



Fabrication of a Polyetherimide/ZIF-8 Composite Membrane for Separating Carbon Dioxide from Methane

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ABSTRACT

In the present work, a polyetherimide/ZIF-8 composite membrane was fabricated by solution casting technique. The prepared membranes were characterized using Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy - attenuated total reflectance (FTIR-ATR), energy dispersive X-ray (EDAX) and X-ray diffraction (XRD). Furthermore, the membrane's performance in separating carbon dioxide and methane was analyzed through single gas permeability measurements. FTIR-ATR spectrum of the prepared membrane confirmed the functional groups of polyetherimide. XRD analysis showed that the additive was well dispersed in the polymer, resulted in a reduction in the membrane's crystallinity. EDAX analysis confirmed the existence and proper dispersion of Zn particles in the membrane. Finally, the results of permeability tests showed that adding ZIF-8 to the membrane significantly increased its permeability and selectivity. The permeability of the composite membrane for CO₂ gas was 5.91 GPU, more than twice that of the pure polyetherimide membrane. Additionally, the permeability for CH₄ gas was 0.31 GPU, representing a significant improvement over the pure membrane's permeability of 0.17 GPU. The carbon dioxide/methane selectivity also rose from 15.3 in the pure membrane to 19.1 in the composite membrane. In conclusion, the study demonstrated that adding ZIF-8 to a polyetherimide matrix can improve the effectiveness of the resulting composite membrane for separating CO₂ from CH₄. The improvement in selectivity was primarily due to the increased solubility coefficient of carbon dioxide compared to methane in the composite membrane.

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1. Introduction

Among the different technologies to reduce CO₂, membrane technology is suggested because of its great performance and environmental friendliness. Typically, polymer and inorganic membranes have been utilized in gas separation, with a specific type of membrane known as mixed matrix membranes being created by incorporating inorganic particles as fillers in polymer membranes. In the fabrication of mixed matrix membranes, polymer materials are commonly used as the membrane network, and other materials such as mineral nanoparticles and ionic liquids are added to improve the polymer structure and its permeability and selectivity characteristics.

Zeolites, molecular sieve carbons and organic-metal frameworks (MOFs) are frequently employed materials in the development of composite network membranes (Setiawan et al., 2019). Since the discovery MOFs, scientists have attempted to utilize them in gas separation membranes. Zeolitic imidazolate frameworks (ZIFs) are a novel category of nanoporous materials that can be produced with various pore sizes and applied as nanofillers in mixed matrix membranes (MMM). Zn(2-methylimidazolate)₂, also known as ZIF-8, has been extensively researched for membrane applications because of its uncomplicated synthesis, strong chemical and thermal stability, widespread availability in the market, and the size of its adsorbent pores (Xia et al., 2014).

Murali et al.(2010) synthesized a membrane based on Pebax 1657 and carbon nanotubes (MWNT) as a filler to investigate the permeability of H₂, N₂, O₂ and CO₂ gases. They used 2,4-toluylene diisocyanate to modify the polymer structure, which led to a reduction in the size of the holes in the polymer chains and amplified the screening properties of the membrane. In 2016, Dai et al.(2016) investigated the gas permeability of the composite matrix membrane

based on Pebax polymer and graphene oxide nanoparticles. Their studies have shown that carbon dioxide shows greater permeability than H₂, CH₄ and N₂ gases due to its higher solubility in polymer matrix. In addition, carbon dioxide gas has a relatively good interaction with the imidazole group and its absorption in graphene increases the selectivity of this gas compared to other gases. Dorosti et al.(2014) investigated the mixed matrix membrane composed of Matrimid polymer and MIL-53 nanoparticles (from the composition of 0 to 20 percent by weight). They used this membrane to separate carbon dioxide from methane.

