

Article

Microporous Adsorbent-Based Mixed Matrix Membranes for CO₂/N₂ Separation

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Abstract: As the atmospheric carbon dioxide (CO₂) concentration rapidly rises, carbon capture, utilization, and storage (CCUS) is an emerging field for climate change mitigation. Various carbon capture technologies are in development with the help of adsorbents, membranes, solvent-based systems, etc. One of the main challenges in this field is the removal of CO₂ from nitrogen (N₂) gas. This paper focuses on mixed matrix membrane technology, for which the CO₂/N₂ separation performance is based on differences in gas permeations. Membrane separation and purification technologies are widely studied for carbon capture. Microporous adsorbents such as zeolites and metal organic frameworks (MOFs) for carbon capture have been attracting researchers' attention due to their highly porous structures, high selectivity values, and tunable porosities. Utilizing microporous adsorbents dispersed within a novel, blended polymer matrix, fourteen membranes were prepared with the commercial MOF ZIF-8, zeolite 13X, and kaolin, with methyl cellulose (MC) and polyvinyl alcohol (PVA), which were tested using a single gas permeation setup in this study. The addition of polyallylamine (PAH) as a chemisorbent was also investigated. These membranes were synthesized both with and without a polyacrylonitrile (PAN) support to compare their performances. MC was found to be an ideal polymeric matrix component to develop free-standing MMMs. At 24 °C and a relatively low feed pressure of 2.36 atm, a free-standing zeolite-13X-based membrane (MC/PAH/13X/PVA) exhibited the highest N₂/CO₂ selectivity of 2.8, with a very high N₂ permeability of 6.9×10^7 Barrer. Upon the optimization of active layer thickness and filler weight percentages, this easily fabricated free-standing MMM made of readily available materials is a promising candidate for CO₂ purification through nitrogen removal.

Keywords: carbon capture; mixed matrix membranes; metal organic frameworks; zeolites; free-standing membranes; permeability; selectivity; CO₂ removal techniques; global warming challenges



Citation: Shervani, S.; Tansug, L.P.; Tezel, F.H. Microporous Adsorbent-Based Mixed Matrix Membranes for CO₂/N₂ Separation. *Energies* **2024**, *17*, 1927. <https://doi.org/10.3390/en17081927>

Academic Editors: Jaber Shabanian and Amin Esmaeili

Received: 18 January 2024

Revised: 2 April 2024

Accepted: 8 April 2024

Published: 18 April 2024



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1. Introduction

Fossil fuel consumption is the main source of greenhouse gas (GHG) emissions, which envelop the earth and trap the sun's heat by absorbing light. The presence of GHGs increase atmospheric temperature, which leads to destructive climate change. The world is warming faster nowadays than at any point in recorded history; the current sustainability goal is to secure global net zero by mid-century and keep a maximum of 1.5 °C degrees of warming within reach, according to the COP26 international climate conference [1]. The mitigation of climate change can be achieved by using renewable energy sources and capturing carbon dioxide (CO₂), the major GHG. Carbon capture, utilization, and storage (CCUS) technologies have attracted the attention of many researchers to mitigate climate change, with various advantages and disadvantages [2].

Membranes have great importance in the scientific world and are used for many applications, such as carbon capture [3], direct contact distillation [4], and oil–water separation [5]. Membrane technology is very promising for carbon capture because it has

potentially low energy requirements and capital costs, and is more environmentally friendly than other methods like cryogenic distillation and absorption. The main obstacle to overcome before employing industrial-sized carbon capture membranes is the development of stable, high-surface-area, high-performing porous materials for this process.

Several materials such as ceramic and composite membranes have been investigated to capture CO₂ and separate it from other gases [6]. Free-standing membranes are studied by researchers for many other applications [7,8]. However, synthesizing these membranes without a polymeric support layer proves challenging due to structural stability issues. Chai et al. have fabricated free-standing mesoporous carbon nanocomposite membranes using the “brick-and-mortar” method, with carbon black as “bricks” and soft-templated phenolic-resin-based mesoporous carbon as the “mortar” for CO₂/N₂ separation. Their results indicate that an increase in the pore diameter of mesoporous carbon–carbon black membranes enhances the CO₂ permeability up to ~180 Barrer, but has little effect on the CO₂/N₂ selectivity (~36) [9]. Kang et al. have also prepared a free-standing membrane, through a base-catalyzed sol–gel reaction. A maximum CO₂ permeability of 48 Barrer was observed with a CO₂/N₂ permselectivity of 30.5 [10].

Polyvinyl alcohol (PVA) and amines like 2-aminoisobutyric acid (AIBA) [11] and microporous adsorbents have been used to fabricate polyacrylonitrile-supported membranes in previous publications [12]. Nitrogen-selective membranes are rare in the literature, with Samputu achieving a maximum nitrogen permeability of 1.8×10^4 Barrer and N₂/CO₂ selectivity of 1.3. Another PVA- and AIBA-based membrane achieved a CO₂ permeability of 2471 Barrer and CO₂/N₂ of 6 at 24 °C and 2.5 atm feed pressure [12]. Although PVA is commonly used in polymeric membranes, PDMS has been frequently used for MMM fabrication. Selyanchyn et al. have prepared PDMS- and Pebax-1657-based membranes by the layer deposition method. The PDMS membrane showed a 3523 GPU (1417 Barrer) permeability of CO₂ and 293 GPU (118 Barrer) permeability for N₂, with a CO₂/N₂ selectivity of 12 [13]. In this study, PVA was chosen over PDMS as a second matrix polymer to blend with MC due to its high solubility in water, allowing the synthesis route to avoid using environmentally unfriendly solvents like toluene.

There is a well-known tradeoff between the selectivity and permeability of membranes, demonstrated by Robeson’s plots for specific gas pairs [14]. Polymeric membranes generally exhibit low selectivities when applied to gas separations, placing them on the lower quadrants of Robeson’s plots. Mixed matrix membranes (MMMs) are advanced membranes synthesized with the purpose of maximizing the permeability and selectivity of one of the gases to be separated. The incorporation of amines and adsorbents serves to enhance the membrane efficiency past the empirical Robeson upper bound, where selectivity and permeability are both high.

In this paper, methyl cellulose (MC)- and adsorbent-based free-standing and supported membranes have been synthesized for carbon capture by a very simple method. Since cellulose and its derivatives are found to be good encapsulation materials [15,16] and MC is a flexible, renewable polymer, it was used as a matrix material to hold and encapsulate all fillers. MC was also blended with polyvinyl alcohol before being impregnated with amine carriers and nanomaterials to improve gas permeance and selectivity.

