing of ZIFs and linking with amine-based bridging ligands implemented to improve the gas separation efficiency of membranes, and their permeability results recorded.

2. Experimental

2.1. Materials

2-methylimidazole (mIM) and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) were procured from Sigma Aldrich (the USA). Acetone, n-hexane, N, N-methyl pyrrolidone (NMP), ammonium hydroxide solution (25%), and isopropyl alcohol obtained from Merck (Germany). Polydimethylsiloxane (PDMS) (Sylgard® 184 Silicone Elastomer) and Polysulfone (PSF Udel® P-3500) were prepared from Dow Corning and Solvay Plastic, respectively. All chemicals used as received and deionized water (DW) used throughout the study.

2.2. Preparation of nanoparticles ZIF-8

ZIF-8 NPs were synthesized according to the procedure described in the literature [32]. 1.17 g of Zn(NO₃)₂·6H₂O was dissolved in 8mL DW, and 22.70 g mIM was dissolved in 80mL DW (molar ratio of Zn²⁺: mIM: H₂O= 1: 70: 1238). ZIF-8 crystals with hexagonal nature produced with the rapid

pouring of the zinc nitrate aqueous solution of into mIM, and then the synthesis solution turned milky. Afterward, after stirring the mixture at room temp for 5 min, the product was collected via continuous centrifugation (0.5h, 6500 rpm) and then washed with DW three times. Finally, the product was dried in a drying oven at 65 °C overnight. Then, the specific amount of synthesized ZIF-8 was uniformly distributed into the ammonium hydroxide solution with additional DW, and then the suspension was sonicated (for 1h). By stirring the resulting solution at definite temperatures for 24h, the sample was collected by centrifugation and washed with DW (three times) before being dried in the oven (60 °C) overnight [30]. Finally, the obtained modified ZIF-8 particles were thermal-annealed in the furnace under vacuum at 300 °C and 1 hour [31].

2.3. Preparation of MMMs

The flat PSF sheet was made from the solution containing of PSF (22 wt%) in NMP (78 wt%). The mixture was stirred till entire polymer pellets dissolved. After an overnight degassing, the solution was cast on a clean glass plate using a casting knife at an ambient atmosphere to a thickness of 350 μm. The cast film was dipped in water for 24h and then air-dried for 24h [33,34].

A homogeneous solution of PDMS (5 wt%) was obtained by dissolving a certain amount of PDMS in n-hexane and stirring for 2 hours at room temp. Synthesized ZIF-8 NPs dispersed in n-hexane for 20 min using a sonicator. The resulting solution then mixed with the PDMS pre-polymer solution, and sonicated for 10 minutes to reduce NP accumulation and sedimentation. At last, the solution was casted rapidly onto a PSF support membrane. After evaporation of the solvent, the membrane dried overnight at 70 °C then this process repeated for the second level of coating. Another MMMs consist of modified ZIF-8 was achieved by the same route as explained above [10,15,22,35,36].

2.4. Characterization

The functional groups and chemical properties of pristine ZIF-8, modified NPs, and prepared membranes characterized by using ATR-IR. XRD analysis employed to confirm the phase similarity of ZIF-8 with other literature and also investigate the crystallinity of membranes. Thermal stability of membranes carried out by using TGA. The small pieces of membranes studied under the N₂ environment and the ramping rate of 10 °C/min from 25 °C to 800 °C. It records the weight changes of the samples under continuous heat condition. Membrane degradation and decomposition estimated from TGA results. The morphologies of the prepared ZIF-8 NPs and membranes characterized by FE-SEM-MIRA3, (TESCAN, Czech). All membrane samples were immersed in nitrogen liquid, then fractured into small pieces, and the NPs were dispersed on smooth silicon and observed after covering with a thin layer of gold. Gas permeation experiments were done using a constant-pressure/variable-volume system. Pure CO₂, N₂, O₂ with high purity (over 99%) were used in the gas permeation tests at 25 °C. The flat membrane with the active permeation area of 15 cm² placed into the permeation cell and exposed to pure gases. Feed pressure was constant at 3 bar for all gases. The liquid flow meter used to record the permeate flow rate and obtain permeability [37]. After the entire permeation system reached steady-state conditions, each measurement calculated at least three times, and gas permeability calculated by using eq. 1.

$$\frac{P}{l} = \frac{j}{A \times \Delta P} \quad (1)$$

The gas permeance is shown with P/l, j is the flux of gas permeated through the membranes (cm³/s), A is the effective membrane area (cm²), and ΔP is the pressure difference (cmHg). Permeance was calculated in gas permeation unit (GPU, 1GPU=1×10⁻⁶cm³(STP)cm⁻²s⁻¹cmHg⁻¹). Separation factor or ideal selectivity (α) is the gas permeability ratio, and is explained as follows:

$$\alpha = \frac{P_A}{P_B} \quad (2)$$

The permeability of pure gas A and B, are shown with P_A and P_B, respectively.

