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Effect of Coating Concentration on Gas Separation Performance of Polysulfone Mixed Matrix Membrane for Biomethane Recovery from Wastewater

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ABSTRACT

Anaerobic membrane bioreactor (AnMBR) provides a range of benefits which include high performance in extracting organic matter and energy production in the form of biogas. In this study, performance of mixed matrix membrane (MMM) to recover biomethane from wastewater was studied. Polymer matrix of polysulfone (Psf) incorporated with different inorganic fillers, halloysite nanotubes (HNT) and activated carbon (AC). Different concentration (3%, 4% and 5%) of MMM's polydimethylsiloxane (PDMS) coating were examined by using scanning electron microscopy (SEM-EDX) and gas permeation tests. The morphological structures as well as permeability and selectivity of MMM towards carbon dioxide (CO_2) and methane (CH_4) were investigated. SEM analysis showed that increasing the concentration increases the thickness of the coated surface of the membrane. For MMMs-HNT, the thickness of the top layer increased 29.1% from the uncoated membrane to the highest concentration of PDMS coating while MMMs-AC showed the thickness of the membrane increased by 64.7%. The EDX results showed that there is 46% increase and 9.63% increased of silicon composition for both MMMs-HNT and MMMs-AC. For the gas separation performance, PDMS coated MMMs showed lower permeability but higher selectivity than uncoated MMMs. The highest selectivity of the membrane can be observed in 3wt% PDMS coated MMMs-HNT which is 15.83 with CO_2 and CH_4 permeance of 0.76 and 0.05 GPU, respectively.

Keywords: Mixed matrix membrane, halloysite nanotubes, activated carbon, membrane bioreactor, gas separation

1.0 INTRODUCTION

Anaerobic treatment technology has been widely implemented and proven over the long run in the treatment of processing wastewater. It provides a range of benefits including high performance in extracting organic matter, low production of excess sludge, stable activity and energy production in the form of biogas [1]. To enhance the performance, anaerobic wastewater treatment will be combined with membrane separation which is known as the anaerobic membrane bioreactor (AnMBR) technology. It has been considered a very promising option for wastewater treatment in

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recent years because of its major advantages over traditional anaerobic treatment and aerobic membrane bioreactor technology [2]. In the early 1980s, Dorr-Oliver first commercialised an anaerobic reactor coupled with a membrane. It was developed to handle wastewater of high strength and was called the anaerobic membrane bioreactor method. Since then, many studies were focusing on the efficacy and treatment efficiencies of AnMBRs [3].

One of the key benefits of anaerobic processes are the amount of biogas depends on the composition of wastewater treated by AnMBRs. Biogas consists mainly of carbon dioxide (25-30%) and methane (60-70%) as well as several other gaseous substances nitrogen (N_2), hydrogen (H_2), hydrogen sulfide (H_2S) and and traces of oxygen (O_2) known as volatile organic compounds (VOC) but they are contained in much smaller concentrations. Biogas is mainly used predominantly for the generation of energy. When upgraded to biomethane, it will be used as a fuel for automobiles [4]. Therefore, to get the biomethane, biogas may be further refined to extract carbon dioxide (CO_2) to get the biomethane.

Anaerobic digestion of wastewater produces biogas by which some of it is used in boilers for heat pumps, while the rest is wasted to flare. As biogas flares, a considerable amount of energy that can be utilized is lost. On the other hand, if the raw biogas content of CH_4 was increased to 90% mol by eliminating CO_2 and other gaseous, upgraded biogas may be used as a non-corrosive fuel. Therefore, biomethane recovery through gas separation is needed to utilize the use of CH_4 in biogas.

Several methods of biomethane recovery by extracting carbon dioxide are now available on a commercial scale such as scrubbing (water, organic, and chemical), pressure swing adsorption, membrane separation and cryogenic technology. Among all these methods, the membrane separation is used of its best efficiency in biomethane recovery with modest energy consumption and methane (CH_4) losses. Moreover, Saha *et al*. reported a recovery of 73983 L CH_4 per tonne of food waste from their integrated AnMBR system [5].

In this research study, membrane separation technology of hybrid membrane or mixed matrix membrane (MMM) is used by dispersing the inorganic filler into the polymer matrix where better gas separation performance is expected than the neat polymer. For gas separation, membrane technology such as polymeric and inorganic membranes are the methods that can be used to recover biomethane. The use of homogeneous membranes such as polymeric and inorganic membrane is of restricted approach owing to its higher costs, low chemical, thermal and stability. Polymeric membrane technique suffers predominantly in the trade-off between permeability and selectivity, as defined earlier by Roberson, as an extremely permeable membrane that is often accompanied by low selectivity and vice versa [6]. Inorganic membranes have rarely been used by the industries due to its high manufacturing expense.