Azizi et al.(2017) studied composite mixed matrix membranes using Pebax 1074 polymer and ZnO nanoparticles with weight percentages of 2, 4, 6 and 8%. They noted that as the proportion of nanoparticles in the polymer matrix rose, the permeability of carbon dioxide gas increased significantly, whereas the increase for nitrogen and methane was much more modest. Perez et al.(2009) assessed the CO₂ and CH₄ permeability of 5-Matrimid/MOF composite matrix membrane. CO₂ permeability increased from 9 to 20.2 bar, while this permeability improvement in CH₄ was weaker. They also found that the CO₂/CH₄ selectivity decreased with the increase of 5-MOF weight percent. They clarified that in some cases, the aggregation of particles at higher concentrations can result in the formation of holes in the polymer and particle common phase, in order to interpret their findings.

Polyetherimide is a thermoplastic polymer known for its outstanding mechanical, thermal, and chemical resistance characteristics. It has high permeability to CO₂ and CH₄ gases due to its amorphous nature and presence of polar ether and imide groups. Polyetherimide also has moderate solubility selectivity for CO₂ over CH₄, which can be enhanced by incorporating porous ZIF-8 particles (Rahman et al., 2023). The dispersed ZIF-8 nanoparticles can facilitate gas

transport through the membrane by providing additional pathways for gas molecules to diffuse through the polymer matrix. Polyetherimide also has good compatibility with ZIF-8, allowing for uniform dispersion of ZIF-8 within the polymer. The high thermal stability of polyetherimide also permits high temperature processing to form mixed matrix membranes with ZIF-8 (Bergaoui et al., 2021). In the present work, a polyetherimide/ZIF-8 mixed matrix membrane was fabricated and its characteristics and potential for separation of CO₂/CH₄ separation was studied.

2. Materials and Methods

2.1. Materials and Reagents

Polyether imide as asymmetric membrane polymer phase and 2-methylimidazole and zinc nitrate (Zn(NO₃)₂·6H₂O) as additive phase and 1-methyl-2-pyrrolidone as solvent were obtained from Merck.

2.2. Membrane Preparation

The PEI substrate with embedded ZIF-8 was created by synthesizing ZIF-8 particles within the casting solution of the PEI membrane. The complete dissolution of 2.2 g of PEI in 9.82 mL of NMP at 70 °C was followed by dissolving 0.1g of Zn(NO₃)₂·6H₂O in 9.82 mL of NMP and then adding it to the PEI mixture solution. The solution was agitated for 2 hours and then allowed to sit for 3 hours to facilitate the growth of ZIF-8 crystals. Following another 24 hours of stirring, the ZIF-8/PEI mixture solution was applied onto a glass sheet onto a glass sheet to form a uniform 0.5mm layer. The entire glass sheet was then submerged in DI water for 24 hours to undergo phase conversion and then dried at 30 °C for another 24 hours. The fabrication process of the pure PEI support was the same as that of the ZIF-8 in-situ embedded PEI substrate. The pure PEI support was fabricated using the same method, involving the dissolution of 2.2 g of PEI in 9.82 mL of NMP.

2.3. Characterization and Gas Permeance Test

FTIR analysis was performed using a Shimadzu 8900-model device. X-ray diffraction (XRD) pattern was conducted using a Philips PW1730 XRD device to identify the phases in the sample and the degree of crystallinity of the membranes. X-ray Energy Diffraction Spectroscopy (EDAX) analysis was performed to identify the constituent elements of the desired sample. Also, mapping images from electron microscope analysis (SEM) using FEI Quanta 200 SEM device were used to analyze the membrane's composition.

Permeability of pure carbon dioxide and methane gases along with selectivity of carbon dioxide/methane were measured and calculated. The flow of carbon dioxide or methane gas, passing through a pressure regulator set to 1 bar, enters the chamber with a known volume and hits the upper surface of the membrane. During the time it is recorded by the data logger, it passes through the mixed matrix membrane and gradually increases the pressure in the output area of the device, which is recorded by the pressure sensor. The raw data obtained from the permeability measurement setup is in the form of pressure changes with time, which will be calculated using the following relation of permeability values:

$$\text{Permeability (GPU)} = \frac{273.15 \times 10^6 \times V \times t}{760 \times ATP_0} \quad (1)$$