3. Results and discussion

3.1. Characterization of ZIF-8 NPs

Changes in the chemical structures of synthesized ZIF-8 NPs studied by FTIR spectra (Figure 1a). Peaks at 3164 and 1569 cm^{-1} are associated to C=C and C=N bonds, respectively. The absorption band at 2948 cm^{-1} attributed to the aromatic C-H stretch of imidazole. The band at 1307 cm^{-1} represents the stretching vibrations of N-H. The peak at 1145 cm^{-1} can be related to the C-N stretching vibrations mode. The peaks at 420 cm^{-1} and 756 cm^{-1} related to Zn-N, and C-H bonds, and peaks at 1425 and 1454 are identified as CH_3 . The FTIR spectrum of the prepared ZIF-8 corresponds well with the FTIR spectrum of ZIF-8 in the other studies that confirmed the prepared NPs are confidently ZIF-8 [38]. The FTIR spectra of NH_2 -ZIF-8 remains almost unchanged because of the same functional groups in their structures; however, a slight increment in peak intensity in C-N, N-H was observed [30,39,40]. Furthermore, the FTIR spectra of annealed samples are similar to the raw samples, just a very slight decrement in the peak intensity of Zn-N bond was observed [31,41]. Figure 1b displays the XRD pattern of prepared ZIF-8. All main peaks of the XRD pattern correspond to the published XRD pattern of ZIF-8 in other works. This affirms that the synthesized NPs are definitely ZIF-8 without other impurities [42]. There are no apparent differences in the XRD patterns of ZIF-8s after alteration even in the peak width of modified and virgin ZIF-8 that it can be said that amendment does not change the size of ZIF-8 particles. However, the intensity of the main XRD peak intensified after amendment and because impurity decomposed during annealing and guest molecules removed in the pores. Figure 1c shows the morphology of the

fabricated ZIF-8 NPs. A uniform rhombic dodecahedral shape with the size range below 100 nm observed that indicating good agreement with literature.

3.2. Membranes characterization

The ATR-FTIR spectrum of the PDMS films similarly corresponds the literature either. The energetic band at 1053, 2962, and 1256 cm^{-1} has been assigned respectively to Si-O-Si, C-H of the $-\text{CH}_3$ groups, and Si-C stretching vibrations. Compared with the spectra of pure PDMS, after incorporating ZIF-8 NPs into PDMS, new peaks were observed. Peaks at 1584, 1296, 1149 cm^{-1} are allotted to C=N, N-H, C-N bands, respectively. C-H bond in MMMs, due to overlapping C-H bond in ZIF-8 and PDMS, increased in comparison with bare PDMS (see Figure 2a) [43].

The XRD picks of MMMs aims to identify structural changes of the membrane after modification via ZIF-8. The horizontal axis based on 2θ and the vertical axis based on peak intensity. As expected, by adding ZIF-8 into the PDMS layer, the membrane crystallization was changed due to its crystallization and larger size of such nanofiller. Besides, a significant increase in peak intensity and the presence of new peaks prove the presence of ZIF-8 in the structure of MMM (see Figure 2b).

The thermal stability of the membranes illustrated in Figure 2c. Compared with the transparent layer, decreasing the total weight of the MMMs in compare to pure membrane indicates that the ZIF-8 incorporation improves their thermal stability. It may be due that the existence of ZIF-8 helped to absorb the thermal energy and therefore keep away the PDMS membrane from the thermal attack.

