



Research Note

Gas separation properties of polyacrylonitrile-polysulfone-iron oxide nanocomposite membrane

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KEYWORDS

Membrane;
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 Polysulfone;
 Polyacrylonitrile.

Abstract. Gas separation by a membrane is performed without phase changing, leading to cost reduction. This study investigates the process of gas separation in the case of polyacrylonitrile (PAN) and polysulfone (PSF) blend membranes. The ratios of polymers to mixed matrix membranes include 100% PAN, 100% PSF, (95% PAN–5% PSF), (90% PAN–10% PSF), (85% PAN–15% PSF). The best combination of membrane mixtures was determined. Then, iron oxide nanoparticles with different weight percentages were placed on the membrane. The impact of adding different amounts of iron oxide nanoparticles to the membrane on gas separation was examined. By adding iron oxide nanoparticles to the membrane by 10% weight and measuring the value of permeability, it was observed that the permeability of this membrane for carbon dioxide, oxygen, nitrogen, and methane gases increased by 117%, 137%, 95%, and 53% compared to membranes without iron oxide nanoparticles. Based on the findings, it was revealed that the optimal value of adding iron oxide to improve the membrane properties was 10% by weight.

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1. Introduction

Some of the most commonly used methods for the absorption and separation of gases are solvent-based methods [1–4], ionic liquid [5–9], and membrane separation [10–13]. The gas separation process by the membrane is conducted without any phase changing, leading to reduced costs. In comparison with other conventional separation methods, membranes use a simpler process, enjoy a lower maintenance cost, and are eco-friendly. The major disadvantage of the gas

separation method is the inverse relationship between permeability and selectivity, though nano-composite membranes are used to solve the complexity of this process to a large extent by improving permeability and selectivity simultaneously. The membrane separation based on the selective passage of gas competes with other gas separation methods. Compared to other methods, membranes are of higher efficiency [10–15].

Significant developments have been made over the past two decades on the performance of polymer membranes in gas separation, and notable efforts have been made to facilitate a deeper understanding of the relationship between the structure of polymer membranes and gas separation properties, including higher permeability and selectivity [16]. In organic membranes, the application of polymer as a membrane component is very common for the sake of better processability and the possibility of optimizing the

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membrane properties for different applications. Hence, the application of this type of membrane has been considered in the separation of gases. Bastani et al. [17] reviewed the membrane of mixed polymer matrices along with zeolite to separate the gas. The findings of the review of papers revealed that nano-sized particles in the mixed matrix membranes showed better performance than micron-sized particles.

Polymers are economically cost effective and are easily converted into spiral modules or formed as hollow fibers due to their flexibility and processability. For this reason, researchers have shown greater interest in polymer membranes, leading to the increasing development of polymer membranes. However, attempts have been made to improve the properties of permeability, selectivity, and mechanical and thermal resistance of these membranes [18]. One of the methods for improving the membrane capabilities is using nanoparticles in the polymeric tissue. Because of the small size of nanoparticles and high contact surfaces between nanoparticles and the polymer phase, the membranes made of these materials will have the desired mechanical and thermal resistance and the ability to make a proper interaction with the separated gas [19,20].

Using new membrane materials or modifying the membrane materials can overcome shortcomings such as operational instability at high temperatures, low permeability and selectivity, low-quality products, and low mechanical stability of the membrane. One of these methods disperses the nanoparticles inside the polymer phase [17,21,22]. Rafiq et al. [23] developed and improved the mixed matrix membrane by applying the fuzzy inversion method. They loaded silica mineral nanoparticles inside the asymmetric membrane mix of polysulfone (PSF) and polyimide. The highest selectivity was obtained in conditions with loading the 15.2% weight of silica and pressure between 2 and 10 bar. Rafiq et al. [23] concluded that a membrane with the 15.2% weight of silica fillers and feed pressure between 2 to 10 bar was characterized by the highest selectivity, leading to the reformation of polymeric chains to be packed well. It consequently reduced the probability of membrane softening.

Dorosti et al. [24] prepared a matrix membrane mixed with PSF and polyimide filled with zeolite particles and examined the function of gas separation. The impact of loading the zeolite and the ratio of two polymers on the membrane passage characteristics was examined in this study. The polymers were immiscible, and a completely homogeneous matrix was formed. Among all the gas tests, Dorosti et al. obtained the minimum permeability and the maximum selectivity in the mixed membranes at a weight percentage ratio of 50 to 50 in PSF and polyimide. The findings revealed that these matrix membranes could provide higher permeability and more acceptable selectivity than sim-

ple membranes. Through a repeated construction of membranes with a 20% weight of zeolite, it was realized that membranes had completely different properties due to the formation of uncontrollable empty cavities.

Ahn et al. [25] constructed a matrix membrane mixed with PSF and silica nanoparticle fillers. The addition of silica nanoparticles also increased the permeability significantly. By increasing silica nanoparticles, the permeability of large gases increased greatly due to an increase in empty space. Sadeghi et al. [26] investigated the properties of gas separation using the nanocomposite membrane of ethylene vinyl acetate and silica. The impact of silica nanoparticles on the properties of gas separation by copolymer membrane containing 28% vinyl acetate was examined. The obtained findings revealed that increasing the number of silica nanoparticles caused a significant increase in gas permeability and an increase in CO₂ selectivity, compared to N₂ and CH₄. They illustrated that this increase in permeability resulted from the increased penetration and solubility of gases in combined membranes. The obtained findings revealed that a mixture of silica nanoparticles and polymer led to consider solubility of the dominant mechanism in the passage of gases as the combined membrane [26].

Chieh-Fang et al. [27] prepared a composite membrane in a laboratory study by combining carbon nanotubes and blend particles of iron with polyvinyl alcohol. Adding iron oxide to the membrane, they prevented the crystallization of polyvinyl alcohol. Accordingly, they prevented the penetration of methanol and, finally, facilitated the passage of ions into the mixture by the immersion of the membrane in potassium hydroxide.

The properties of the cellulose acetate membrane through silver nanoparticles were enhanced [28]. Kim and Bruggen [29] reviewed various types of ceramic and polymer membranes with nanoparticles. Among the polymer membranes with nanoparticles, we can refer to polyvinylidene fluoride (PVDF) polymer membrane with alumina nanoparticles, in which dimethyl acetamide is used as a solvent. In this membrane, polymer is added by 19% weight, and nanoparticles are added with an average particle size of 10 nm in the concentration of 0 to 4% weight. Their study revealed that silver and silica nanoparticles were used as nanoparticles, which were added to polymeric membranes.