On the other hand, as it is low in mechanical strength and easily porous, the inorganic membrane cannot be the ideal replacement for the polymeric membrane for gas separation. This problem continues to be the major challenge and motivation for the present study using MMM. As a result, a lot of research has been conducted to create novel and more efficient gas polymers to address this trade-off problem for gas separation. The most effective approach for enhancing the

permeation properties of these polymers is the creation of mixed matrix membranes.

Mixed matrix membrane (MMM), a common study currently ongoing, is a membrane that is formed by the integration fillers in polymer matrix [7]. The procedure to prepare mixed matrix membranes mainly involve blending and phase inversion. Inorganic materials such as zeolite, carbon nanotube and metal organic frame with unique features (shape, pore size and surface interaction) are typically the fillers used to enhance the efficiency of the mixed matrix membrane in this structure [8]. In MMMs, membrane coating is usually carried out to prepare the MMMs prior to gas separation to eliminate surface defects of the membrane. Coating of membrane is commonly conducted by using PDMS solution that can seal non-selective surface defects successfully due to its low surface tension. Therefore, it is often used as coating film for different asymmetric membranes for gas separation. According to previous work, polydimethylsiloxane (PDMS) coating on the P84 co-polyimide membrane was able to improve the average air separation efficiency and selectivity by up to 60% [9]. Chung Chong *et al*. studied the performance of Polysfulfone (Psf) hollow fiber membrane using different coating which were PDMS and poly(ether block amide) (PEBAX) at various concentration for gas separation in oxygen enrichment. They found that PDMS coated Psf membrane offered higher permeability and selectivity compared to the PEBAX coated membrane [10].

Therefore, in this work, MMM is fabricated to study the effect of membrane coating concentration on the permeability and selectivity of gas separation for CO_2/CH_4 to recover biomethane from wastewater. Psf was chosen as the polymer and halloysite nanotubes (HNT) as well as activated carbon (AC) were chosen for the inorganic filler. Psf is widely used because of its good permeability, gas separation selectivity, low cost and degradation resistance [11]. HNT was selected because of its larger lumen diameter that allows to make space for larger molecules such as CH_4 while AC was chosen due to its greater surface area and extremely porous superior to excellent adsorptive ability for gases [12]. The objective of this study is to identify the effects of three different concentration of membrane coating (3%, 4% and 5% PDMS) on the biomethane recovery by looking at the separation performance of the membrane.

2.0 METHODS

2.1 Materials

In this research, the as fabricated membrane from the previous work were used [13]. The polymer matrix used during the previous work was polysulfone provided by Sigma Aldrich Co. in the form of clear pellets, while n-hexane provided by Merck. N-methyl-2-pyrrolidone (NMP) also provided by Sigma Aldrich Co. was used as the solvent. The fillers used for this research which were halloysite nanotubes (HNT) and activated carbon (AC). HNT was also supplied by Sigma Aldrich Co. while AC was supplied by Southern Clay Products, Inc., USA. The PDMS used for the coating of the membrane were provided by Dow Corning.

2.2 Membrane Coatings with PDMS

The method for membrane coating is adapted from Ismail *et al*. (2020) [14]. 13.5cm^2 area circular discs of fabricated

membrane, Psf/HNT as well as Psf/AC were prepared. Membrane coating was carried out by immersing the 13.5cm^2 area of fabricated MMM with highly permeable elastomeric silicone polymer of different concentration from 3wt%, 4wt% to 5wt% of polydimethylsiloxane (PDMS) in n-hexane. Uncoated samples were prepared as controlled membranes.

2.3 Membrane Characterizations

The fabricated neat and mixed matrix membranes will be characterized by using Scanning electron microscopy (SEM-EDX) (S-3400N, Hitachi). The membrane will be fractured on liquid nitrogen to obtain the cross section area to be observed by SEM. The sample was then mounted on stab by using carbon tape, and then sputter-coated with gold/platinum before analyzing it by using SEM. The surface and cross section area of the membrane will be observed under the magnification of 500x, 1500x and 10kx. All the elemental composition in the samples will be analyzed by using the elemental dispersion composition (EDX). EDX method plots the abundance of an element alongside a line.