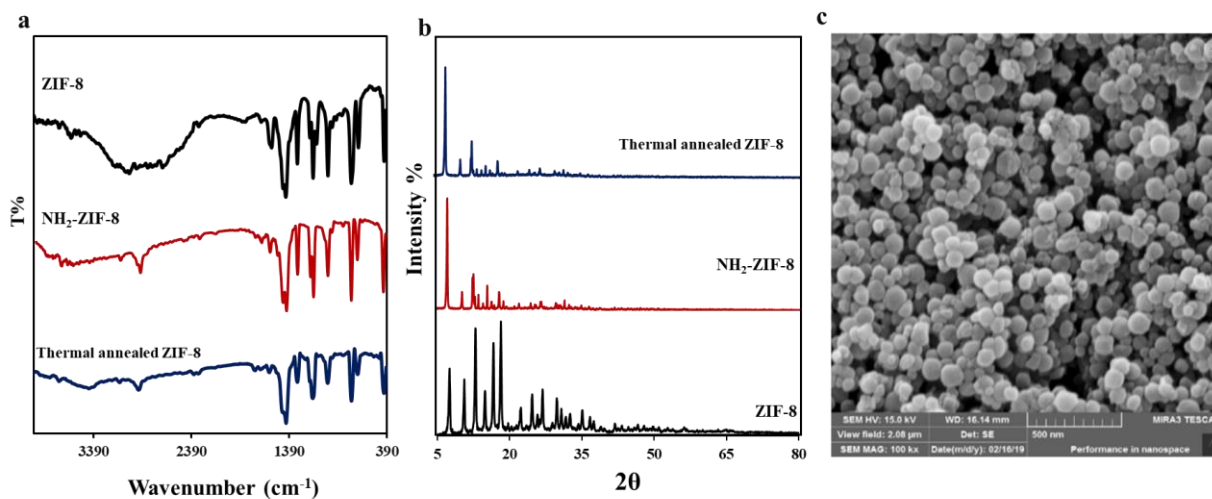


Fig. 1. (a) Fourier transform infrared (FTIR) spectra of ZIFs nano particles, (b) XRD patterns of ZIFs nano particles, (c) SEM image of ZIF-8 nanoparticles.

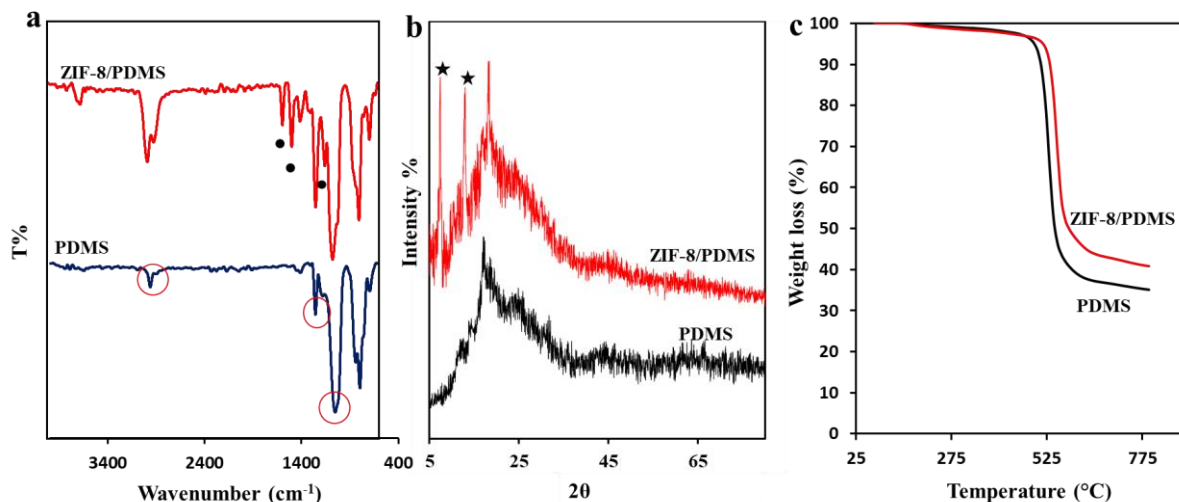


Fig. 2. (a) Attenuated total reflectance-infrared spectroscopy (ATR) of membranes, (b) XRD patterns of PDMS and MMM, (c) TGA curves of PDMS and MMM.