Polyallylamine hydrochloride was incorporated as a fixed amine carrier (chemisorbent), and zeolite 13X, ZIF-8, or kaolin were used as physisorbent fillers for the membranes. Table 1 presents the literature separation data of some MMMs using similar materials.

In spite of MOFs’ high expense, ZIF-8 was chosen as a filler in this study due to its commercial availability and resistance to degradation by water, making it appropriate for the solution-based membrane fabrication. Despite its lack of molecular sieving capabilities, kaolin was investigated as an alternative to 13X because it is a natural and abundantly found aluminum silicate material. The selectivity and permeability values of the prepared membranes were determined with a single gas permeation setup in this study.

Table 1. The literature CO₂/N₂ separation data of MMMs using similar fillers, where P_{CO2} is the carbon dioxide permeability, P_{N2} is the nitrogen permeability, and T and p represent the experimental temperature and pressure, respectively.

Membrane	CO ₂ /N ₂	P _{CO2} (Barrer)	P _{N2} (Barrer)	T (°C)	p (atm)	Ref.
[C ₂ mim][Tf ₂ N]/MC-CB-75	36	180	5	22	1.35	[9]
LPG64	30	48	1.6	35	1	[10]
PVA/AIBA/Pam-OH	6	2471	416	24	2.5	[12]
PDMS ⁵ /O ₂ ^{0.7} /Pebax ^{0.1}	12	1417	118	25	1.97	[13]
PEBAX + ZIF-8	59	118	2.0	35	10.9	[17]
15wt%Cu(6L)@13X	117	1034	8.8	25	2	[18]
PDMS/4A/PAN	24	12,000	508	25	3	[19]
PEBA-13X	57	194	3	25	13.8	[20]
PEBAX 1657/ZIF-8	71	261	4	30	2	[21]

2. Materials and Methods

Gas cylinders used for N₂, and CO₂ were purchased from Messer Canada Ltd. (Mississauga, ON, Canada) of grade 4.0 with 99.99% purities. Methyl cellulose (MC) (CAS: 9004-67-5), ZIF-8 (CAS: 59061-53-9), 13X (CAS: 63231-69-6), polyallylamine hydrochloride (PAH) (CAS: 71550-12-4), polyvinyl alcohol (PVA) (CAS: 9002-89-5), and kaolin (CAS: 1332-58-7) were purchased through Sigma-Aldrich (Toronto, ON, Canada). The polyacrylonitrile (PAN) flat sheet support with a 30 kDa molecular weight cutoff and 150 µm thickness was purchased from Synder Filtration (CAS: 500-06-9095). The membranes were cast by the perpendicular layer deposition method [22]. Two sets of membranes using ZIF-8, kaolin, and 13X have been synthesized. One set contained PVA, and the other set did not contain PVA. All of these membranes were also tried with and without the PAN support, with a total of 14 membranes being prepared in this study.

2.1. Synthesis of Mixed Matrix Membranes

A total of 2 g of MC was stirred in 50 mL deionized (DI) water. The solution was stirred at 600 rpm on a hot plate and heated at 50 °C until it formed a gel (30 min). Then, 0.5 g ZIF-8 or 13X or kaolin was stirred in 10 mL ethanol and poured into the MC solution. Also, 0.5 g PAH was stirred in 10 mL of DI water and poured into the MC solution. For MMMs containing PVA as well as MC, an additional 1 g of PVA was stirred in 10 mL of DI water and poured into the MC solution. The solution was stirred rigorously for 30 min at 50 °C.

For free-standing membranes, once the solution had cooled down, 50 vol% of the solution was deposited on a fixed area of a hydrophobic plastic tray and air-dried in the dark. The second half was deposited on top when the first layer dried fully. The membrane was air-dried overnight and was gently removed from the plastic substrate.

For supported membranes, the 50 vol% of the solution was cast onto the same, fixed area of a PAN layer using a casting bar. After air-drying, the second half of the solution was cast perpendicularly to the first casting direction, and left to fully air-dry. The synthesized flat sheet membranes were then cut into 4 cm discs using a circular cutter, to fit the membrane module. A micrometer was used to measure the thicknesses of the MMMs in five areas per disc to ensure a homogeneous distribution of the components and the average of the five measurements was recorded as the thickness.

2.2. Single Gas Permeation Characterization

The membrane permeation characteristics were measured using the lab-scale single gas permeation setup shown in Figure 1. In the setup, two feed gas cylinders were connected to the membrane module and the feed flowrate was controlled through the rotameters connected to each gas cylinder. During the experiments, the single gas feed flow of N₂ or CO₂ gas was passed through the membrane at 1.36 atm differential pressure with the

permeate open to atmospheric pressure. The two outlet streams of the module were connected to two bubble flow meters, one for the permeate and the other for the retentate stream. Permeate and retentate flow rates were measured using these bubble flowmeters every 5 min for 60 min, until constant flow rates were observed for both the permeate and the retentate streams.

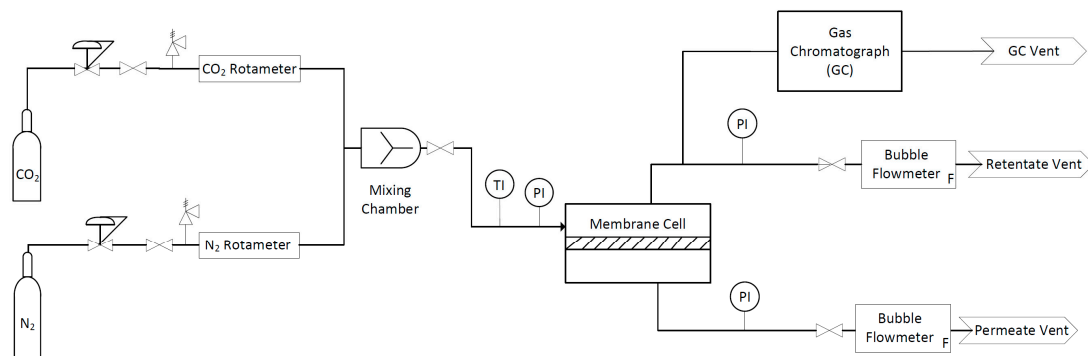


Figure 1. Schematic diagram of the lab-scale single gas permeation testing setup used in this study [12].