Gas with a feed pressure of 2 bar was used during the gas permeation test. The test was based on the pressure on feed steam and measure the gas flux across a known area and thickness of the membrane on the permeate phase. All the test was carried out at a temperature of 25°C. The data measurement was taken for the permeate gas to reach a volume of 1 cm. By using a bubble flow meter, the gas for volume was measured. Then, the pressure-normalized flux or gas permeance was calculated by using the Equation 1 below:

$$\left(\frac{P}{l}\right)_i = \left(\frac{Q_i}{(A) \times (\Delta P)}\right) \quad \ldots\ldots\text{Equation 1}$$

where ΔP is the differential pressure across the membrane (bar), A is the surface area of membrane (cm^2), Q is the volumetric flow rate of gas at standard temperature and pressure. The gas permeance can be expressed in the unit of GPU, which stated in Equation 2 below:

$$\text{GPU} = 1 \times 10^{-6}\left(\frac{\text{cm}^3\,(\text{STP})}{\text{cm}^2\ \text{sec cm Hg}}\right) \quad \ldots\ldots\text{Equation 2}$$

The ideal selectivity of the membrane is the ratio of gas permeance calculated by Equation 1 CO_2 and CH_4 as in Equation 3:

$$\alpha_{i/j} = \frac{P_i/_l}{P_j/_l} \quad \ldots\ldots\text{Equation 3}$$

3.0 RESULTS AND DISCUSSIONS

3.1 Morphological Properties of Uncoated and Coated MMM

The typical MMM morphological properties consists of active skin layer and the porous structure. For ideal membrane, there are two types of substructures in a membrane's porous layer which are spongy substructure and finger-like substructure. For coated MMMs, additional layers are observed on the top surface of the membrane due to PDMS coating. From the observations, it is evident that the top surface of the membrane appeared thicker compared to uncoated membrane and increasing coating concentration increases thickness of the coating layer. SEM cross-sectional images of MMMs-HNT are shown in Figure 1. From this figure, a thin layer of PDMS coating can be seen in Figure 1(b-d). The thickness of 5wt% PDMS coating concentration membrane is 13.6μm as shown in Figure 1(d). The thickness of the top layer increased by 29.1% compared to uncoated membrane.

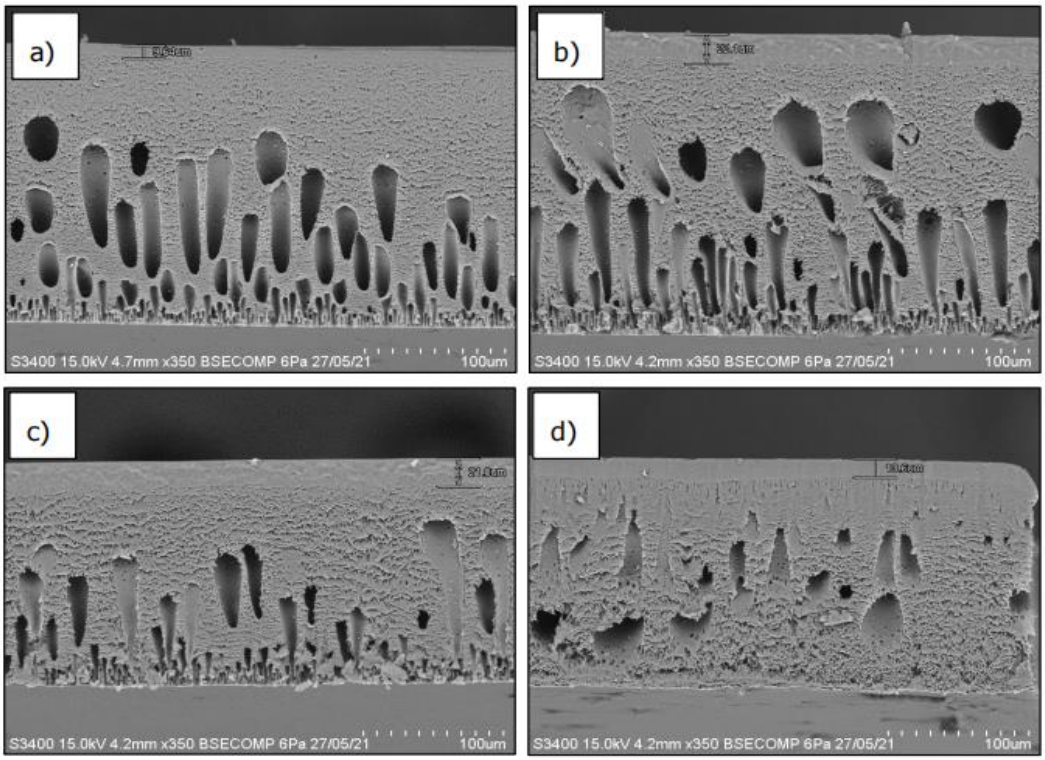

Figure 1 Cross sectional images at magnification of x350 (a) uncoated MMM Psf-HNT, (b) 3wt% PDMS MMM Psf-HNT, (c) 4wt% PDMS MMM Psf-HNT and (d) 5wt% PDMS MMM Psf-HNT