3.3. Morphological investigation (SEM)

In order to investigate the cross-sectional and surface morphologies of membranes, FE-SEM used, and the related results respectively are shown in Figures 3 and 4. The Cross-sectional morphologies of the membranes, which based on the support of PSF with finger cavities shown in Figure 3a. The cross-sectional images affirm the presence of thin-film PDMS on the top of the PSF support surface, and a typical asymmetric structure could be observed. The lack of agglomeration of nanoparticles in the formation of PDMS in lower percentages is proper evidence that proves the uniform distribution of nanoparticles in the upper layer of all MMMs. Moreover, the images indicate the desired adhesion of the PDMS layer to the support. In a high percentage of nanoparticles, a small agglomeration inside the PDMS would be observed.

Figure 4 illustrated the surface characteristics of the prepared membranes. Figure 4a shows the surface of the neat PSF membrane before covering with PDMS. As can be seen, the smart layer showed lots of cavities and cracks on the surface that make the membrane undesirable to perform well in gas separation. Figure 4b clearly showed a perfectly smooth surface of the created PDMS layer on the top of PSF. Oppositely, the images Figure 4c-f illustrated covers with a condensed and shrunk thin layer of PDMS, confirming the dispersion and consistency of nanoparticles into the surface of MMMs. Micrographs represented the MMMs composed of zero, 3, and 6 wt% of nanoparticles, respectively. Further percentage of nanoparticles into the structure of PDMS presumably helps to improve the separation efficiency of MMMs owing to the separation characteristics of nanofillers.

3.4. Permeation Analysis

The gas permeation conducted to evaluate the ideal separation of gases in both neat and MMMs (Figure 5). Permeation tests were undertaken in the pressure 3 bar at ambient temperature. All experiments were repeated 3 times and the average values reported. Regarding the results, the order of permeability of gases is $\text{CO}_2 > \text{O}_2 > \text{N}_2$, respectively. It could be explained in terms of:

1. The porous structure of ZIF-8 nanoparticles that provide a network of cavities for gas molecules that facilitate gaseous penetration, and since the kinematic diameter of the CO_2 is smaller than N_2 and O_2 , and it leads to higher penetration of CO_2 .
2. There are suitable places close to Imidazole rings (open metal sites in ZIF-8 pores) that have good interaction between quadrupole moment of CO_2 , resulting in higher permeability of CO_2 .

Moreover, the interaction between ZIF-8 NPs and the polymer phase induces excess free volume among polymeric chains, so by increasing the percentage of ZIF-8, the permeability of all gases increased owing to facilitating the transfer of gases by the filler. At 1 wt% of ZIF-8, the maximum permeability of CO_2 , O_2 , and N_2 achieved at 89.77, 6.59, and 18.92barrier, respectively (Figure 5a). Adversely, by more increasing the amount of nanoparticles in the composite membrane, there is also a decrease in permeability, which can be owing to an increase in tortuosity of the permeation path in the attendance of the large number of fillers NPs, which mass transport resistance increases.

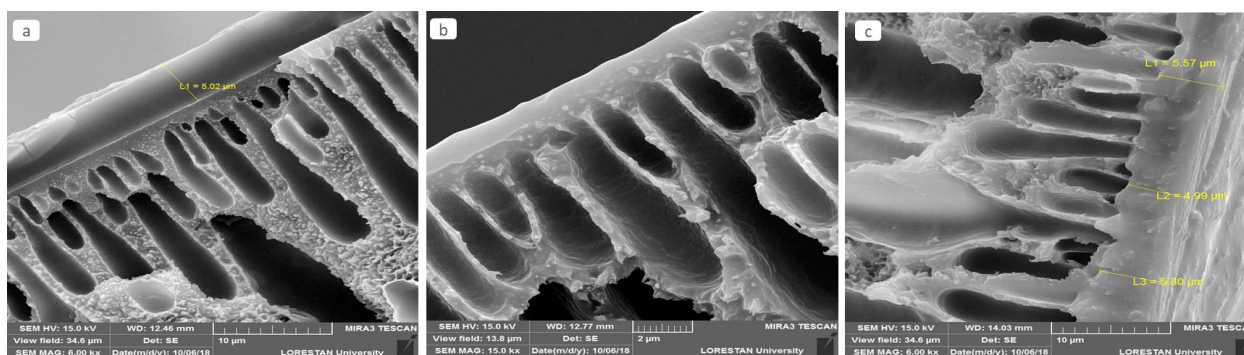


Fig. 3. SEM images of cross section morphology of ZIF-8/PDMS MMMs, (a) PDMS, (b) 3%wt, (c) 6%wt.