In the given equation, P represents gas permeability, V stands for chamber volume (measured in cm³), A denotes the membrane surface area (measured in cm²), T represents the test temperature (measured in Kelvin), P₀ signifies the pressure of the gas feed to the system (measured in mmHg), and dp/dt indicates the rate of change in pressure of the permeable gas over time. The ideal selectivity is achieved by dividing the permeability of pure gases using the following formula:

$$\alpha_{AB} = \frac{p_A}{p_B} \quad (2)$$

3. Results and Discussion

The FTIR-ATR graph of the fabricated composite membrane is depicted in (Figure 1). The peak at $\sim 1715\text{ cm}^{-1}$ is related to the symmetric stretching vibration of carbonyl imide C=O and the peak at $\sim 1775\text{ cm}^{-1}$ is related to the asymmetric stretching vibration of carbonyl imide C=O. The peaks at $\sim 1475\text{ cm}^{-1}$ and $\sim 1596\text{ cm}^{-1}$ are related to the stretching vibrations of the C=C vibration

of the aromatic ring. The peak in the range of $\sim 1232\text{ cm}^{-1}$ indicates the ethereal C-O bond. The peak at $\sim 1442\text{ cm}^{-1}$ is caused by the stretching vibrations of the C-N bond, and the peak at $\sim 2959\text{ cm}^{-1}$ is related to the stretching vibration of the aromatic C-H ring and the peak at $\sim 740\text{ cm}^{-1}$ indicates the out-of-plane C-H vibration (Chen et al., 2006; Singh et al. 2011).

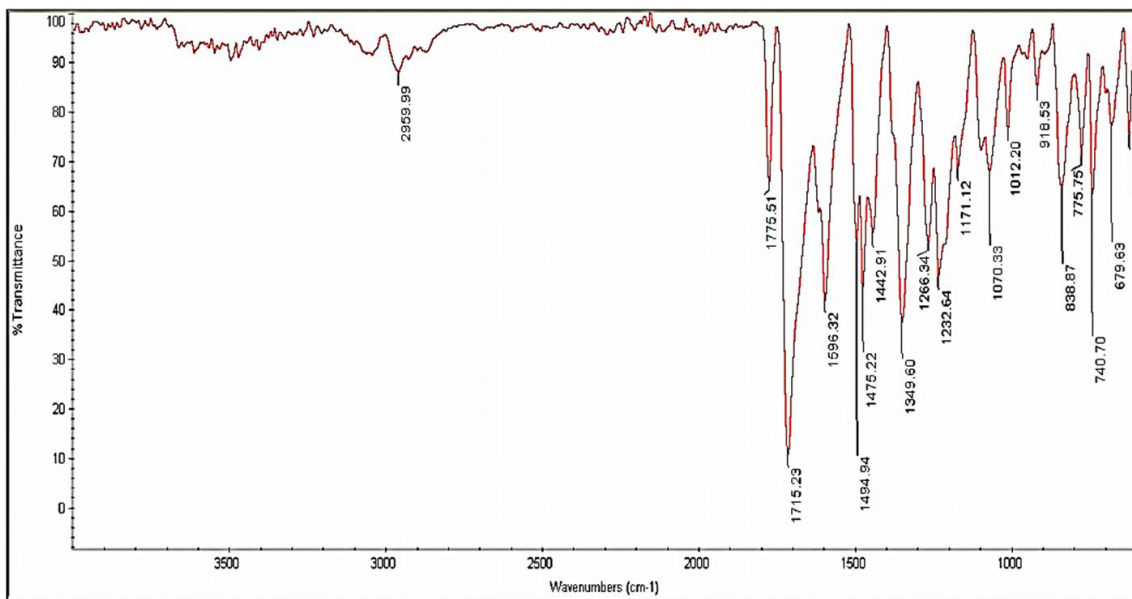


Figure 1. FTIR-ATR Spectra of PEI/ZIF-8 Membrane

The XRD patterns for both the pure polyetherimide membrane and the composite membrane are shown in (Figure 2). In the XRD

pattern of the fabricated membranes, a broad diffraction peak is observed at 2θ of 14.24° , consistent with references (Eiras et al., 2016).