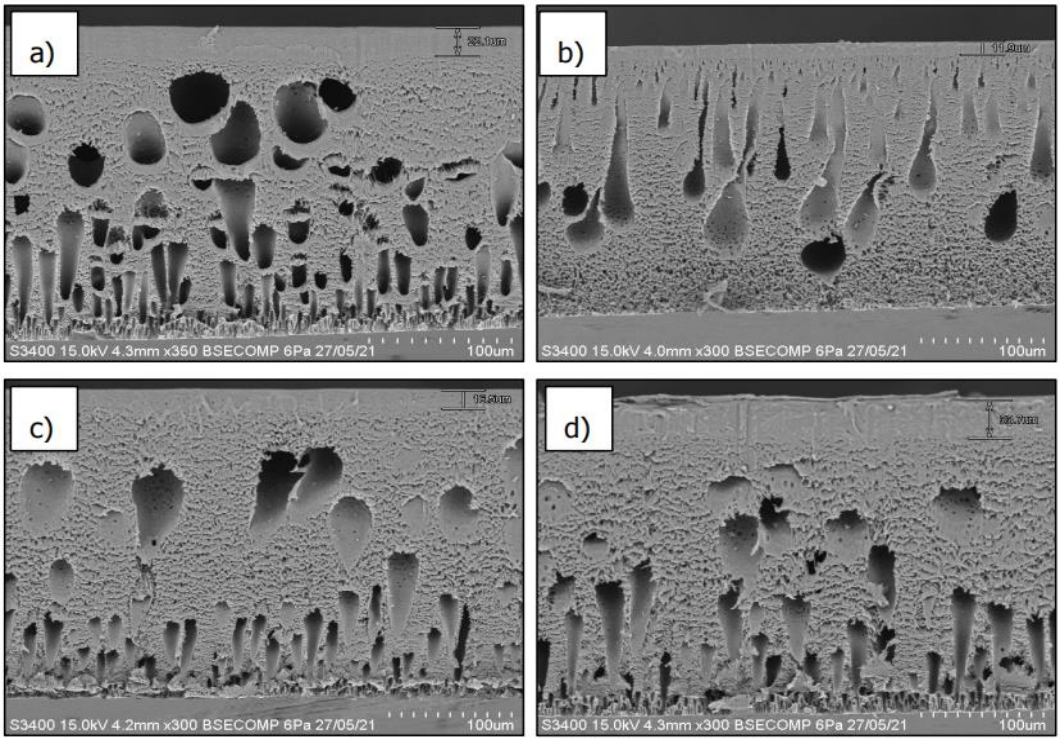

Figure 2 Cross sectional images at magnification of x300 (a) uncoated MMM Psf-AC, (b) 3wt% PDMS MMM Psf-AC, (c) 4wt% PDMS MMM Psf-AC and (d) 5wt% PDMS MMM Psf-AC

For MMMs-AC membrane, the SEM cross-sectional images at magnification of x300 are shown in Figure 2, the thickness of the skin layer of the membrane is increasing from 11.9μm for 3wt% PDMS coating [Figure 2(b)], 16.5μm for 4wt% PDMS coating [Figure 2(c)] to 33.7μm [Figure 2(d)] for the highest concentration of PDMS coating which is 5wt%. Hence, the thickness of the membrane increased by 64.7% from 3wt% to 5wt%. This showed that increasing the concentration causes the PDMS coating of the membrane to increase. On the other hand, there are some discrepancies on the thickness of the membrane in 3wt% and 4wt% PDMS MMM-HNT where its thickness was greater than 5wt% PDMS MMM-HNT and it shows a declining trend. This is speculated to be due to poor spreading, uneven film formation or different solvent evaporation rates during the coating process.

This result is supported by Chung Chong *et al*. (2018) in their study of Psf hollow fiber membrane with PEBAX or PDMS coating for oxygen (O_2) enhancement process and also supported by Wang *et al*. (2014) [10, 15]. The thickness of the coating layer is proportional to the viscosity of the coating solvent, according to the LandauLevich theorem [16]. The viscosity of PDMS solution improved as the concentration of PDMS solution increased. As a result, when the PDMS concentration increased, so did the thickness of the PDMS coating as mentioned before. Moreover, the presence of a thick PDMS top layer on a porous support layer provides resistance for diffusing species, allowing various permeants to be separated such as CO_2 and CH_4. This explains the lower permeability and higher selectivity of gases through the coated membrane compared to the uncoated membrane. Basically, it is said that PDMS on the top surface of the membrane forms selective region towards the gases.