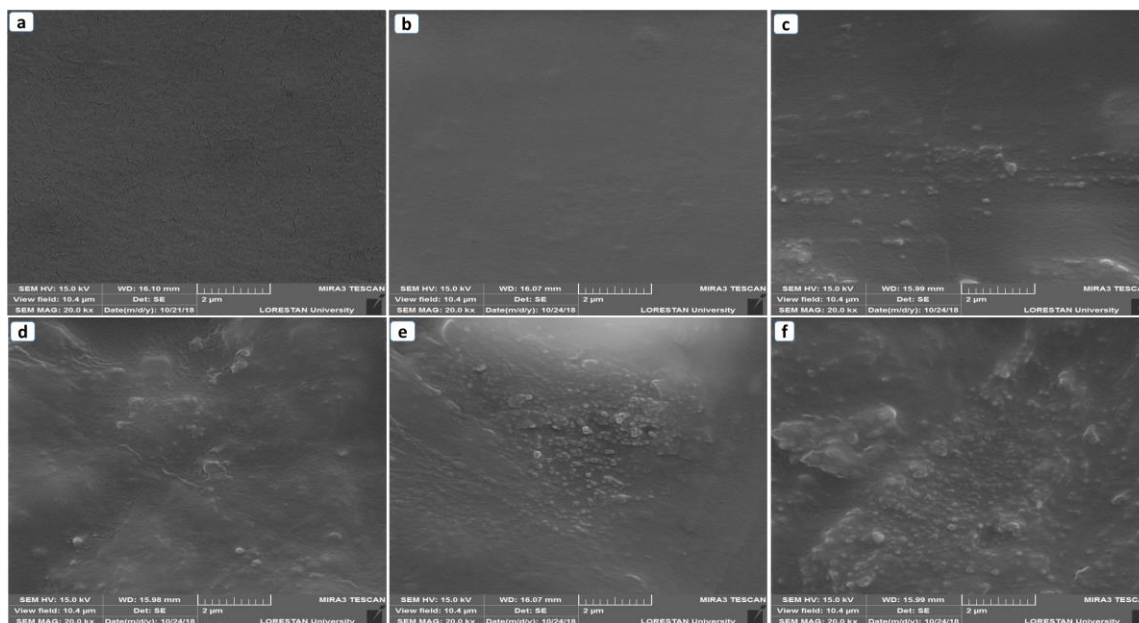


Fig. 4. SEM images of surface morphology of ZIF-8/PDMS MMMs, (a) PSF, (b) PDMS, (c) 1%wt, (d) 2%wt, (e) 3%wt, (f) 6%wt.

The selectivity of O_2/N_2 and CO_2/N_2 is shown in Figure 5b, which reaches from 2.4 and 10.45 in the bare membrane to 2.95 and 13.62 in 2 wt% of ZIF-8. ZIF-8 NPs, like other MOFs, have necessary molecular sieving that can distinct gaseous molecules based on the size of their cavities and the kinematic diameter of gases (the kinematic width of gases is CO_2 (3.3Å), N_2 (3.64 Å) and O_2 (3.46Å)). The ZIF-8 nanocrystals have large cavities (11.6 Å) and window opening approximately 3.4 Å [31,44]. Furthermore, the strong interaction of C=C groups with CO_2 makes this filler act as a selectable filler. By increasing the percentage of nanoparticles, the ideal selectivity of membranes has been raised in comparison to the neat layer, which be ascribed to the inherent selectivity of ZIF-8 NPs.

By more increasing the percentage of nanoparticles, a slight decrement in the selectivity of the pair gases was observed; it can be attributed to the intense accumulation of nanoparticles, which is carried out at higher percentages, restrict the penetrate the pores. Also, formation hunk and increase the non-selective cavities in membrane structure caused a reduction in selectivity. The highest selectivity of O_2/N_2 and CO_2/N_2 was observed at 2 wt% of nanoparticles.