Moghadam et al. [30] studied the impact of adding TiO₂ nanoparticles on the mixed matrix membrane. With the addition of 15% volumes of TiO₂, the permeability value of N₂, CH₄, and CO₂ turned out to be 2.76, 3.3, and 1.86 times more than that in the membrane without nanoparticles. The investigation of the polythene and polyurethane mixture matrix membrane along with the silica nanoparticles revealed that by increasing the value of silica nanoparticles, the

permeability of N_2 , O_2 , and CH_4 gases decreased, while the permeability of carbon dioxide increased with an increase in the nanoparticles. The greater permeability of carbon dioxide results from its smaller kinetic diameter, greater condensation, and higher interaction of this polar gas with polar groups than oxygen, methane, and nitrogen [31].

The role of the nano-composite membrane of polyvinyl acetate/titanium oxide in the separation of gases was examined. In this investigation, Field Emission Scanning Electron Microscopy (FESEM), X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), and Thermal Gravimetric Analysis (TGA) were carried out. The addition of titanium oxide nanoparticles to polymer vinyl acetate improved their properties [32]. Momeni and Pakizeh [33] examined the membrane composed of PSF containing aluminum oxide nanoparticles for the separation of gas. Their study revealed that the value of permeability of the polymer membrane increased by adding magnesium oxide nanoparticles. The addition of the layers of silica to the PSF matrix was examined. The impact of the percentage of nanoparticles on the selectivity and permeability of the membrane was examined for carbon dioxide separation [34].

Sun et al. [35] investigated the matrix membrane mixed with carbon nanoparticles. The findings of their study revealed that the permeability coefficient of carbon dioxide permeation increased by 292% at 3% weight of carbon nanoparticles. Sadeghi et al. [36] investigated the impact of titanium oxide nanoparticles on gas separation in polyurethane-titanium oxide nanocomposite membranes. By increasing the value of nanoparticles, the permeability of nitrogen, oxygen, methane, and carbon dioxide gases decreased, while the selectivity of N_2/CO_2 increased. However, the selectivity of N_2/O_2 and CH_4/CO_2 did not change significantly.

This study applies PSF and polyacrylonitrile (PAN) blend membranes to investigate the process of gas separation. The best weight percentage of PSF and PAN membranes was determined for the proposed purpose. Then, the effects of adding iron oxide nanoparticles on gas separation and the permeability and selectivity properties of the nanocomposite membrane were examined. Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Thermal Gravimetric Analysis (TGA) analyses were conducted to identify and examine the membranes.

2. Experimental

2.1. Materials

PSF polymer was purchased from BASF Company in Germany. PAN polymer was received from the

Polyacrylic Company of Isfahan. Dimethylformamide and iron nanoparticles were purchased from Merck Company. Methane gas with a purity degree of 99.5% was obtained from TGS Company. Nitrogen, oxygen, and carbon dioxide gases with a purity degree of 99.9% were purchased from Ardestan Gas Company.

2.2. Characterization

SEM analysis was carried out to investigate the membrane cross-sectional form and the distribution of iron oxide particles in the polymer. FT-IR analysis was conducted to examine the structure of constructed membranes. The model used in this test is Spectrum 65 FT-IR Perkin Elmer. To study the degradation temperature and the impact of iron oxide nanoparticles on thermal behavior, weight heat analysis test was applied. In this method, sample were heated in argon at a ramp of $10^\circ C/min$.

2.3. Membranes preparations

A PAN-PSF mixed membrane and a polymer-oxide iron nano-composite membrane were prepared by applying the solvent evaporation method [37]. PAN and PSF were dissolved at different percentages in dimethyl for amide solvent in a concentration of 10% by weight at $50^\circ C$ for 3 hours. The prepared solution passed through a 30-micron ceramic filter and was poured into a clean and dry ridged glass container. This container was placed in a conventional oven at $65^\circ C$ for 24 hours. Then, in order to separate the solvent from the polymer chains, the membrane was placed in a vacuum oven at a temperature of $75^\circ C$ for 4 hours so that the solvent could be separated completely.

To construct polymer-iron oxide composite membranes, the polymeric solution prepared at the considered weight ratio was mixed with iron oxide nanoparticles well to obtain a uniform homogeneous solution. The obtained solution was poured into a glass container and, then, placed in a conventional and vacuum oven so that the solvent could be separated. The prepared membrane was 45-micron thick and measured by a micrometer

2.4. Gas permeation measurements

After constructing the PAN-PSF mixed membrane, which was obtained by adding 5%, 10%, and 15% weights of PSF to the PAN pure membrane, the permeability ratio was tested for these membranes and for nitrogen, oxygen, methane, and carbon dioxide gases using a constant pressure method. The delay time method was used to examine the permeability of pure gases. The delay time method is the most common method used to test the permeability of gases in polymeric membranes [38]. In this method, the penetration of gas in the polymer is measured from zero time to the permeability speed of the polymer, reaching a constant number. To examine the amount

of gas passing through the membrane and to record the gas flow, a constant pressure method was used. In the course of applying constant pressure method, the downstream pressure is considered as environment pressure and, also, the changes in the volume of gas passing through the membrane are recorded.

3. Results and discussion

3.1. FTIR analysis

Findings of the analysis of the FT-IR spectrum of the PAN-PSF mixed membrane and polymer-iron oxide nanocomposites membranes are shown in Figure 1. As illustrated in Figure 1, the widespread absorption in the FT-IR spectrum in the case of pure iron oxide is found to be 471 cm^{-1} . This absorption can be observed in other FT-IR spectra related to nano-composite membranes by combining different percentages of iron oxide, and its intensity increases as the iron oxide value increases.

3.2. SEM analysis

Figure 2 illustrates the SEM image of the PAN-PSF nanocomposite membrane with 2.5% iron oxide. The SEM image of PAN-PSF nanocomposite membrane with 20% iron oxide is shown in Figure 3. The SEM image illustrates the presence of small nano-scale particles along with the accumulated iron oxide particles in nano-composite membranes with higher percentages of iron oxide. As seen earlier, iron oxide nanoparticles at lower weight percentages showed a highly uniform distribution in the polymeric network, and an insignificant nanoparticle agglomeration phenomenon was seen, which represents one of the disadvantages of nano-composites membranes. In addition, there is no cavity at the interface of two phases, suggesting good compatibility with organic and mineral phases. The average size of distributed nanoparticles was obtained between 80 and 110 nm.