3.2 Energy Dispersive X-ray Analysis (EDX)

Energy Dispersive X-ray Analysis (EDX) is used in this research to analyse elements present on the membrane outer surface. Elements present in EDX were used to confirm the existence of coating layer as well as to study the effect of PDMS coating concentration on the amount of element present [17]. The incorporation of different concentration of PDMS coating on 1wt% of HNT and AC in MMM are further analysed. Table 1 and Table 2 showed the EDX elemental composition analysis for the three concentrations for both MMMs-HNT and MMMs-AC. From the analysis, it is observed that increased in PDMS coating solution results in higher amount of silicon detected. For MMMs-HNT, the weight percentage of silicon in the membrane increased from 16.3, 30.02 to 30.50 for 3wt%, 4wt% and 5wt% PDMS coated MMMs-HNT membranes (Table 1). There is 46% increase of silicon composition from the lowest concentration of PDMS coating to the highest concentration of PDMS coating.

An increased in silicon composition is also observed in MMMs-AC. The weight percentage of silicon in MMMs-AC increased from 27.69 to 30.64 for 3wt% PDMS coated MMMs-AC and 5wt% PDMS coated MMMs-AC. However, the weight percentage for 4wt% PDMS coated MMMs-AC showed a declining value which was 14.36% due to errors during coating of the membrane. Silicon (Si) element is usually used to confirm the existence of PDMS coating layer because PDMS is a silicon-based organic polymer that is optically clear, and non-toxic that

commonly used as coating solvent. Therefore, higher amount of Si is detected as the coating layer thickened due to the use of higher concentration of PDMS solution. The rise in the number of silicon detected corresponds well with the increased in the thickness of the corresponding coating layer. This conclusion is also supported by Chong *et al*. (2018) through their analysis of PEBAX/PDMS coating on membrane [17].

Table 1 EDX elemental composition of 3wt%, 4wt% and 5wt% PDMS coated MMMs-HNT

Elements	Coatings		
	3wt% PDMS	4wt% PDMS	5wt% PDMS
Carbon, C	12.03	9.08	9.10
Oxygen, O	8.68	8.32	6.97
Sulphur, S	7.82	-	-
Tungsten	5.60	-	-
Silicon, Si	16.34	30.02	30.50
Gold	49.53	52.59	53.43

Table 2 EDX elemental composition of 3wt%, 4wt% and 5wt% PDMS coated MMMs-AC

Elements	Coatings		
	3wt% PDMS	4wt% PDMS	5wt% PDMS
Carbon, C	10.00	13.09	8.18
Oxygen, O	8.49	7.45	8.06
Sulphur, S	-	7.88	-
Tungsten	-	6.03	-
Silicon, Si	27.69	14.36	30.64
Gold	53.82	51.18	53.11

3.3 Effect of Coating on Gas Separation Performance

The gas permeation test is used to investigate the gas separation performance of uncoated and coated mixed matrix membrane as CO_2 and CH_4 gasses pass into them. The effect of uncoated as well as different coating concentration on the gas permeability and selectivity for both Psf/HNT and Psf/AC at pressure of 2 bar are studied in this section. The result for permeability and selectivity is shown in Figure 3 to Figure 6. Based on the results, the CO_2 permeance showed an overall decreasing trend with increasing PDMS coating concentration. From Figure 3, the CO_2 permeance for uncoated membrane of MMMs-HNT shows 6.120 and declining to 0.686 for 5wt% PDMS coating concentration while CH_4 permeance also shows declining from 7.470 to 0.119. This shows a decrease of permeability of 88.8% for CO_2 and 98.4% for CH_4 gas in MMMs-HNT membrane.

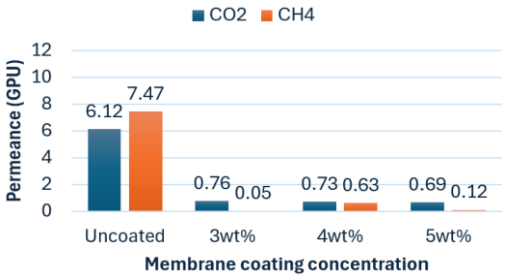

Figure 3 Permeance of uncoated, 3, 4 and 5wt% PDMS coating concentration MMMs-HNT at pressure of 2 bar