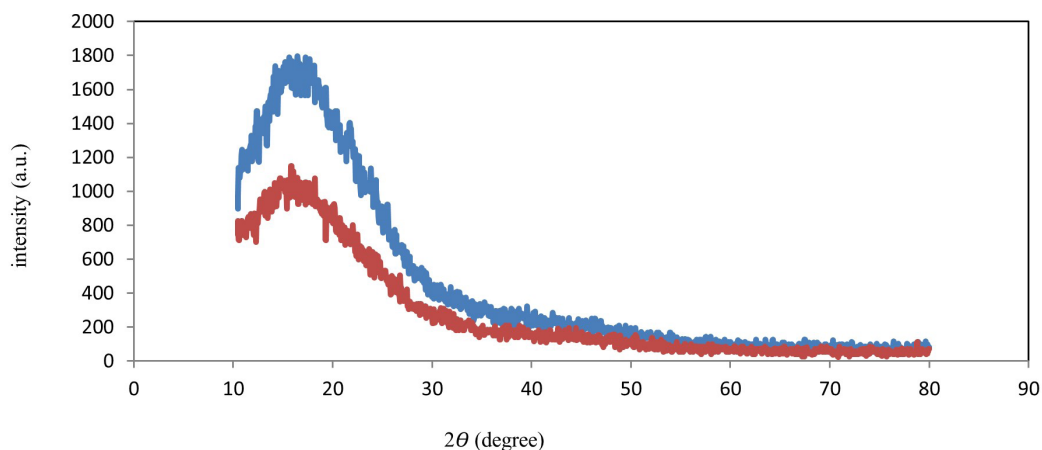


Figure 2. XRD Spectrum of Pure PEI (a) and PEI/ZIF-8 Membrane (b)

As depicted in the above figure, the intensity of the peak for pure polyetherimide has diminished by adding zinc nitrate, which means a decrease in crystallinity. Additives have reduced the crystallinity of the membrane and disrupted its structural unity. In fact, adding additives to the polymer body reduces the structural unity of the membrane due to the increase of amorphous parts. In amorphous materials, the rays weaken each other and the phenomenon of diffraction does not occur, but if the atoms are in the form of a crystalline material, i.e. they are placed next to each other with a certain order and distance, the difference in the path traveled is a multiple of the wavelength of the X-ray and so on. Which is seen in the pure polyether imide membrane, diffraction takes place. Typically, the addition of additives changes the degree of crystallinity of the membranes. The figure illustrates that the membrane's crystallinity decreased with the incorporation of additives. Adding additives to the structure of the polymer membrane causes more stimulation of the polymer chain, which is the reason for the reduction of inter-chain hydrogen bonds.

In order to identify the constituent elements of the desired sample and also to check the distribution of elements inside the membrane, X-ray Energy Dispersive Spectroscopy (EDAX) analysis and mapping images were used for the polymer composite membrane. The result of the EDAX test of the mixed matrix membrane confirms the existence of zinc (Zn) in the polymer matrix, which is shown in (Figure 3) with the Zn peak and it suggests that the ZIF-8 particles are evenly distributed across the membrane's cross-sectional area. The mixing of zeolite particles in the polyetherimide membrane has led to the accumulation of particles in the membrane, primarily because of the insufficient adhesion between the polyether imide membrane and additive particles. When a higher percentage of zeolite particles are included inside the membrane, the aggregation of particles that are in the form of aggregates becomes larger, which causes the formation of large pores, which leads to low performance in CO_2/CH_4 selectivity (Ma et al., 2018).