A similar behavior was seen in the membrane of the matrix mixed with titanium oxide nanoparticles. SEM images showed that particles were distributed properly at all points at low values of titanium oxide nanoparticles, while, at a higher level of titanium oxide, particles tend to be placed together as a mass [30]. In the nano-composite membrane of polyvinyl acetate/titanium oxide, FESEM analysis revealed that the addition of titanium oxide nanoparticles up to 10% by weight had a proper distribution throughout the membrane. By increasing the value of titanium oxide, the density of particles in the membrane increased [32].

3.3. TGA analysis

The impact of increasing the iron oxide nanoparticles on the thermal stability of the nano-composite membrane using the TGA analysis is shown in Table 1 and Figure 4. By increasing the weight percentage of iron

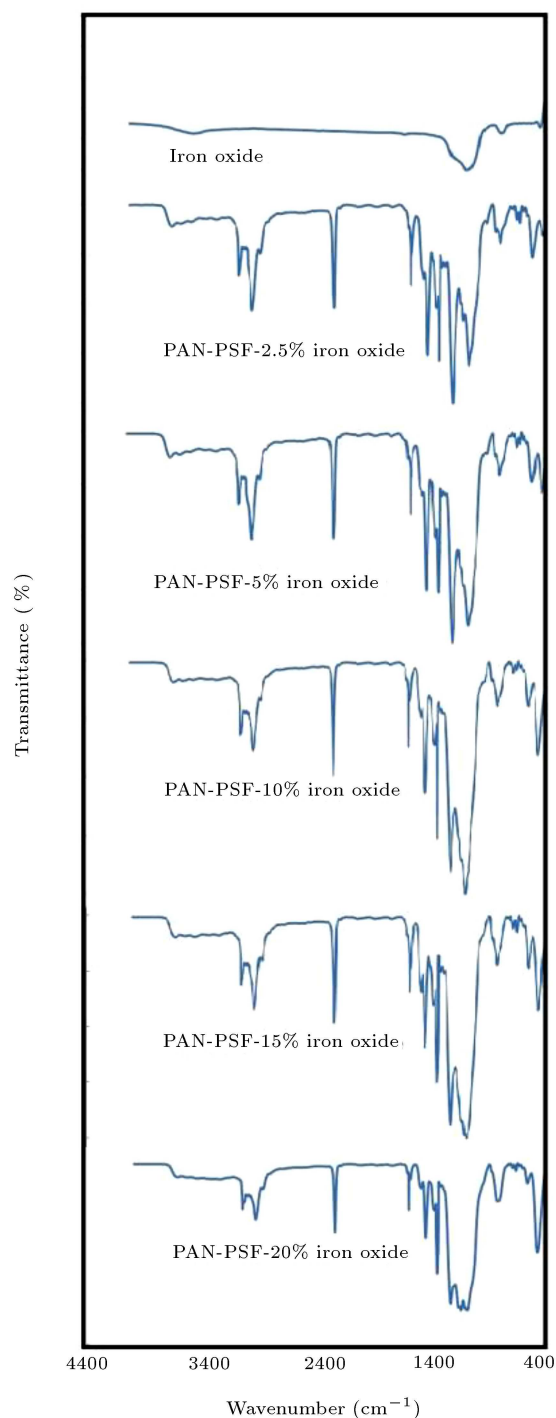


Figure 1. Fourier Transform Infrared Spectroscopy (FTIR) spectra of pure iron oxide and PAN-PSF-iron oxide membrane.

oxide nanoparticles, the thermal stability of the nano-composite membrane increases; further to this, such an increase in thermal resistance results from the presence of iron oxide nanoparticles in the polymer membrane tissue. It can be mentioned that the mineral membranes have proper thermal resistance, and increasing oxide nanoparticles in the polymer membrane tissue

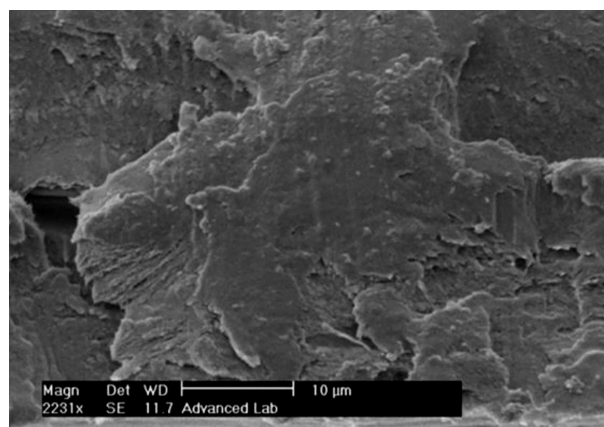


Figure 2. Scanning Electron Microscope (SEM) image of the membrane with 2.5% iron oxide.

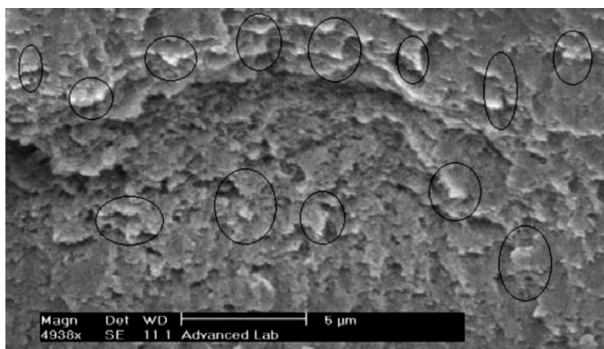


Figure 3. Scanning Electron Microscope (SEM) image of the membrane with 20% iron oxide.