Based on Figure 4, for Psf/AC, it also shows the same trend with a decreasing of CO_2 and CH_4 permeance as the membrane goes from uncoated to 5wt% PDMS coating concentration. The CO_2 permeance decreasing from 4.460 to 0.598 which is 86.6% declining from the uncoated Psf/AC membrane to 5wt% (highest) PDMS coating concentration. While the CH_4 permeance also shows the same pattern from 4.110 to 0.144 which is 96.5% decreases from uncoated to 5wt% PDMS coating concentration. For selectivity of the membrane, uncoated MMM shows lower selectivity compared to coated MMM. The selectivity of the MMMs-HNT increases from 0.819 for the uncoated

MMM to 5.746 for the 5wt% PDMS coated MMM (Figure 5) whereas the selectivity of MMMs-AC increases from 1.085 for the uncoated MMM to 4.152 for the 5wt% PDMS coated MMM (Figure 6). The highest selectivity of the membrane can be observed in 3wt% PDMS coated MMM for both types of MMM.

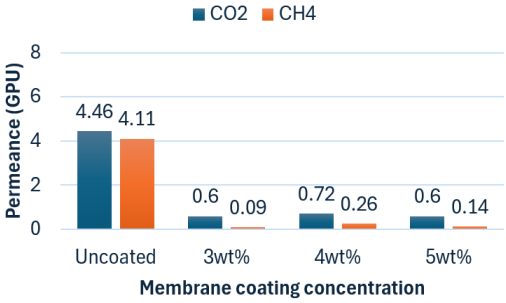

Figure 4 Permeance of uncoated, 3, 4 and 5wt% PDMS coating concentration MMMs-AC at pressure of 2 bar

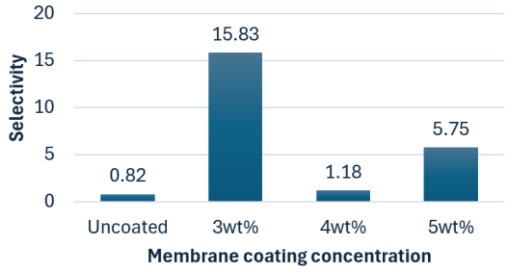

Figure 5 Selectivity of uncoated, 3, 4 and 5wt% PDMS coating concentration MMMs-HNT at pressure of 2 bar.

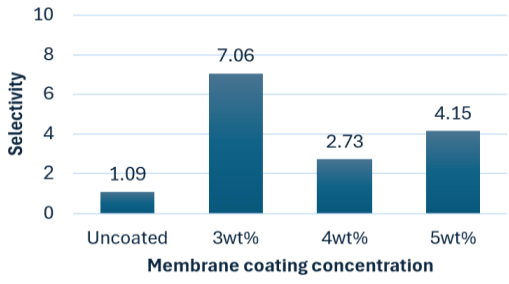

Figure 6 Selectivity of uncoated, 3, 4 and 5wt% PDMS coating concentration MMMs-AC at pressure of 2 bar

Uncoated MMM has higher CO_2 and CH_4 permeability compared to PDMS coated MMM. However, the selectivity for uncoated MMM is lower compared to PDMS coated MMM. This is because coating of the membrane reduces surface defects and pinholes on the surface of the membrane causing both the gas to be less permeable. Therefore, this explains the results obtained which showed decreasing pattern in permeability of the gases. The kinetic diameter of CO_2 is about 3.3 Å whereas CH_4 has a larger kinetic diameter of 3.8 Å. For this reason, CH_4 has a lower permeability since the larger kinetic diameter restricts its movement when passing through the membrane compared to CO_2. The selectivity of the MMM increases when the membrane is coated with PDMS by decreasing the permeance of both CO_2 and CH_4. Surface defects and pinholes on the surface of the membrane are reduced by the PDMS coating as it forms selective layer on the surface of the membrane consequently reducing the permeability and as a result increases the selectivity of the MMM. According to the current findings, the PDMS thin film plays an important role as a selective barrier in regulating gas flow. For this research, 3wt% PDMS coating membrane for both MMMs-HNT and MMMs-AC are preferred since it gives better selectivity that is needed for separation of gas in order to recover biomethane. 3wt% PDMS coated MMMs is called the optimum concentration of coating because too high concentration of PDMS causes increase resistance diffusivity for the membrane due to thicker PDMS layer [17].