The permeability and selectivity values were calculated using Equations (1) and (2), respectively.

$$P = F_i \left(\frac{T_{STP}}{T_{permeate}} \right) \left(\frac{p_{permeate, absolute}}{p_{STP}} \right) \left(\frac{L}{A \Delta p} \right) 10^{10} \text{ Barrer} \quad (1)$$

where P is the permeability [Barrer]; F_i is the volumetric flow rate [cm^3/s] of the permeate for component i at room temperature (24°C); A is the surface area of the membrane [cm^2]; T_{STP} is the standard temperature in K with 273.15 K being used; p_{STP} is the atmospheric pressure [atm]; $T_{permeate}$ is the temperature of the permeate; $p_{permeate, absolute}$ is the absolute pressure of the permeate [atm]; Δp is the difference between the retentate and permeate pressure [cm Hg]; and L is the thickness of the membrane [cm]. The multiplication by 10^{10} converts the permeability from $\{\text{cm}^3 (\text{STP})\text{cm}/(\text{s cm}^2 \text{cmHg})\}$ units to Barrer. Accounting for the membrane thickness in the permeability calculation allows the results of membranes with different thicknesses to be comparable.

The membrane selectivity is defined as the ratio of the permeability values for the membrane for different components. For example, for the selectivity of gas 1 over gas 2:

$$\alpha_{1/2} = P_1/P_2 \quad (2)$$

where $\alpha_{1/2}$, is the selectivity of the membrane for component 1 over component 2, P_1 is the permeability of gas 1, and P_2 is the permeability of gas 2.

3. Results and Discussion

3.1. Structural and Chemical Characterizations

Table 2 presents the filler and polymer combinations for the synthesized membranes for this study, and Figure 2 depicts the SEM images of the surface of these synthesized membranes. Figure numbers in parentheses correspond to the membrane numbers shown in Table 2.

Table 2. CO₂ and N₂ permeability (P_{CO2}, P_{N2}) and selectivity values (CO₂/N₂, N₂/CO₂) for the synthesized membranes in this study, tested at a feed pressure of 2.36 atm ($\Delta p = 1.36$ atm) and 24 °C.

No.	Membrane	CO ₂ /N ₂	N ₂ /CO ₂	P _{CO2} (Barrer)	P _{N2} (Barrer)
1	MC	-	-	-	-
2	MC/PAN	0.9	1.1	2.8×10^3	3.0×10^3
3	MC/PAH/ZIF-8	0.9	1.1	4.8×10^6	5.2×10^6
4	MC/PAH/ZIF-8/PAN	0.5	1.9	8.6×10^5	1.6×10^6
5	MC/PAH/ZIF-8/PVA	1.6	0.6	4.8×10^6	2.9×10^6
6	MC/PAH/ZIF-8/PVA/PAN	0.8	1.3	8.6×10^5	1.1×10^6
7	MC/PAH/13X	1.0	1.0	3.0×10^5	3.0×10^5
8	MC/PAH/13X/PAN	0.9	1.2	9.4×10^5	1.1×10^6
9	MC/PAH/13X/PVA	0.4	2.8	2.5×10^7	6.9×10^7
10	MC/PAH/13X/PVA/PAN	0.9	1.1	1.1×10^6	1.2×10^6
11	MC/PAH/kaolin	1.1	0.9	1.1×10^6	9.6×10^5
12	MC/PAH/kaolin/PAN	0.9	1.1	1.1×10^6	1.2×10^6
13	MC/PAH/kaolin/PVA	0.7	1.5	1.3×10^6	2.1×10^6
14	MC/PAH/kaolin/PVA/PAN	0.9	1.1	1.0×10^6	1.1×10^6

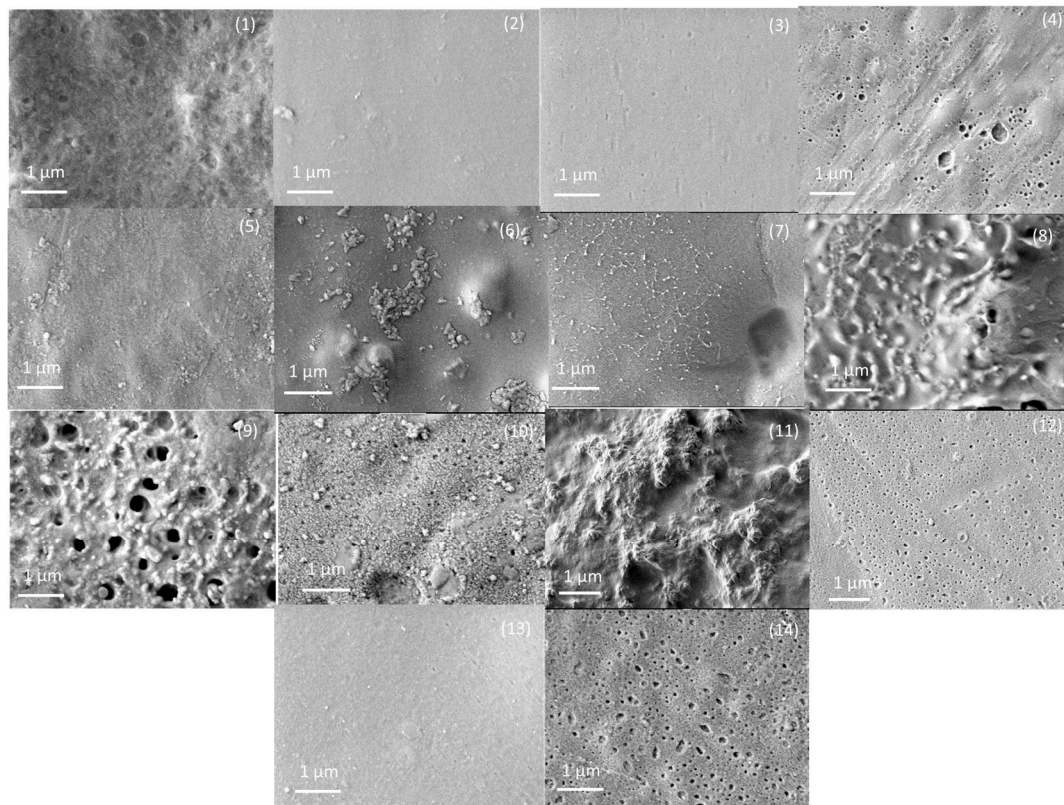


Figure 2. SEM images of the surfaces of membranes (1–14) prepared in this study. Figure numbers in parentheses correspond to the membrane numbers shown in Table 2.

Figure 2(1) shows the surface of a free-standing MC membrane with shallow pores smaller than 0.5 μm . Figure 2(2) belongs to MC cast on a PAN substrate, showing a uniform surface structure. Figure 2(9) is a free-standing 13X membrane with PVA, which has approximately 0.5 μm pores and visible 13X agglomerations, suggesting that the dispersion of the particles in the MMM solution must be improved to achieve a higher homogeneity. The supported version of the same membrane in Figure 2(10), 13X cast on a PAN substrate with PVA, has smaller pores and suffers from the same agglomeration issue. Comparing the free-standing membranes with supported ones, the PAN appears to minimize the

pore expansion during the drying of the membrane, which is expected, since this is one of the purposes of using support layers. Interestingly, as seen in Table 2, membrane 9 achieved the highest nitrogen permeability due to these defects, while maintaining the highest nitrogen selectivity over carbon dioxide. Therefore, the pinholes seen in Figure 2(9) had a positive impact on permeability while the adsorbents served to keep the carbon dioxide in the retentate.