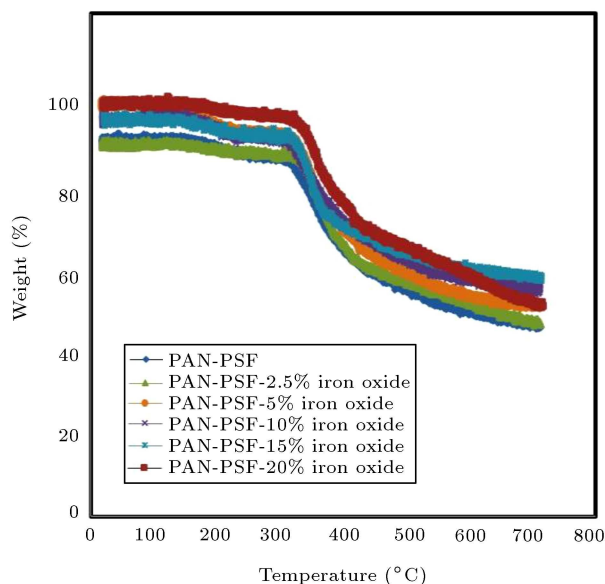


Figure 4. Thermal Gravimetric Analysis (TGA) analysis of polyacrylonitrile-polysulfone (PAN-PSF) and (PAN-PSF-iron oxide) membranes.

facilitates the compatibility of the properties of the membrane with the properties of mineral membranes. The initial degradation that occurred at temperatures

Table 1. The decomposition temperature of polyacrylonitrile-polysulfone (PAN-PSF) and PAN-PSF-iron oxide membranes investigated by Thermal Gravimetric Analysis (TGA) analysis.

Membrane	Decomposition temperature (°C)
PAN-PSF	311.23
PAN-PSF-2.5% iron oxide	320.27
PAN-PSF-5% iron oxide	321.91
PAN-PSF-10% iron oxide	324.1
PAN-PSF-15% iron oxide	332.17
PAN-PSF-20% iron-oxide	334.1

lower than 200°C occurred due to the presence of water or additional solvent in the membrane.

Momeni and Pakizeh [33] found the same trend in the nano-composite membrane of magnesium oxide and PSF. By increasing the magnesium oxide nanoparticles, the thermal stability of the nano-composite membrane increased. The thermal resistance of the polyvinyl acetate membrane also increased as titanium oxide nanoparticles increased [32]. Ahmadizadeghan et al. [10] observed the same trend. The same results were shown in the case of the polycaprolactone-based polyurethane-silica nano-composite membrane.

3.4. Gas permeation

The permeability of nitrogen, oxygen, methane, and carbon dioxide gases and the selectivity of gas pairs in polymer membrane and mixed membranes are reported in Table 2. The ratio of permeability changes of gases was tested. According to the findings obtained from the PAN-PSF mixed membranes, the mixed PAN membrane with 10% PSF showed good permeability and selectivity and, thus, was selected as the best membrane. In this study, the impact of adding different weight percentages of iron oxide to the mixed membranes was examined. The findings of permeability and selectivity of pure gases of CO₂, O₂, N₂, and CH₄ at 10 bar pressure and 30°C by the mixed membrane and nanocomposites membranes with different weight percentages of iron oxide are illustrated in Table 2. Based on the findings shown in Table 2, by increasing iron oxide nanoparticles, the permeability of all gases increases.

This increase in permeability stands in contrast with the model predicted by Maxwell. Maxwell's model cannot analyze the permeability of nano-composite membranes efficiently, because the interface between the polymer and the nanoparticles is not considered as a separate phase similar to that in Maxwell's model [39]. A simultaneous increase in permeability and selectivity of nano-composite membranes with low percentages of iron oxide nanoparticles is seen; how-

Table 2. Gas permeability and selectivity of polyacrylonitrile-polysulfone (PAN-PSF) and PAN-PSF-iron oxide membranes.

Membranes	Permeability (barrer)				Selectivity		
	CO ₂	CH ₄	N ₂	O ₂	CO ₂ /N ₂	CO ₂ /CH ₄	O ₂ /N ₂
PAN-PSF	1.16658	0.22874	0.27448	0.41732	4.25002	5.10002	1.52035
PAN-PSF-2.5% iron oxide	1.62634	0.26762	0.37055	0.59701	4.38888	6.07705	1.61111
PAN-PSF-5% iron oxide	2.14101	0.32938	0.47349	0.78170	4.52174	6.50000	1.65093
PAN-PSF-10% iron oxide	2.53215	0.34997	0.53525	0.98815	4.73076	7.23527	1.84615
PAN-PSF-15% iron oxide	3.19093	0.638185	0.844051	1.31754	3.780494	5.000008	1.560972
PAN-PSF-20% iron-oxide	3.80852	0.782292	1.09109	1.64693	3.490564	4.868412	1.509436

ever, at higher percentages of iron oxide nanoparticles, permeability increased and selectivity decreased. By adding iron oxide nanoparticles to the PAN membrane and 10%, the permeability of all gases increased. In the investigation of PSF/polyamide polymer with zeolite nanoparticles in the study of Dorosti et al., the same trend was observed [24].

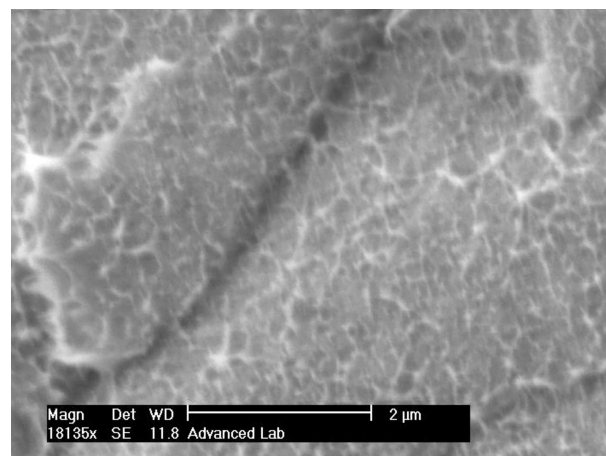
The permeability value of N₂, CH₄, H₂, and CO₂ in the PSF and PSF/MgO membranes was investigated by Momeni and Pakizeh [33]. The permeability of all gases into the membrane increased as the percentage of magnesium oxide nanoparticles increased, the cause of which can be attributed to the increase of free volumes in the polymer phase. This increase in free volume increases the penetration coefficient and solubility, the consequence of which is the high permeability [33]. Nanoparticles of zinc oxide placed on poly amide-6-B-ethylene oxide/zinc oxide (PEBA/ZnO) membrane showed higher permeability than PEBA membrane [40]. By increasing the value of titanium oxide nanoparticles to that of the mixed matrix membrane, the permeability of N₂, CH₄, O₂, CO₂, and He increased [30].