To better stability of nanoparticles in a polymer solution and to increase the gas separation and permeation efficiency of membranes, the nanoparticles were modified by amine functional groups. As shown in Table 1, the permeability of gases after modification generally decreased. As a consequence of the results, it can be explained that entrapping the CO_2 within and inside the filler hindered its diffusion owing to strong "quadrupole- π electron" interaction between CO_2 and N-H group. Also, by modifying the nanoparticles via $-NH_2$ anchoring, the contribution of mesopores decreased; nevertheless, micropores increased. Accordingly, the permeability of all gases decreased. Besides, selectivity has increased by increasing the participation micropores in the permeation path; thus, CO_2 with a smaller kinetic diameter illustrated better passing throughout the membrane [30].

Another idea which was also performed to improve the separation properties of the MMMs was to treat the NH_2 -ZIF-8 nanoparticles with thermal annealing procedure under 300 °C for one hour, resulting in breakage of the Zn-N bond [31]. Thermal annealed NH_2 -ZIF-8 NPs embedded in the PDMS layer, and the performance of 2 wt% nanofiller is shown in Table 1. By thermal annealing, the Zn-N weak bond is broken. The interaction between CO_2 and ZIF nanofiller would be increased due to the lone pair electrons in N atom formed from annealing.

Figure 6 implied the efficiency of the fabricated membranes on Robeson's upper bound limit for CO_2/N_2 (Figure 6a) and O_2/N_2 (Figure 6b). As can be seen, the performance of nano-composite membranes filled with

modified ZIF is closer to the boundary compared to the layers filled with raw ZIF-8.

Table 2 illustrated and compared the CO_2/N_2 selectivity of MMMs primed in the current work to literatures. Despite the lower percentage of nanoparticles compared to other studies, the MMMs incorporated with thermal annealed ZIF-8 nanoparticles showed a comparable and desired performance.

Table 1

Gas permeation results of MMMs.

| Membrane | P_{N_2} (BARRER) | P_{O_2} (BARRER) | P_{CO_2} (BARRER) | α_{O_2/N_2} | α_{CO_2/N_2} |
|--------------------------|-----------------------|-----------------------|------------------------|--------------------|---------------------|
| ZIF-8 @PDMS, 2%W | 6.121 | 18.083 | 83.416 | 2.95 | 13.62 |
| NH_2 -ZIF-8 @PDMS, 2%W | 1.99 | 9.98 | 43.69 | 4.97 | 21.75 |
| THERMAL ZIF-8 @PDMS, 2%W | 2.40 | 13.42 | 53.69 | 5.5 | 22.37 |

Table 2

Comparison the gas separation efficiency of this investigation with other literature.

| Membrane | Filler | Selectivity CO_2/N_2 | P_{CO_2} (Barrer) | ref. |
|------------|---------------------------|------------------------|---------------------|-----------|
| PSF | ZIF-8/GO | 24 | 79.9 GPU | [45] |
| PVC-g-POEM | 10% ZIF-8 | 31.4 | 197.6 | [46] |
| SEBS | ZIF-8 | 12 | 454.6 | [25] |
| PMPS | ZIF-8 | 7 | 827 | [47] |
| Ultem | 17% ZIF-8 | 36 | 26 GPU | [48] |
| PEBAX | 5% ZIF-8 | 29.6 | 365 | [49] |
| PDMS | - | 11 | 3395 | [50] |
| PDMS | KIT-6 silica | 1.9 | 12 | [51] |
| PDMS | 2% Thermal annealed ZIF-8 | 22.37 | 53.69 | This work |