Comparison of Figure 2(7,8) shows that casting 13X without PVA as a free-standing membrane without the PAN support produces a flatter surface topology. The same trend is seen for ZIF-8 with PVA when Figure 2(5,6) are compared. The PVA and kaolin combination in Figure 2(13,14) show similar structures, with a larger variation in the pore sizes for the free-standing version. The kaolin membranes without PVA seen in Figure 2(11,12) show a drastic difference between the supported and free-standing versions, with significant agglomerations in the unsupported case.

Figure 3 shows the cross-sectional SEM images of the membranes listed in Table 2. Figure numbers in parentheses correspond to the membrane numbers shown in Table 2. The active layer thicknesses of the MMMs are within the range of 6 to 20 μm . The deposited solution volume and casting area were kept constant during synthesis; however, the final active layer thickness of the membrane is dependent on various factors such as the component compatibilities, presence of agglomerations, and the drying speed. The permeability calculations account for the active layer membrane thickness producing a comparable data set, and the thickest membrane, number 9 (Figure 3(9)), had the best separation performance compared to the others. This indicates that increasing the active layer thickness improves the selectivity of the MMMs, as expected.

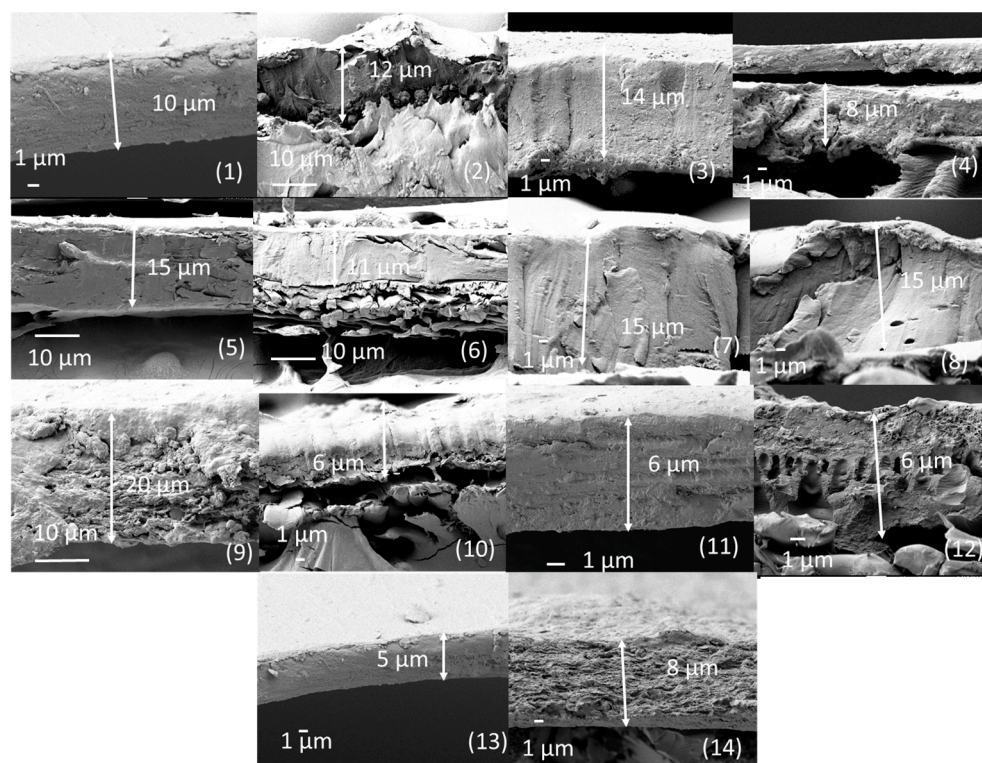


Figure 3. Cross-sectional SEM images of membranes (1–14). Figure numbers in parentheses correspond to the membrane numbers shown in Table 2.

Fourier-transformed infrared spectroscopy (FTIR) was used to confirm the molecular makeup of the membranes. Figure 4 presents the FTIR spectra of only the free-standing membranes, since the identical membrane solutions were cast on their PAN-supported counterparts.

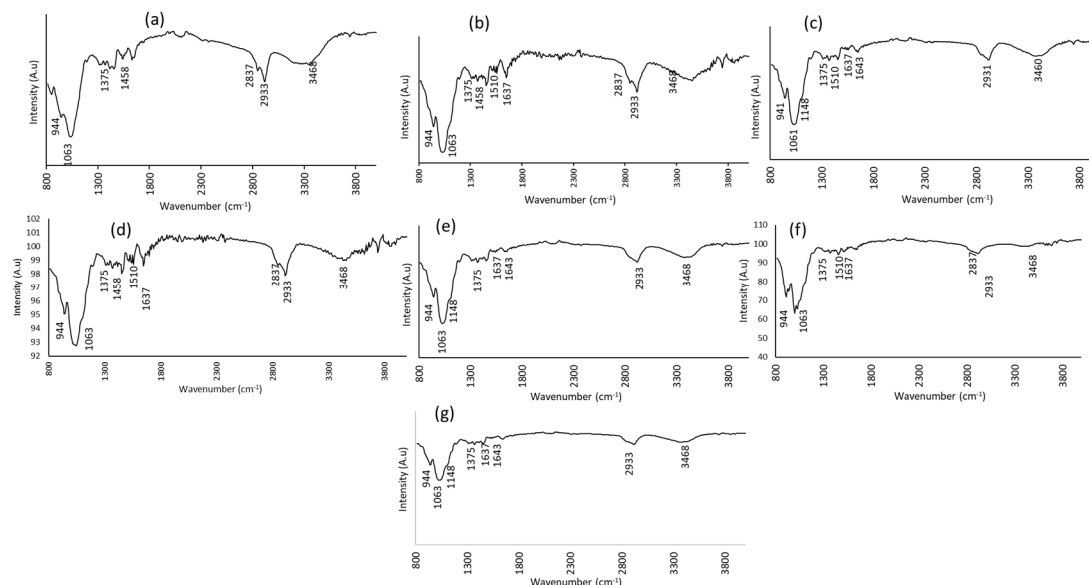


Figure 4. FTIR spectra of (a) MC, (b) MC/13X/PAH, (c) MC/13X/PAH/PVA, (d) MC/ZIF-8/PAH, (e) MC/ZIF-8/PAH/PVA, (f) MC/kaolin/PAH, and (g) MC/kaolin/PAH/PVA.