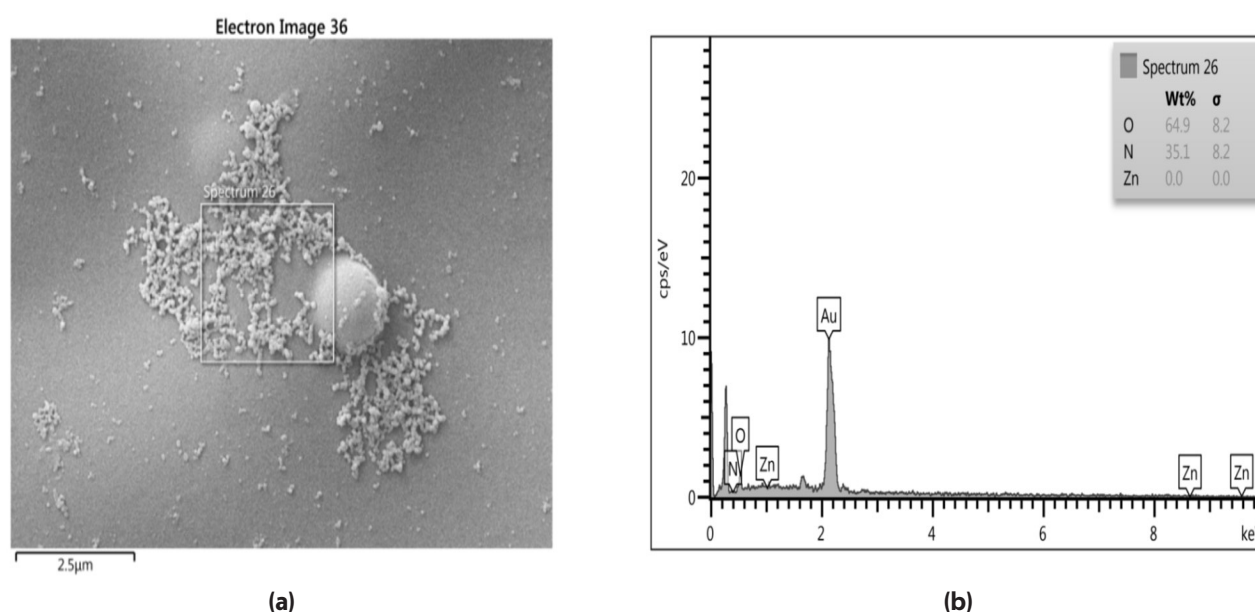


Figure 3. SEM (a) Image and EDAX Analysis (b) of the PEI/ZIF-8 Membrane

The pressure changes over time for the constructed membranes are depicted in (Figure 4), while (Table 1) presents the calculated permeation

values for both gases and the ideal carbon dioxide/methane selectivity for all constructed membranes, alongside similar investigations. It

was noted that the permeability of both gases rose with the introduction of additives to the pure polymer solution in the polymer matrix. This rise in permeability was more pronounced for carbon dioxide gas than for methane gas. One factor that contributed to the enhanced selectivity in the composite, as opposed to the pure membrane, was the selective absorption of CO_2 by the additive. This absorption facilitated and enhanced the passage of this gas, ultimately leading to an increase in selectivity. Moreover, the existence of additives

enhanced the movement of the polymer chain, leading to chain breakage and increased free volume. Consequently, CO_2 exhibited higher permeability than CH_4 due to its greater solubility, thereby increasing the selectivity [20]. When comparing the obtained results with those of similar works, it's worth mentioning that the gas permeability and selectivity values varied due to differences in the thickness of the polymer films and the incorporation of additives with varying weight percentages, making direct comparisons challenging.