The results are also supported by previous studies done Madaeni, *et al.* that shows increasing PDMS coating would affect the permeability [18]. According to their work, it seems that further increase in PDMS concentration results in thicker separation layer leading to low gas permeability. However, the dipped coated samples show promising results with the CO_2/CH_4 selectivity of 9.8. Their

results are also supported by Wijiyanti *et al*. [19]. Based on their study, PDMS coating solution able to reduce active layer defects that causes the permeances of the slower and larger kinetic diameter gases such as CH_4 were greatly decreased, resulting in a significant improvement in selectivity of the membrane. The coated samples show a 30.98 of CO_2/CH_4 selectivity with CO_2 permeance of 51.51 GPU, an improvement of 210.1% from the uncoated Psf/ZTC membrane. Gunawan *et al*. has also observed a 47.2% of increased in selectivity for PDMS coated Psf membrane for CO_2/CH_4 separation [20]. In a recent work by Khan *et al*. [21], PSf/NH_2-ZIF-8 showed a range of 60-72% of increase in selectivity for CO_2/CH_4 separation when samples were coated. Meanwhile, higher selectivity was achieved for PDMS/Psf compared to uncoated Psf membrane which is 4.69 at 10 bar with 1.0 GPU of CO_2 permeance [22].

However, inconsistency results were observed for the 4wt% PDMS coating concentration of both MMMs reflected in the higher permeability compared to 3wt% PDMS coating concentration. This variation is postulated due to the insufficient drying of PDMS solution which affected the separation performance of the membrane.

4.0 CONCLUSION

In this study, the performance of gas separation for biomethane recovery when polymer matrix was incorporated into two different types of inorganic fillers; HNT and AC at different PDMS coating concentration were studied by using standard method of variable-pressure constant-volume. For membrane characterisation, the morphological structure of the uncoated and coated MMMs are studied by using SEM-EDX analysis. Based on the results, SEM images for coated MMMs showed the presence of PDMS layer on the top surface of the MMMs. SEM analysis revealed that raising the coating concentration increases the thickness of the PDMS coating layer. The thickness of the coating layer is proportional to the viscosity of the coating solvent. EDX findings revealed the presence of coating layer on the surface of both membranes by observing the silicon element. Amount of silicon element increased with increasing PDMS coating concentration. In terms of gas separation performance, PDMS coated MMMs showed better selectivity but lower permeability compared to uncoated MMMs. For both types of MMMs, 3wt% PDMS coated MMMs have the best membrane selectivity. 3wt% PDMS coated MMMs-HNT achieved a CO_2/CH_4 selectivity of 15.83 with permeability of 0.76 for CO_2. A significant improvement was achieved with a selectivity of 1830.5% higher compared to uncoated MMMs-HNT. Meanwhile, 55.4% of decreased in selectivity of MMMs-AC was observed compared to MMMs-HNT at the optimum PDMS coating which illustrates a better potential of HNTs as the fillers for the MMMs. Therefore, high selectivity of membrane will give the best membrane for biomethane recovery from wastewater as biomethane may be used as a direct alternative for natural gas and as a fuel in applications such as heating, transportation and power production. This is a key component in future efforts to resolve the problems in membrane separation technology of mixed matrix membrane to separate biomethane from biogas to fully utilize it.

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CONFLICTS OF INTEREST

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

REFERENCES

[1] C. Ramos, A. Garcia and V. Diez. (2014). Performance of an AnMBR pilot plant 50 treating high-strength lipid wastewater: Biological and filtration processes. *Water Res., 67*, 203–215.

[2] L. Dvořák, M. Gómez, J. Dolina, A. Černín, M.Gó Mez and C. Ernín. (2015). Anaerobic membrane bioreactors-a mini review with emphasis on industrial wastewater treatment: applications, limitations and perspectives. *Desalin Water Treat., 57*, 19062–19076.

[3] M. A. Musa, S. Idrus, H. C. Man and N. N. N. Daud. (2018). Wastewater treatment and biogas recovery using anaerobic membrane bioreactors (AnMBRs): Strategies and achievements. *Energies, 11*(7), 1675.

[4] K. Arrhenius, A. Fischer and O. Büker. (2019). Methods for sampling biogas and biomethane on adsorbent tubes after collection in gas bags. *Appl. Sci., 9*(6), 1171.

[5] S. Saha, A. Hussain, J. Lee, E. Lee, H.-S. Lee. (2023). An integrated leachate bed reactor – anaerobic membrane bioreactorsystem (LBR-AnMBR) for food waste stabilization and biogas recovery. *Chemosphere. 311*, 137054.

[6] N. M. Ismail, A. F. Ismail, A.Mustafa, A. K. Zulhairun and N. A. H. M. Nordin. (2016). Enhanced carbon dioxide separation by polyethersulfone (PES) mixed matrix membranes deposited with clay. *J. Polym. Eng., 36*(1), 65–78.