In Figure 4a, the peaks at 944, 1063, 1375, 1485, 2837, 2933, and 3468 cm^{-1} are due to the presence of MC [23]. Figure 4b shows peaks at 944, 1063, 1375, 1485, 2837, 2933, and 3468 cm^{-1} due to the presence of MC [23], and the peaks at 1510 and 1637 cm^{-1} are from PAH [24]. The additional peaks at 1148 and 1643 cm^{-1} in Figure 4c are due to PVA [25]. The 941, 1061, 1375, 2931, and 3460 cm^{-1} peaks are due to MC, and those at 1510 and 1637 cm^{-1} are due to PAH. Similarly, the peaks corresponding to PAH, PVA, and MC are observed in Figure 4d–f. This confirms the presence of PAH and PVA in the MC/adsorbent membranes.

3.2. Gas Permeation Characterization

The permeability and selectivity values obtained for the membranes prepared in this study are listed in Table 2 for CO_2 and N_2 gases. Both CO_2/N_2 and N_2/CO_2 selectivity values are listed in this table to highlight the nitrogen removal potential of some MMMs, as opposed to only CO_2 removal. Among all membranes, MC/PAH/13X/PVA (membrane 9) exhibits the highest selectivity (2.8) for N_2/CO_2 , which also showed the highest permeability for both CO_2 (2.5×10^7 Barrer) and N_2 (6.9×10^7 Barrer) due to the presence of larger defects. This suggests that the combination of 13X and PAH in a blended polymer matrix increases the separation performance and casting more than two layers of a more homogeneous solution, as a free-standing membrane may further improve the nitrogen separation.

It is clear from Table 2 that upon the incorporation of PVA, the separation performance of the ZIF-8-containing free-standing membrane increases, as MC/PAH/ZIF-8 (membrane 3) has a CO_2/N_2 selectivity of 0.9, and the MC/PAH/ZIF-8/PVA (membrane 5) has a CO_2/N_2 selectivity of 1.6. The same trend was observed for the 13X-based free-standing membranes, with MC/PAH/13X (membrane 7) having no N_2/CO_2 or CO_2/N_2 selectivity ($\text{N}_2/\text{CO}_2 = 1.0$), and the similar membrane with PVA (MC/PAH/13X/PVA, membrane 9) having a N_2/CO_2 selectivity of 2.8.

The kaolin-containing free-standing membrane without PVA (MC/PAH/kaolin, membrane 11) has a N_2/CO_2 selectivity of 0.9. With the addition of PVA for MC/PAH/kaolin/PVA (membrane 13), N_2/CO_2 selectivity increased to 1.5. So, for all free-standing membranes, the separation is improved by the addition of PVA.

It is noteworthy that the ZIF-8-, 13X-, and kaolin-containing membranes with PAN support did not show significant differences in CO_2/N_2 or N_2/CO_2 selectivity by the incorporation of PVA. In the case of free-standing membranes, PVA not only improves the structural integrity of the membranes but also improves their selectivity.

Membranes without the PAN support performed better in comparison to membranes with support. This is likely due to the entire membrane thickness of unsupported MMMs being composed of the active layer only, containing adsorbents and amines, while the supported membranes are composed of mostly PAN with a thin layer of active coating deposited on them. The adsorbent fillers do not appear to improve the MMMs as significantly as expected, which may be due to the operating conditions lowering their potential. All experiments were conducted at 24 °C and 2.36 atm feed pressure, with the permeate side open to atmospheric pressure, to develop successful MMMs that minimize the operating costs of potentially scaled-up membranes. There are various limitations of the adsorbents. The amine groups in PAH would have higher carbon dioxide adsorption capacities in the presence of moisture; however, only dry conditions were tested to prevent the adsorption competition between water and CO₂ on 13X and kaolin. ZIF-8's CO₂ adsorption capability has been shown to maximize with much higher operating pressures [26], so this MOF was found to be unsuitable for the desired operating conditions in this study. The lack of significant separation improvement by filler addition may be due to pinholes and issues with organic–inorganic interactions and incompatibilities when forming the membrane solution. The permeability and selectivity values for pure MC membrane are not shown in Table 2 since they could not be measured. This was due to the fact that the pressure differential could not be achieved between the feed and permeate for this membrane during the experiments.

Figures 5 and 6 chart the MMM permeability and selectivity values, respectively, for the two gases (N₂, CO₂), for the membranes prepared in this study. For these figures, the membrane numbers shown on the x-axis correspond to the numbers in Table 2.

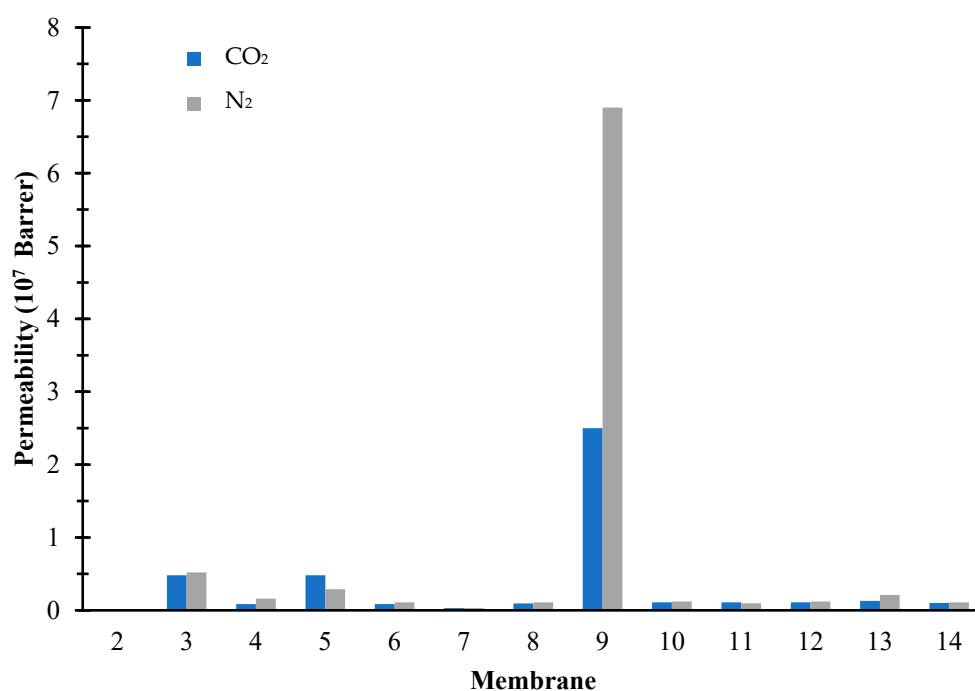


Figure 5. Permeability values of the two gases for the membranes prepared in this study, tested at a feed pressure of 2.36 atm ($\Delta p = 1.36$ atm) and 24 °C. The membrane numbers shown on the x-axis correspond to the numbers in Table 2.