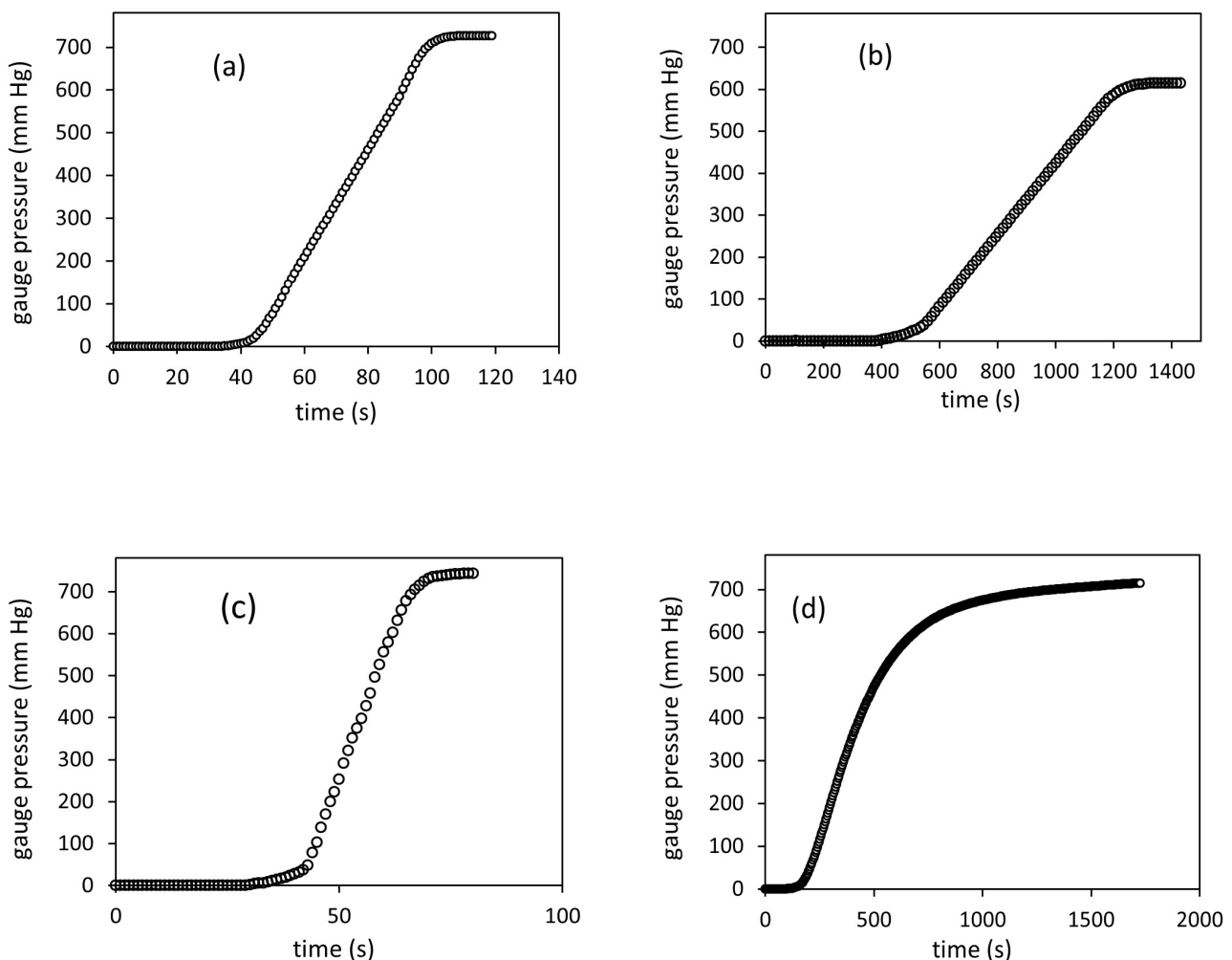


Figure 4. Diagram of Pressure Changes of Membranes:

- a) Pure Polyetherimide Membrane for CO_2 Gas,**
- b) Pure Polyetherimide Membrane for CH_4 Gas,**
- c) Mixed Matrix Membrane for CO_2 Gas,**
- d) Mixed Matrix Membrane for CH_4 Gas**