To investigate the significant characteristics of gas transfer from polymer nano-composite membranes, it is important to note that a significant increase in permeability is observed by increasing the volume fraction of nanoparticles despite the nonporosity of nano-fillers, compared to the conventional perceptions. The unusual behavior of nanoparticles is due to the larger interface area (common surface area relative to the volume of nano-composite) in comparison to filler particles with micron sizes or larger [41]; therefore, the interaction of nanoparticles and the polymer matrix at a contact point causes certain changes and accelerates the penetration of gas molecules and their solubility. In other words, structural changes made at the interface of the nanoparticle and the polymer matrix cause an increase in the permeability of gas molecules. Increased non-organic nanoparticles affected the properties of gas transfer into three ways of increasing the free volume, increasing solubility, and increasing empty volume [19].

Examining the interface layer in polymer nano-

composite membranes is very important, since it leaves significant impact on the permeability of the gas. On the other hand, it is essential to consider the role of three phenomena of increasing free volume, creating empty volume, and increasing the solubility in selecting the type of nanoparticles and polymer matrix in designing polymer nano-composite membranes, considering their interactions with each other. On the other hand, to model gas permeability in this type of the membrane, considering the interface layer as a separate phase is of great importance, such that almost none of the current two-phase models, such as Maxwell and Brugman models, has successfully determined the properties of polymer nano-composite membranes. The reason why these models are often subject to failure is two-fold: (a) assuming the polymer matrix to be ideal and (b) failing to consider the interactions of nanoparticles and polymer matrices [39].

As illustrated in Table 2, the presence of iron oxide by 10% weight in the membrane caused a simultaneous increase in selectivity and permeability. For this reason, the SEM image of the cross-sectional surface of the membrane containing 10% weight of iron oxide was examined. As illustrated in Figure 5, iron oxide nanoparticles, weighing 10%, exhibit a uniform

**Figure 5.** Scanning Electron Microscope (SEM) image of the membrane with 10% iron oxide.

distribution in a polymeric network, and the agglomeration phenomenon of nanoparticles is not significantly observed, which is one of the disadvantages of nano-composite membranes. In addition, no cavity is seen at the interface of two phases, suggesting good compatibility between the organic and inorganic phases; this issue increased the permeability and selectivity simultaneously.

A similar behavior by the membrane of titanium oxide/polystyrene was observed [42]. Suhaimi et al. [43] studied the impact of adding palladium nanoparticles to the PSF membrane and observed a similar trend. Based on the investigation of the membrane of polyvinyl chloride/silica nanoparticles, it was seen that the permeability of CO₂ and O₂ increased as the percentage of nanoparticles increased, while the addition of nanoparticles did not have much impact on the permeability of N₂ and CH₄ [44].

The mixed membrane along with nanoparticles that were filled with iron oxide for all gases showed higher permeability than the mixed membrane without iron oxide, and permeability reduced as the percentages of iron oxide weight decreased. Findings obtained from the permeability of nano-composite membranes are in contrast with Maxwell's model, predicting the gas permeability from the nano-composite membrane including non-porous fillers to be less than pure membranes. Maxwell also predicted that, due to the increase of the non-porous fillers, permeability reduced, resulting from increased turbulence in the polymer matrix [39].

Figure 6 shows that the permeability of oxygen and carbon dioxide gas increases as nanoparticles increase, while nitrogen and methane gases show an insignificant increase in the permeability of the nano-composite membrane with 2.5, 5, and 10% weights of iron oxide nanoparticles and provide required con-

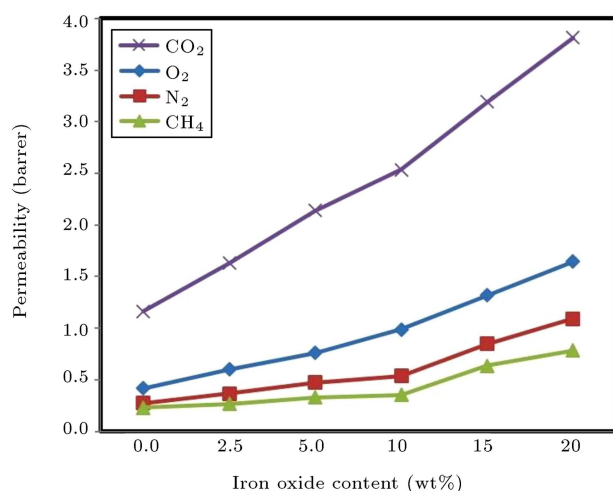


Figure 6. The effect of iron oxide content in (PAN-PSF-iron oxide) membranes on gas permeability.

ditions to improve the membrane selectivity. The significant increase was observed in the permeability of gases at a higher molecular weight in the nano-composite membrane with 15 and 20% weights of iron oxide nanoparticles, while the permeability of gases at a lower molecular weight remained constant, leading to the reduced selectivity of nano-composite membranes at high percentages of iron oxide nano-particles.

The addition of nanoparticles to the polymer membrane does not produce the same results [45,46]. Adding silica nanoparticles to the mixed matrix of polyurethane/polyvinyl alcohol caused a reduction in permeability of methane, oxygen, and nitrogen; however, carbon dioxide permeability increased. In polymer systems, changes in the solubility at the interface of particle-polymer caused an increase in permeability compared to the systems not filled with nanoparticles. The conducted study indicates that, by adding silica to membrane, penetration is reduced. Reduced penetration restricts the movement of gas molecules in this membrane. The investigation of the gas solubility in a matrix membrane filled with silica nanoparticles revealed that these nanoparticles improved solubility coefficient. Thus, the reduced permeability of N₂, O₂, and CH₄ gases results from reduced penetration, and the increased permeability of CO₂ by adding silica is due to the increase of the gas solubility [31].

Increasing the weight percentage of titanium oxide nanoparticles to that of the membrane of polyethylene glycol/polyether black amide increased the permeability of CO₂ and CH₄ [47]. The gas permeance of the carbon/polyimide/TiO₂ composite membranes increased by increasing the ratio of TiO₂/carbon [10].

According to the findings obtained, the gas penetration properties were examined in the polymer matrix-iron oxide matrix membrane. The correlation between permeability and selectivity for O₂/N₂, CO₂/CH₄, and CO₂/N₂ is illustrated in Figures 7, 8, and 9, respectively. The permeability chart in terms of selectivity is one of the important charts in examining the gas separation property with polymer membranes, indicating the ability of the membrane to overcome the upper limit of Robson. At the same time, by increasing selectivity and permeability, membranes can become closer to the upper limit of Robson [48].