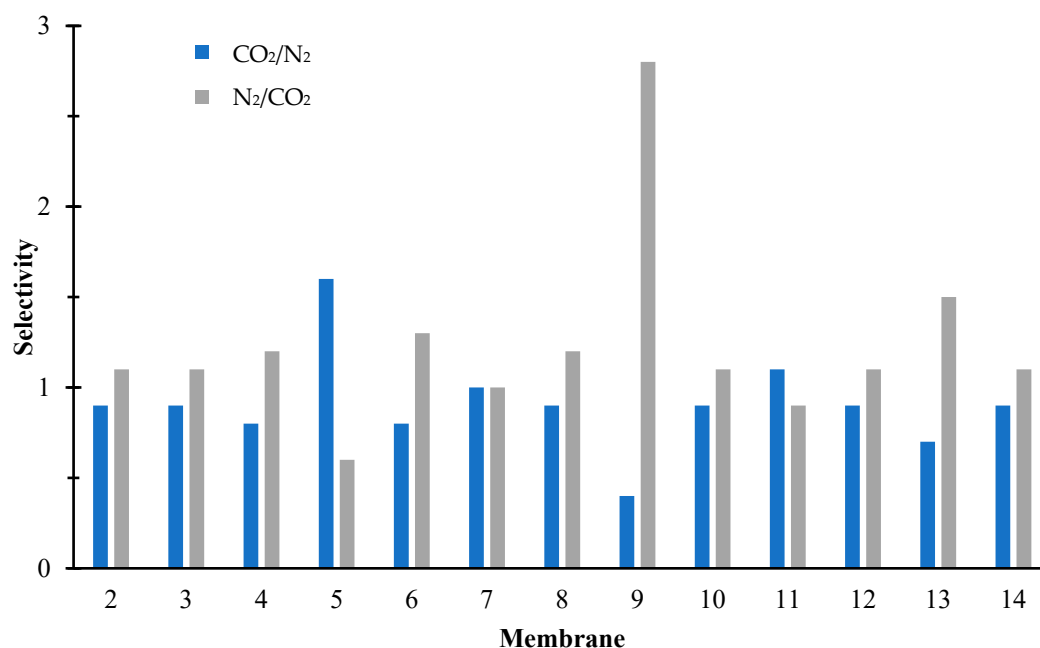


Figure 6. Selectivity values of the membranes prepared in this study for the two gases (N₂, CO₂), tested at a feed pressure of 2.36 atm ($\Delta p = 1.36$ atm) and 24 °C. The membrane numbers shown on the *x*-axis correspond to the numbers in Table 2.

The permeability and selectivity results of the free-standing membranes and membranes with PAN support indicate that the combination of methyl cellulose and PVA with a PAH amine carrier and a 13X filler yields the most promising carbon-capture membrane in this study. Methyl cellulose and PVA have different structural properties, and their combination was found to provide excellent flexibility to the matrix holding the carriers and adsorbents together. Brittle active layers on supported membranes tend to obtain cracks and flake off of the casting tray easily, whereas all free-standing membranes produced in this study can be curled, rolled up, and even bent without forming visible cracks. In terms of permeability and selectivity, the trends in the figures highlight the superior separation of free-standing membranes, with unsupported MMMs having higher selectivity for one gas over another compared with the membranes with PAN support. For example, MC/PAH/13X/PVA (membrane 9) has $P_{N_2} = 6.9 \times 10^7$ Barrer and a N₂/CO₂ selectivity of 2.8; however, the corresponding membrane with PAN support, MC/PAH/13X/PVA/PAN (membrane 10), has $P_{N_2} = 1.2 \times 10^6$ Barrer and a N₂/CO₂ selectivity of 1.1. Another example is MC/PAH/kaolin/PVA (membrane 13), with $P_{N_2} = 2.1 \times 10^6$ Barrer and a N₂/CO₂ selectivity of 1.5; however, the corresponding membrane with PAN support, MC/PAH/kaolin/PVA/PAN (membrane 14), has $P_{N_2} = 1.1 \times 10^6$ Barrer and a N₂/CO₂ selectivity of 1.1. Note that all even numbered membranes have PAN support.

Figure 7 presents the CO₂/N₂ Robeson's plot, which illustrates the relationship between carbon dioxide permeability and CO₂/N₂ selectivity. There is a widely known tradeoff between membrane permeability and selectivity, which causes there to be an empirical upper bound for performance. Both the 2008 upper bound equation and the 2019 revisited equation were used to compare this study's results with the literature data on the Robeson plot [14,27]. The purpose of incorporating inorganic filler materials into polymers is to help overcome this tradeoff by increasing selectivity while maintaining the highest permeability possible.