4. Conclusion

On this research, the effect of an additive such as zinc nitrate on the permeability properties of CO₂ and CH₄ gases of asymmetric composite membranes using polyetherimide by solution casting was evaluated. The prepared membranes were analyzed by Fourier transform infrared spectroscopic analysis (FTIR), X-ray diffraction analysis (XRD), energy dispersive X-ray spectroscopic analysis (EDAX) and scanning electron microscope image (SEM). Moreover, the effectiveness of the resulting membranes was checked by measuring the permeability of carbon dioxide and methane

gases and also calculating the selectivity of carbon dioxide /methane. Fourier infrared spectroscopy analysis and X-ray diffraction showed the proper distribution of the additive or filler inside the polymer matrix, and the result of X-ray energy diffraction spectroscopy analysis confirmed the existence of zinc (Zn) in the membrane. The gas permeability test confirmed that the addition of additives to polymer membranes increases the permeability of gases (especially CO₂) and in addition to this, the Selectivity CO₂ / CH₄ has also had an upward trend in line with permeability.

Table 1. Comparison of Permeability and Selectivity of Pure Polymer and Mixed Matrix Membrane with other Reported Polymer Membrane

Membrane type	CO ₂ permeability (GPU)	CH ₄ Permeability (GPU)	CO ₂ /CH ₄ selectivity	2005
Pure PEI	0.4333	0.0278	15.59	(Vega et al., 2019)
Mixed matrix membrane	0.5810	0.0458	12.68	
Pure PEI	1.535	0.0405	37.9	(Eiras et al., 2017)
Mixed matrix membrane	11.1	0.274	40.4	
Pure PEI	2.60	0.17	15.3	This Research
PEI/ZIF-8	5.91	0.31	19.1	

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References

- Azizi, N., Mohammadi, T. and Behbahani, R. M., 2017. Synthesis of a new nanocomposite membrane (PEBAX-1074/PEG-400/TiO₂) in order to separate CO₂ from CH₄. *J. Nat. Gas. Sci. Eng.*, 37, 39. <https://doi.org/10.1016/j.jngse.2016.11.038>
- Bergaoui, M., Khalfaoui, M., Awadallah, F. A. and Al-Muhtaseb, S., 2021. A review of the features and applications of ZIF-8 and its derivatives for separating CO₂ and isomers of C₃-and C₄-hydrocarbons. *J. Nat. Gas Eng.*, 96, 104289. <https://doi.org/10.1016/j.jngse.2021.104289>
- Chen, B. K., Su, C. T., Tseng, M. C. and Tsay, S. Y., 2006. Preparation of Polyetherimide Nanocomposites with Improved Thermal, Mechanical and Dielectric Properties. *Polym. Bull.*, 57 (5), 671. <http://dx.doi.org/10.1007/s00289-006-0630-3>
- Dorosti, F., Omidkhah, M. and Abedini, R., 2014. Fabrication and characterization of Matrimid/MIL-53 mixed matrix membrane for CO₂/CH₄ separation. *Chem. Eng. Res. Des.*, 92 (11), 2439.