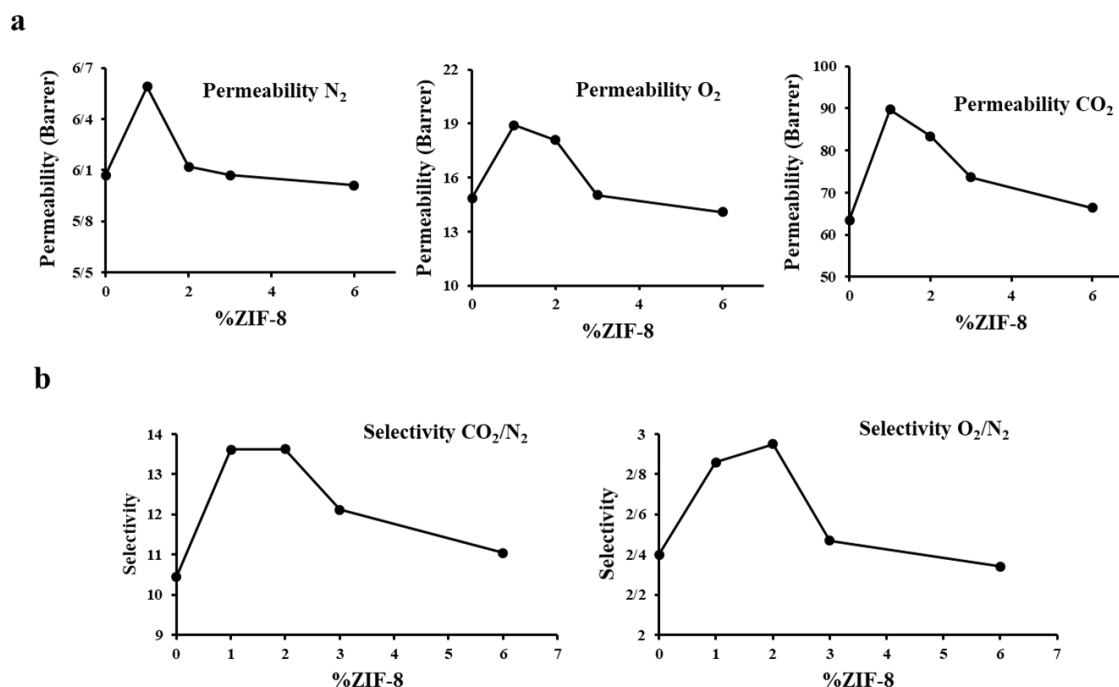


Fig. 5. (a) Gas permeability of membranes, (b) Selectivity of pair gases through membranes.

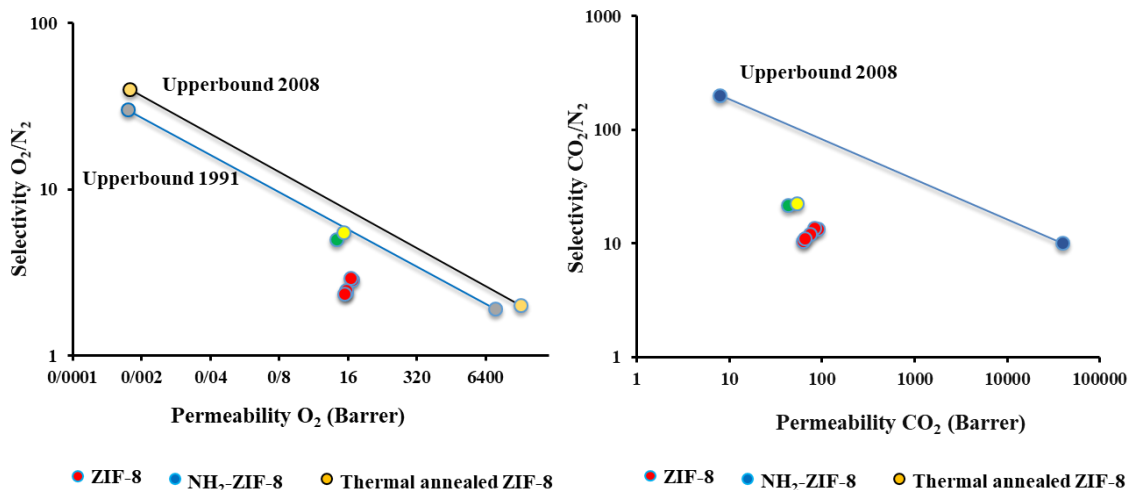


Fig. 6. (a) The Robeson upper bound relationship of O₂ permeability and O₂/N₂ selectivity and comparison with the present work performed, (b) The Robeson upper bound relationship of CO₂ permeability and CO₂/N₂ selectivity and comparison with the present work performed.

4. Conclusions

The current study, ZIF-8 and its derivatives embedded into a double layer of PDMS fabricated via coating method, and then the performance for gas separation explored. In comparison with pure PDMS membranes, all MMMs with ZIF-8 NPs and its derivatives showed substantial improvement in O₂/N₂ and CO₂/N₂ selectivity, especially for thermal treated ZIF-8 that showed an appropriate selectivity over 22. The results illustrated that the existence of ZIF-8 nanofillers and its derivatives inside the rubbery PDMS polymeric layer on the top of the PSF membrane causes a great potential to become better the efficiency for gas separation.

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