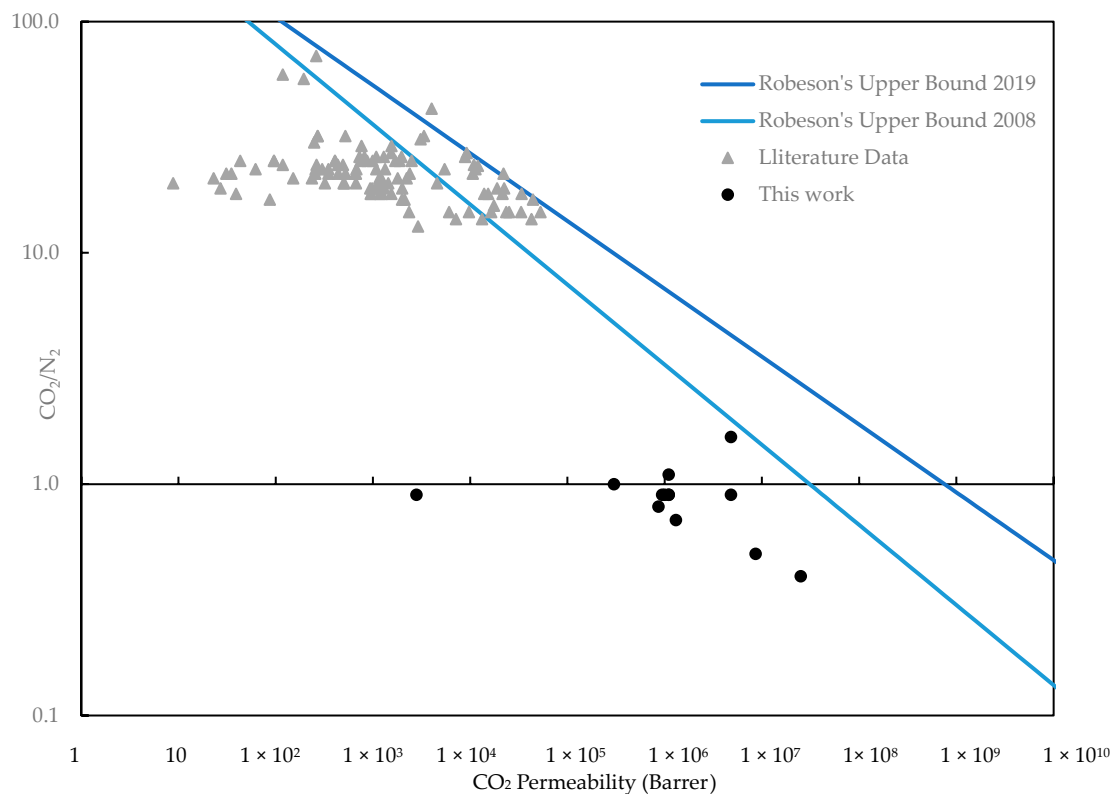


Figure 7. CO_2/N_2 Robeson's plot for membranes, comparing the literature membrane data with the membranes used in this study [17–21,27].

The Robeson's plot in Figure 7 compares the performance of the membranes used in this study with the carbon dioxide permeation performance of MMMs in the literature [27]. Because none of the membranes exhibit high enough CO_2/N_2 selectivity, the membranes included in this study could not surpass the upper bounds. However, the permeability values of the membranes are remarkably high. Upon further improvement of the selectivity by increasing filler weight percentages or incorporating different filler materials for these MMMs, it is possible to overcome the upper bound.

Under dry, ambient conditions (24 °C) with a relatively low pressure drop (1.36 atm), the combination of MC/PAH/13X/PVA (membrane 9) is a promising candidate to optimize for nitrogen removal from carbon dioxide. The N_2/CO_2 -selective membrane number 9 could be a promising candidate for industrial carbon capture. With a N_2/CO_2 selectivity value of 2.8, it could separate these gases by retaining most of the CO_2 in the retentate stream and allowing most of the nitrogen to permeate into a storage tank. However, additional matrix components that facilitate the further permeation of N_2 should also be introduced to develop a higher-performing membrane in terms of N_2/CO_2 selectivity. The filler amounts, final MMM thickness, and operating pressure could be studied to maximize the nitrogen diffusion while inhibiting CO_2 diffusion.

4. Conclusions

In this study, zeolite-, kaolin-, and MOF-based membranes were synthesized with and without a support layer using MC and PVA. It was found that the membranes without support are superior to membranes with support. It was also discovered that a blend of PVA and methyl cellulose forms an excellent polymer matrix in terms of flexibility. The most promising nitrogen-selective membrane was MC/13X/PAH/PVA, which also has the highest permeability for both gases. The selectivity of this membrane is 2.8 for N_2/CO_2 , and the permeability values for CO_2 and N_2 are high at 2.5×10^7 Barrer, and 6.9×10^7 Barrer, respectively. This membrane may be a good candidate for carbon capture upon further optimization to maximize its nitrogen selectivity.

Author Contributions: Conceptualization, F.H.T., L.P.T. and S.S.; methodology, S.S. and L.P.T.; validation, S.S. and L.P.T.; formal analysis, S.S. and L.P.T.; investigation, S.S. and L.P.T.; resources, F.H.T.; writing—original draft preparation, S.S.; writing—review and editing, L.P.T., F.H.T. and S.S.; visualization, F.H.T., S.S. and L.P.T.; supervision, F.H.T.; project administration, F.H.T.; funding acquisition, F.H.T. All authors have read and agreed to the published version of the manuscript.

Funding: The authors would like to acknowledge the funding received from Natural Resources Canada (NRCan), Grant number: 3000702663, and the Natural Sciences and Engineering Research Council (NSERC) of Canada through the Discovery Grant Program, Grant number: RGPIN-2018-05763. Both of these funds were received by F.H.T. at the University of Ottawa.

Data Availability Statement: The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author.

Acknowledgments: The authors thank Natural Resources Canada for supporting this project, in addition to the Natural Sciences and Engineering Council of Canada Discovery Grant Program, the Tezel research group, and the technical staff at the University of Ottawa.

Conflicts of Interest: The authors declare no conflicts of interest.

Nomenclature

A	Membrane area [cm^2]
F	Volumetric flowrate [cm^3/s]
L	Membrane thickness [cm]
p	Pressure [atm]
P	Permeability [Barrer]
p_{STP}	Standard atmospheric pressure [atm]
STP	Standard pressure and temperature [K, atm]
T	Temperature [K]
T_{STP}	Standard temperature [K]
α	Selectivity [dimensionless]
Δp	Pressure differential [atm]

Abbreviations

CAS	Chemical abstracts service
CCUS	Carbon capture, utilization, and storage
CO_2	Carbon dioxide
COP26	Conference of the Parties 26
DI	Deionized
FTIR	Fourier-transform infrared spectroscopy
GHG	Greenhouse gas
KOH	Potassium hydroxide
MC	Methyl cellulose
MMM	Mixed matrix membrane
MOF	Metal organic framework
N_2	Nitrogen
PAA	Poly-N-isopropylallylamine
PAH	Polyallylamine hydrochloride
PAN	Polyacrylonitrile
PVA	Polyvinyl alcohol
ZIF-8	Zeolitic imidazolate framework

References

1. European Association of Remote Sensing Companies. A reporting service for environment and development negotiations. *Earth Negot. Bull.* **2021**, *12*.
2. Khalid, M.; Dharaskar, S.A.; Sillanpa, M.E.T.; Siddiqui, H. *Emerging Carbon Capture Technologies: Towards a Sustainable Future*; Elsevier: Amsterdam, The Netherlands, 2022.