- <https://doi.org/10.1016/j.cherd.2014.02.018>
- Eiras, D., Labreche, Y. and Pessan, L. A., 2016. Ultem®/ZIF-8 Mixed Matrix Membranes for Gas Separation: Transport and Physical Properties. *Mater. Res.*, 19 (1), 220. <https://doi.org/10.1590/1980-5373-MR-2015-0621>
- Ma, Y., Sun, Y., Yin, J., Sun, H., Wu, H. and Wang, H., 2019. A MOF membrane with ultrathin ZIF-8 layer bonded on ZIF-8 in-situ embedded PSf substrate. *J. Taiwan Inst. Chem. Eng.*, 104, 273. <https://doi.org/10.1016/j.jtice.2019.08.012>
- Murali, R. S., Sridhar S., Sankarshana, T. and Ravikumar, Y. V. L., 2010. Gas Permeation Behavior of Pebax-1657 Nanocomposite Membrane Incorporated with Multiwalled Carbon Nanotubes. *Ind. Eng. Chem. Res.*, 49 (14), 6530. <http://dx.doi.org/10.1021/ie9016495>
- Perez, E. V., Balkus, K. J., Ferraris, J. P. and Musselman, I. H., 2009. Mixed-matrix membranes containing MOF-5 for gas separations. *J. Membr. Sci.*, 328(1-2), 165. <http://dx.doi.org/10.1016/j.memsci.2008.12.006>
- Rahman, S. N., Saleem, H. and Zaidi, S. J., 2023. Progress in membranes for pressure retarded osmosis application. *Desalination.*, 549, 116347. <http://dx.doi.org/10.1016/j.desal.2022.116347>
- Setiawan, W. K. and Chiang, K. Y., 2019. Silica applied as mixed matrix membrane inorganic filler for gas separation: a review, *Sustain. Environ. Res.*, 29 (1), 1. <https://doi.org/10.1186/s42834-019-0028-1>
- Singh, K., Devi, S., Bajaj, H. C., Ingole, P., Choudhari, J. and Bhrambhatt, H., 2014. Optical Resolution of Racemic Mixtures of Amino Acids through Nanofiltration Membrane Process, *Sep. Sci. Technol.*, 49 (17), 2630. <https://doi.org/10.1080/01496395.2014.911023>
- Vega, J., Andrio, A., Lemus, A. A., Díaz, J. A. I., del Castillo, L. F., Gavara, R. and Compañ, V., 2019. Modification of polyetherimide membranes with ZIFs fillers for CO₂ separation. *Sep. Purif. Technol.*, 212, 474. <https://doi.org/10.1016/j.seppur.2018.11.033>
- Xia, W., Zhu, J., Guo, W., An, L., Xia, D. and Zou, R., 2014. Well-defined carbon polyhedrons prepared from nanometal-organic frameworks for oxygen reduction. *J. Mater. Chem. A.*, 2 (30), 11606. <http://dx.doi.org/10.1039/C4TA01656D>.

تولید غشای کامپوزیت پلی‌اترایمید/ZIF-8 برای جداسازی دی‌اکسید کربن از متان

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چکیده

در این مطالعه، غشای کامپوزیت پلی‌اترایمید/ZIF-8 به روش ریخته‌گری حلال تولید شد. طیف‌سنجی فوریه تبدیل مادون قرمز - بازتاب کاهش یافته (FTIR-ATR) غشای تهیه شده تأیید کرد که گروه‌های عاملی پلی‌اترایمید وجود دارند. پراش اشعه ایکس (XRD) نشان داد که ذرات افزودنی به خوبی در پلیمر پخش شده است که منجر به کاهش بلورینگی غشا شد. پراش اشعه ایکس پراکنده انرژی (EDAX) وجود و پخش مناسب ذرات روی در غشا را تأیید کرد. در نهایت، نتایج آزمون‌های عبور نشان داد که افزودن ZIF-8 به غشا به طور قابل توجهی میزان عبور و انتخاب‌پذیری آن را افزایش داده است. عبور غشای کامپوزیت برای گاز دی‌اکسید کربن ۵/۹۱ GPU بود، بیش از دو برابر غشای پلی‌اترایمید خالص. علاوه بر این، عبور گاز متان ۰/۳۱ GPU بود که نشان دهنده بهبود قابل توجهی نسبت به نفوذیت غشای خالص با عبور ۰/۱۷ GPU بود. همچنین، انتخاب‌پذیری دی‌اکسید کربن/متان هم از ۱۵/۳ در غشای خالص به ۱۹/۱ در غشای کامپوزیت افزایش یافت. در نتیجه، این مطالعه نشان داد که افزودن ZIF-8 به ماتریس پلی‌اترایمید می‌تواند کارایی غشای کامپوزیت حاصل را در جداسازی CO₂ از CH₄ بهبود بخشد. این بهبود انتخاب‌پذیری را می‌توان بیش از همه به افزایش ضریب حلالیت دی‌اکسید کربن نسبت به متان در غشای کامپوزیت ارتباط داد.

واژگان کلیدی: پلی‌اترایمید، غشای ماتریس آمیخته، ZIF-8، جداسازی گاز