PAN is a membrane material and is characterized by low permeability and selectivity. It is an example of glass polymers used for gas separation. The addition of iron oxide nanoparticles to the membrane structure of the PAN improves the separation properties of this membrane. Furthermore, the addition of iron oxide nanoparticles at low levels caused a simultaneous increase in permeability and selectivity.

As the value of iron oxide nanoparticles in the membrane increases, selectivity decreases, but permeability increases. As shown in Figure 7, in the

mixed membrane containing the 10% weight of iron oxide, the relative permeability of oxygen increases gradually to 137%, and the O_2/N_2 selectivity increases by 21.45%. Based on the findings of experiments illustrated in Figures 8 and 9, carbon dioxide gas permeability increased gradually to 117% and the selectivity of CO_2/CH_4 and CO_2/N_2 increased by 41.76% and 11.29%, respectively, in a membrane with the 10% weight of iron oxide. Findings indicate that there is good compatibility between the polymer and the iron oxide. However, permeability increased in the case of loading higher than 10%, i.e., 15% and 20% weights of iron oxide. However, selectivity decreased. In the membrane containing the 20% weight of iron oxide, despite a 67.66% increase in oxygen permeability, O_2/N_2 selectivity decreased by 10.8% compared to the 10% weight of the iron oxide membrane.

Moghadam et al. [30] investigated the impact of titanium oxide nanoparticles on a mixed matrix membrane. Their research revealed that, by increasing titanium oxide nanoparticles, the permeability and selectivity increased and decreased, respectively. After studying the permeability and selectivity of gases with the nano-composite membrane of polyvinyl acetate/titanium oxide, it was found that the addition of 10% titanium oxide increased the selectivity and permeability of O_2/N_2 , CO_2/N_2 , and H_2/N_2 gases. A simultaneous increase in permeability and selectivity in the 10% weight of titanium oxide indicated that mixing these two materials left a significant impact on transitional properties and created a resistant membrane. At values greater than this value, i.e., 15% weight of titanium oxide, a reduction in selectivity is seen. In this membrane with 15% of titanium oxide, a greater agglomeration of nanoparticles occurred due to the creation of microscopic cavities and, thus, increased permeability and reduced selectivity [32].

4. Conclusion

The addition of polysulfone as a polymer with high permeability and selectivity, compared to polyacrylonitrile, improved the gas separation properties by a mixed membrane of polyacrylonitrile-polysulfone. By adding polysulfone to polyacrylonitrile, the permeability of all gases increased. Among the mixed membranes, the highest selectivity was obtained for that with 10% polysulfone. Thus, the iron oxide nanoparticles were added to a combination of these two polymers. By adding the 10% weight of iron oxide nanoparticles to the mixed membrane of polyacrylonitrile-polysulfone, permeability and selectivity increased simultaneously. The reason for a simultaneous increase in permeability and selectivity at low percentages of iron oxide nanoparticles is the proper compatibility of the polymer and the iron oxide nanoparticles. In other words,

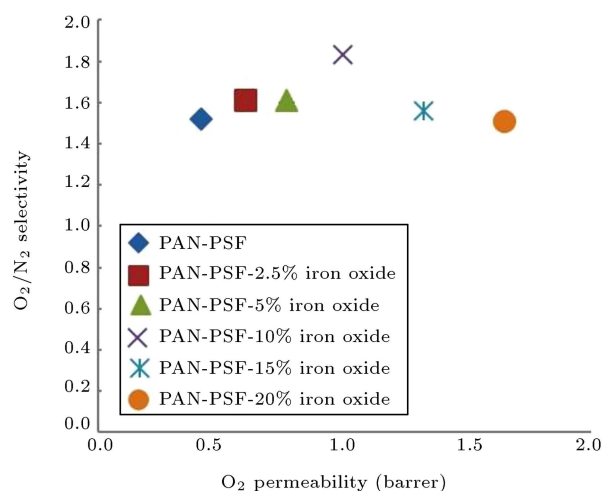


Figure 7. Relation between O_2 permeability and O_2/N_2 selectivity with different wt% of iron oxide in membranes.

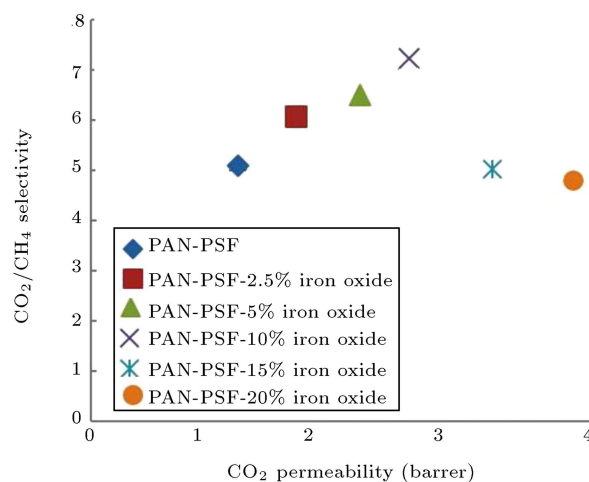


Figure 8. Relation between CO_2 permeability and CO_2/CH_4 selectivity with different wt% of iron oxide in membranes.

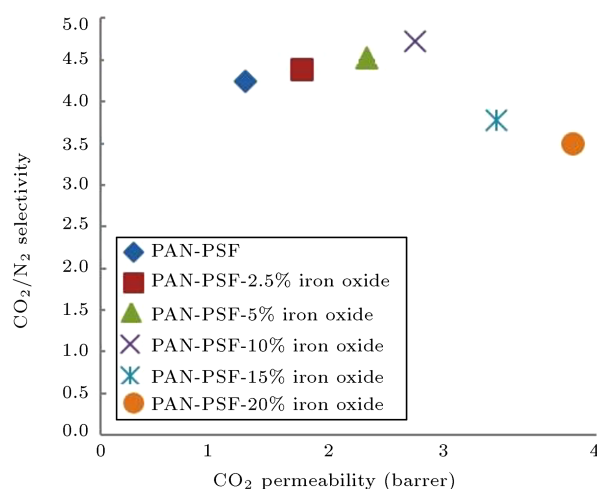


Figure 9. Relation between CO_2 permeability and CO_2/N_2 selectivity with different wt% of iron oxide in membranes.

this combination did not form large cavities. Increased selective surface spaces at the interface between the polymer and iron oxide nanoparticles and the proper spread of nanoparticles in the polymer matrix were other reasons for a simultaneous increase in permeability and selectivity.