3. Chen, G.; Wang, T.; Zhang, G.; Liu, G.; Jin, W. Membrane materials targeting carbon capture and utilization. *Adv. Membr.* **2022**, *2*, 100025. [\[CrossRef\]](#)
4. Criscuoli, A. Membrane Distillation Process. *Membranes* **2021**, *11*, 144. [\[CrossRef\]](#)
5. Jiang, S.; Meng, X.; Chen, B.; Wang, N.; Chen, G. Electrospinning superhydrophobic–superoleophilic PVDF-SiO₂ nanofibers membrane for oil–water separation. *J. Appl. Polym. Sci.* **2020**, *137*, 49546. [\[CrossRef\]](#)
6. Zagho, M.M.; Hassan, M.K.; Khraisheh, M.; Al-Maadeed, M.A.A.; Nazarenko, S. A review on recent advances in CO₂ separation using zeolite and zeolite-like materials as adsorbents and fillers in mixed matrix membranes (MMMs). *Chem. Eng. J. Adv.* **2021**, *6*, 100091. [\[CrossRef\]](#)
7. Athanasiou, M.; Manoli, A.; Papagiorgis, P.; Georgiou, K.; Berezovska, Y.; Othonos, A.; Bodnarchuk, M.I.; Kovalenko, M.V.; Itskos, G. Flexible, Free-Standing Polymer Membranes Sensitized by CsPbX₃ Nanocrystals as Gain Media for Low Threshold, Multicolor Light Amplification. *ACS Photonics* **2022**, *9*, 2385–2397. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Stogin, B.B.; Gockowski, L.; Feldstein, H.; Claire, H.; Wang, J.; Wong, T.-S. Free-standing liquid membranes as unusual particle separators. *Sci. Adv.* **2018**, *4*, eaat3276. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Chai, S.-H.; Fulvio, P.F.; Hillesheim, P.C.; Qiao, Z.-A.; Mahurin, S.M.; Dai, S. “Brick-and-mortar” synthesis of free-standing mesoporous carbon nanocomposite membranes as supports of room temperature ionic liquids for CO₂–N₂ separation. *J. Memb. Sci.* **2014**, *468*, 73–80. [\[CrossRef\]](#)
10. Kang, W.R.; Lee, A.S.; Park, S.; Park, S.-H.; Baek, K.-Y.; Lee, K.B.; Lee, S.-H.; Lee, J.-H.; Hwang, S.S.; Lee, J.S. Free-standing, polysilsesquioxane-based inorganic/organic hybrid membranes for gas separations. *J. Memb. Sci.* **2015**, *475*, 384–394. [\[CrossRef\]](#)
11. Zou, J.; Ho, W.S.W. CO₂-selective polymeric membranes containing amines in crosslinked poly(vinyl alcohol). *J. Memb.* [\[CrossRef\]](#)
12. Samputu, I. Optimization of Using Polymeric and Mixed Matrix PVA Amine-Based Membranes for CO₂/N₂ and CO₂/CH₄ Separation. Master’s Thesis, University of Ottawa, Ottawa, ON, Canada, 2022.
13. Selyanchyn, O.; Selyanchyn, R.; Fujikawa, S. Critical Role of the Molecular Interface in Double-Layered Pebax-1657/PDMS Nanomembranes for Highly Efficient CO₂/N₂ Gas Separation. *ACS Appl. Mater. Interfaces* **2020**, *12*, 33196–33209. [\[CrossRef\]](#)
14. Robeson, L.M. The upper bound revisited. *J. Memb. Sci.* **2008**, *320*, 390–400. [\[CrossRef\]](#)
15. Wang, Z.; Li, M.; Zhang, X.-F.; Zhou, Y.; Yao, J. Integration of natural clay into cellulose membrane for efficient CO₂/N₂ separation. *Cellulose* **2022**, *29*, 1873–1881. [\[CrossRef\]](#)
16. Tezel, F.H.; Shervani, S.; Strong, C. Composite Material for Thermochemical Energy Storage and Method of Making Same. U.S. Patent US20230332033A1, 19 October 2023.
17. Meshkat, S.; Kaliaguine, S.; Rodrigue, D. Comparison between ZIF-67 and ZIF-8 in Pebax® MH-1657 mixed matrix membranes for CO₂ separation. *Sep. Purif. Technol.* **2020**, *235*, 116150. [\[CrossRef\]](#)
18. Mashhadikhan, S.; Moghadassi, A.; Amooghin, A.E.; Sanaeepur, H. Interlocking a synthesized polymer and bifunctional filler containing the same polymer’s monomer for conformable hybrid membrane systems. *J. Mater. Chem. A Mater.* **2020**, *8*, 3942–3955. [\[CrossRef\]](#)
19. Alavi, S.A.; Kargari, A.; Sanaeepur, H.; Karimi, M. Preparation and characterization of PDMS/zeolite 4A/PAN mixed matrix thin film composite membrane for CO₂/N₂ and CO₂/CH₄ separations. *Res. Chem. Intermed.* **2017**, *43*, 2959–2984. [\[CrossRef\]](#)
20. Asghari, M.; Mosadegh, M.; Harami, H.R. Supported PEBA-zeolite 13X nano-composite membranes for gas separation: Preparation, characterization and molecular dynamics simulation. *Chem. Eng. Sci.* **2018**, *187*, 67–78. [\[CrossRef\]](#)
21. Jomekian, A.; Bazoooyar, B.; Behbahani, R.M.; Mohammadi, T.; Kargari, A. Ionic liquid-modified Pebax®1657 membrane filled by ZIF-8 particles for separation of CO₂ from CH₄, N₂ and H₂. *J. Memb. Sci.* **2017**, *524*, 652–662. [\[CrossRef\]](#)
22. Rose, L. Carbon Dioxide Gas Separation from Syngas to Increase Conversion of Reverse Water Gas Shift Reaction via Polymeric and Mixed Matrix Membranes. Master’s Thesis, University of Ottawa, Ottawa, ON, Canada, 2018.
23. Nadour, M.; Boukraa, F.; Ouradi, A.; Benaboura, A. Effects of Methylcellulose on the Properties and Morphology of Polysulfone Membranes Prepared by Phase Inversion. *Mater. Res.* **2017**, *20*, 339–348. [\[CrossRef\]](#)
24. Meléndez-Ortiz, H.I.; Puente-Urbina, B.; León, G.C.-D.; Mercado-Silva, J.A.; Saucedo-Salazar, E.; García-Cerda, L.A. Covalent attachment of poly(allylamine hydrochloride) onto ordered silica foams. *J. Porous Mater.* **2020**, *27*, 929–937. [\[CrossRef\]](#)
25. Kharazmi, A.; Faraji, N.; Hussin, R.M.; Saion, E.; Yunus, W.M.M.; Behzad, K. Structural, optical, opto-thermal and thermal properties of ZnS-PVA nanofluids synthesized through a radiolytic approach. *Beilstein J. Nanotechnol.* **2015**, *6*, 529–536. [\[CrossRef\]](#)
26. Jiang, S.; Liu, J.; Guan, J.; Du, X.; Chen, S.; Song, Y.; Huang, Y. Enhancing CO₂ adsorption capacity of ZIF-8 by synergetic effect of high pressure and temperature. *Sci. Rep.* **2023**, *13*, 17584. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Lee, W.H.; Seong, J.G.; Hu, X.; Lee, Y.M. Recent progress in microporous polymers from thermally rearranged polymers and polymers of intrinsic microporosity for membrane gas separation: Pushing performance limits and revisiting trade-off lines. *J. Polym. Sci.* **2020**, *58*, 2450–2466. [\[CrossRef\]](#)

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