[7] A. Torre-Celeizabal, C. Casado-Coterillo, A. Gomis-Berenguer, J. Iniesta and A. Gare. (2023). Chitosan-based mixed matrix composite membranes for CO_2/CH_4 mixed gas separation. Experimental characterization and performance validation. *Sep. Purif. Technol., 325*, 124535.

[8] S.-Y. Suen. (2015). Mixed matrix membranes for adsorption application. *J. Chem. Eng. Process Technol., 6*(1), 1000e119.

[9] N. Widiastuti, T. Gunawan, H. Fansuri, W. N. W. Salleh, A. F. Ismail and N. Sazali. (2020). P84/zcc hollow fiber mixed matrix membrane with pdms coating to enhance air separation performance. *Membr., 10*(10), 267.

[10] K. Chung Chong, S. Onn Lai, W. Jye Lau, H. San Thiam, A. Fauzi Ismail and R. Azwa Roslan. (2018). Polymers preparation, characterization, and performance evaluation of polysulfone hollow fiber membrane with PEBAX or PDMS coating for oxygen enhancement process. *Polymers, 10*(2), 126.

[11] N. S. Fadaly and F. Aziz. (2020). Preparation and characterization of mixed matrix membrane based on polysulfone (PSF) and lanthanum orthoferrite ($LaFeO_3$) for gas separation. *J. Appl. Membr. Sci. Technol., 24*(1), 27–38.

[12] S. A. Hashemifard, A. F. Ismail and T. Matsuura. (2011). Mixed matrix membrane incorporated with large pore size halloysite nanotubes (HNTs) as filler for gas separation: Morphological diagram. *Chem. Eng. J., 172*(1), 581–590.

[13] A. Gunasakaran, J. Jafa, S. Saalah, C. S. Sipaut, N. Yusof, F. Aziz, A. F. Ismail, M. R. Bilad, N. Y. Yahya and N. M. Ismail. (2021). Activated carbon and halloysite nanotubes membrane for CO_2 and CH_4 separation. *IOP Conf. Ser.: Mater. Sci. Eng.,* 1142 012012.

[14] N. M. Ismail, N. A. Yusaini, J. Jafa, S. M. Anissuzaman, C. C. Ken, N. Bolong, A. R. Razali and A. F. Ismail. 2020. Carbon dioxide/methane separation performance by mixed matrix membrane. *J. Teknol., 3*, 91–100.

[15] L. Wang, Y. Li, S. Li, P. Ji and C. Jiang. (2014). Preparation of composite poly(etherblock amide) membrane for CO_2 capture. *J. Energy Chem., 23*(6), 717–725.

[16] X. Tang and X. Yan. (2017). Dip-coating for fibrous materials: mechanism, methods and applications. *J. Sol-Gel Sci. Technol., 81*, 78–404.

[17] K. C. Chong, S. O. Lai, W. J. Lau, H. S.Thiam, A. F. Ismail and R. A. Roslan. 2018. Preparation, characterization, and performance evaluation of polysulfone hollow fiber membrane with PEBAX or PDMS coating for oxygen enhancement process. *Polymers, 10*(2), 126.

[18] S. S. Madaeni, M. M. S. Badieh and V. Vatanpour. (2013). Effect of coating method on gas separation by PDMS/PES membrane. *Polym. Eng. Sci., 53*(9), 1878–1885.

[19] R. Wijiyanti, A. R. K. Wardhani, R. A. Roslan, T. Gunawan, Z. A. Karim, A. F. Ismail and N. Widiastuti. (2020). Enhanced gas separation performance of polysulfone membrane by incorporation of zeolite-templated carbon. *Mal. J. Fund. Appl. Sci., 6*(2), 128–134.

[20] T. Gunawan, S. R. Lusman, S. N. P. Wahyudhie, A. R. Widyanto, N. Widiastuti, H. Fansuri, S. D. Nurherdiana and D. Prasetyoko. (2024). Introducing PDMS layer on Psf membrane to enhance CO_2/CH_4 separation. *AIP Conf. Proc.*, 3071, 020007.

[21] I. U. Khan, M. H. D. Othman, M. A. Rahman, M. Iftikhar, Z. Ali, M. Muqeet, J. Jaafar, A. Jilani, M. K. N. Ramli. (2025). Enhanced CO_2/CH_4 separation using amine-modified ZIF-8 mixed matrix membranes. *Mat. Chem. Phys., 334*, 130404.

[22] M. S. Suleman, K. K. Lau, Y. F. Yeong. (2024). Development and performance evaluation of Polydimethylsiloxane/Polysulfone (PDMS/PSF) composite membrane for CO_2/CH_4 separation. *IOP Conf. Ser. Earth Environ. Sci., 36*, 012014.