References

- Shi, H., Huang, M., Huang, Y., Cui, M., and Idem, R. "CO₂ absorption efficiency of various MEA-DEA bled with aid of CaCO₃ and MgCO₃ batch and semi-batch processes", *Sep. Purif. Technol.*, **220**, pp. 102–113 (2019).
- Wang, J., Deng, S., Sun, T., Xu, Y., Li, K., and Zhao, J. "Thermodynamic and cycle model for MEA-based chemical CO₂ absorption", *Energy Procedia*, **158**, pp. 4941–4946 (2019).
- Yin, Y., Fu, T., Zhu, Ch., Guo, R., Ma, Y., and Li, H. "Dynamics and mass transfer characteristics of CO₂ absorption into MEA/[Bmim][BF₄] aqueous solution in a microchannel", *Sep. Purif. Technol.*, **210**, pp. 541–552 (2019).
- Akinola, T.E., Oko, E., and Wang, M. "Study of CO₂ removal in natural gas process using mixture of ionic liquid and MEA through process simulation", *Fuel*, **236**, pp. 135–146 (2019).
- Gao, H., Bai, L., Han, J., Yang B., Zhang, S., and Zhang, X. "Functionalized ionic liquid membrane for CO₂ separation", *Chem. Commun.*, **54**, pp. 12671–12685 (2018).
- Zhao, Y., Gani, R., Afzal, R.M., Zhang, X., and Zhang, S. "Ionic liquids for absorption and separation of gases: An extensive database and a systematic screening method", *AIChE J.*, **63**, pp. 1353–1367 (2017).
- Zhao, Y., Pan, M., Kang, X., Tu, W., and Gao, H. "Gas separation by ionic liquids: A theoretical study", *Chem. Eng. Sci.*, **189**, pp. 43–55 (2018).
- Sasikumar, B., Arthanareeswaran, G., and Ismail, A. F. "Recent progress in ionic liquid membrane for gas separation", *J. Mol. Liq.*, **266**, pp. 330–341 (2018).
- Ilyas, A., Muhammad, N. Gilani, M.A., Vankelecom, I.F.J., and Khan, A.L. "Effect of zeolite surface modification with ionic liquid [APTMS][AC] on gas separation performance of mixed matrix membranes", *Sep. Purif. Technol.*, **205**, pp. 176–183 (2018).
- Ahmadizadeghan, H., Tahriri, M., Tahriri, M., Padam, M., and Ranjbar, M. "Polyimide-TiO₂ nano composites and their corresponding membranes: Synthesis, characterization, and gas separation applications", *Solid State Sci.*, **89**, pp. 25–36 (2019).
- Wong, K.C., Goh, P.S., Taniguchi, T., Ismail, A.F., and Zahri, K. "The role of geometrically different carbon-based fillers on the formation and gas separation performance of nanocomposite membrane", *Carbon*, **149**, pp. 33–44 (2019).
- Nigiz, F.U. and Hilmioglu, N.D. "Enhanced hydrogen purification by graphene-poly (dimethyl Siloxane) membrane", *Int. J. Hydrogen Energy*, **45**, pp. 3549–3557 (2020).
- Torstensen, J.Q., Helberg, R.M.L., Deng, L., Gregersen, Q.W., and Syveud, K. "PVA/nanocellulose nanocomposite membranes for CO₂ separation from flue gas", *Int. J. Greenhouse Gas Control*, **81**, pp. 93–102 (2019).
- Takht Ravanchi, M., Kaghazchi, T., and Kargari, A. "Application of membrane separation processes in petrochemical industry: a review", *Desalination J.*, **235**(1), pp. 199–244 (2009).
- Xiang, L., Pan, Y., Zeng, G., Jiang, J., Chen, J., and Wang, C. "Preparation of poly(ether-block-amid) /at-tapoltgite mixed membranes for CO₂/N₂ separation", *J. Membrane Sci.*, **500**, pp. 66–75 (2016).
- Pandey, P. and Chauhan, R.S. "Membranes for gas separation", *Prog. Polym. Sci.*, **26**, pp. 853–893 (2001).
- Bastani, D., Esmeaili, N., and Asadollahi, M. "Poly-meric mixed matrix membranes containing zeolites as a filler for gas separation applications: A review", *J. Ind. Eng. Chem.*, **19**, pp. 375–393 (2013).
- Koros, W.J. "Gas separation membranes: needs for combined material science and processing approaches", *Macromol. Symp.*, **188**, pp. 13–22 (2002).
- Cong, H., Radosz, M., Towler, B.F., and Shen, Y. "Polymer-inorganic nanocomposite membranes for gas separation", *Sep. Purif. Technol.*, **55**, pp. 281–291 (2007).
- Safak Boroglu, M. and Burcu Yumru, A. "Gas separation performance of 6FDA-DAM-2IF-11 mixed-matrix membranes for H₂/CH₄ and CO₂/CH₄ separation", *Sep. Purif. Technol.*, **173**, pp. 269–279 (2017).
- Ozturk, B. and Demirciyeva, F. "Comparison of bio-gas upgrading performance of different mixed matrix membranes", *Chem. Eng. J.*, **222**, pp. 201–217 (2013).
- Tseng, H.H., Chuang, H.W., Zhuang, G.L., Lai, W.H., and Wey, M.Y. "Structure-controlled mesoporous SBA-15-derived mixed matrix membranes for H₂ purification and CO₂ capture", *Int. J. Hydrogen Energy*, **42**(16), pp. 11379–11391 (2017).
- Rafiq, S., Man, Z., Maulud, A., Muhammad, N., and Maitra, S. "Separation of CO₂ from CH₄ using polysulfone. polyimide silica nanocomposite membranes", *Sep. Purif. Technol.*, **90**(27), pp. 162–172 (2012).
- Dorosti, F., Omidkhah, M.R., Pedram, M.Z., and Moghadam, F. "Fabrication and characterization of polysulfone/polyimide-zeolite mixed matrix membrane for gas separation", *Chem. Eng. J.*, **171**, pp. 1469–1476 (2011).

25. Ahn, J., Chung, W.J., Pinnau, I., and Guiver, M.D. "Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation", *J. Membrane Sci.*, **314**, pp. 123–133 (2008).
26. Sadeghi, M., Khanbabaei, G., Dehaghani, A.H.S., Sadeghi, M., Aravand, M., Akbarzade, A.M., and Khatti, S. "Gas permeation properties of ethylene vinyl acetate-silica nanocomposite membranes", *J. Membrane Sci.*, **322**, pp. 423–428 (2008).
27. Chieh-Fang, L., Jung-Fen, W., Hsieh-Yu, L., Wie-Sung, H., Chao-Ming, S., Chien-Chieh, H., Ying-Ling, L., and Shinjiang, L. "Novel poly vinyl alcohol nano composites containing carbon nano-tubes with Fe₃O₄ pendants for alkaline fuel cell applications", *J. Membrane Sci.*, **444**, pp. 41–49 (2013).
28. Madaeni, S.S. and Akbarzade Arbatan, T. "Preparation and characterization of microfiltration membrane embedded with silver nano-particles", *Iran. J. Chem. Eng.*, **29**, pp. 105–111 (2010).
29. Kim, J. and Bruggen, B.V. "The use of nano particles in polymeric and ceramic membrane structures: Review of manufacturing procedures and performance improvement for water treatment", *Environ. Pollut.*, **158**, pp. 2335–2349 (2010).
30. Moghadam, F., Omidkhah, M.R., Vasheghani Farahani, E., Pedram, M.Z., and Dorosti, F. "The effect of TiO₂ nanoparticles on gas transport properties of matrimid 5218-based mixed matrix membranes", *Sep. Purif. Technol.*, **77**, pp. 128–136 (2011).
31. Semsarzadeh, M.A. and Ghalei, B. "Preparation, characterization and gas permeation properties of polyurethane-silica/polyvinyl alcohol mixed matrix membranes", *J. Membrane Sci.*, **432**, pp. 115–125 (2013).
32. Ahmad, J. and Britt Hagg, M. "Polyvinyl acetate/titanium dioxide nanocomposite membranes for gas separation", *J. Membrane Sci.*, **445**, pp. 200–210 (2013).
33. Momeni, S. and Pakizeh, M. "Preparation, characterization and gas permeation study of PSf/MgO nanocomposite membrane", *Braz. J. Chem. Eng.*, **30**, pp. 589–597 (2013).
34. Zuhariun, A.K. and Ismail, A.F. "The role of layered silicate loadings and their dispersion states on the gas separation performance of mixed matrix membrane", *J. Membrane Sci.*, **468**, pp. 20–30 (2014).
35. Sun, H., Wang, T., Xu, Y., Gao, W., Li, P., and Niu, Q.J. "Fabrication of polyimide and functionalized multi-walled carbon nanotubes mixed matrix membrane by in-situ polymerization for CO₂ separation", *Sep. Purif. Technol.*, **77**, pp. 327–336 (2017).
36. Sadeghi, M., Taheri Afarani, H., and Tarashi, Z. "Preparation and investigation of the gas separation properties of polyurethane-TiO₂ nanocomposite membranes", *Korean J. Chem. Eng.*, **32** (1), pp. 97–103 (2015).
37. Ismail, A.F. and Lai, P.Y. "Development of defect-free asymmetric polysulfone membranes for gas separation using response surface methodology", *Sep. Sci. Technol.*, **40**, pp. 191–207 (2004).
38. Semsarzadeh, M.A. and Ghalei, B. "Characterization and gas permeability of polyurethane and polyvinyl acetate blend membranes with polyethylene oxide-polypropylene oxide Block Copolymer", *J. Membrane Sci.*, **401-402**, pp. 97–108 (2012).
39. Maxwell, C., *Treatise on Electricity and Magnetism*, Oxford University, London (1873).
40. Sheikh, M., Asghari, M., and Afshari, M. "Effect of nano zinc oxide on gas permeation through mixed matrix poly (amide-6-b-ethylene oxide) based membranes", *Int. J. Nano Dimens.*, **8**(1), pp. 31–39 (2017).
41. Xue, L., Borodin, O., and Smith, D. "Modeling of enhanced penetrant diffusion in nanoparticle-polymer composite membranes", *J. Membrane Sci.*, **286**, pp. 293–300 (2006).
42. Safaei, P. Marjani, A., and Salimi, M. "Mixed matrix membranes prepared from high impact polystyrene with dispersed TiO₂ nanoparticles for gas separation", *J. Nanostruct.*, **6**(1), pp. 74–79 (2016).
43. Suhaimi, H.S.M., Khir, M.N.I.M., Leo, C.P., and Ahmad, A.L. "Preparation and characterization of polysulfone mixed matrix membrane incorporated with palladium nanoparticles dispersed in polyvinylpyrrolidone for hydrogen separation", *J. Polym. Res.*, **21**(428), pp. 1–8 (2014).
44. Mohaghehian, M., Sadeghi, M., Pourafshari Chenar, M., and Naghsh, M. "Gas separation properties of polyvinylchloride (PVC)-silica nanocomposite membrane", *Korean J. Chem. Eng.*, **31**(11), pp. 2041–2050 (2014).
45. Sadeghi, M., Talakesh, M.M., Ghalei, B., and Shafiei, M. "Preparation, characterization and gas permeation properties of a polycaprolactone based polyurethane-silica nano-composite membrane", *J. Membrane Sci.*, **427**, pp. 21–29 (2013).
46. Isfahani, A.P., Sadeghi, M., Saeedi Dehaghani, A.H., and Aravand, M.A. "Enhancement of the gas separation properties of polyurethane membrane by epoxy nanoparticles", *J. Ind. Eng. Chem.*, **44**, pp. 67–72 (2016).
47. Azizi, N., Mohammadi, T., and Mosayebi Behbahani, M. "Synthesis of a new nanocomposite membrane (PEBAX-1074/PEG-400/TiO₂) in order to separate CO₂ from CH₄", *J. Nat. Gas Sci. Eng.*, **37**, pp. 39–51 (2017).

48. Robeson, L.M. “Correlation of separation factor versus permeability for polymeric membranes”, *J. Membrane Sci.*, **62**, pp. 165–185 (1991).

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