

Formulation of Mixed-Matrix Membrane (PSF/Zeolite) for CO₂/N₂ Separation: Screening of Polymer Concentration

Chen Chee Lek, Sunarti Abd Rahman*

Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Kuantan, Malaysia
Email: [*sunartirahman@gmail.com](mailto:sunartirahman@gmail.com)

Received 6 March 2015; accepted 10 May 2015; published 13 May 2015

Copyright © 2015 by authors and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY).
<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

This research investigates the permeability of CO₂ and N₂ as well as selectivity of CO₂ over N₂ of polysulfone (PSF) mixed matrix membranes filled with zeolite 4Å particles. The membranes were prepared by solution-casting method and utilized to determine the permeation rates of N₂ and CO₂. It was characterized by FTIR and the gas separation performance was analysed by Design of Expert (DOE) method. FTIR result revealed the intensity of peak for sulfone S=O vibration at 1322 cm⁻¹; it was related to O=S=O bound of polysulfone in the sample. The single concentration variable has low outcome, however the mixture concentration interaction was effectively to lead better selectivity of CO₂ over N₂. In terms of interaction between mixture concentrations, interaction between PSF and N-Methyl-2-pyrrolidone (NMP) has considerable effect on the permeability of CO₂ with the highest F value of 0.46 membrane. NMP exhibited a high degree of polarity and hydrogen bonding which led to effect of selective skin and permeation rate. The model regression equations were developed as the potential use for screening the permeability of CO₂ and N₂ based on the deviation effect of polymer concentration.

Keywords

Mixed-Matrix Membranes, CO₂/N₂ Separation, Polymer

1. Introduction

Mixed-matrix membranes (MMMs) have turned into an apparent morphology to prevail over the gas selectivity

*Corresponding author.

How to cite this paper: Chee Lek, C. and Abd Rahman, S. (2015) Formulation of Mixed-Matrix Membrane (PSF/Zeolite) for CO₂/N₂ Separation: Screening of Polymer Concentration. *Journal of Materials Science and Chemical Engineering*, 3, 65-74.
<http://dx.doi.org/10.4236/msce.2015.35008>

limitation by conventional polymeric membranes. In previous researches, several filler materials like silica [1], zeolites [2], conductive polymers [3] or carbon molecular sieves [4] [5] were studied to embed into polymer matrix. The notable attainment has been achieved to fabricate MMMs by using glassy polymers and zeolites as polymeric matrix and filler respectively [6] [7]. The selection of filler was based on its molecular sieve mechanism on the polymer matrix which relied on its stiffness and higher intrinsic selectivity. Nearly all MMMs experienced the deficiency of interaction between zeolite and glassy polymer; hence it was the outcome of investigating the effect of non-selective voids at the polymer-zeolite membrane interface [8] [9]. Several methods have been proposed and inspected to refine the interaction between polymer and zeolite [2] [10]. These approaches can be categorized into the adaptability of polymer during membrane fabrication and affinity between zeolite and polymer. Based on the research, the polyimides, polyesters, polysulfones and polyamides resulted in higher gas separation performance [11] [12]. The influences contributing to the result of membrane fabrication are the mixture concentration of polymer and solvent, type of solvent and effect of solvent evaporation on the permeability and selectivity of membranes [13].

To date, many researches have examined to improve and optimize the membrane morphology [14]-[16] and gas separation attainment [17] through a statistical approach. In the research, the further investigation on the interaction of mixed matrix membrane variables is statistically designed with minimum experimental runs to locate ideal setting of mixture concentration factors for improving permeability of CO₂ and N₂ as well selectivity of CO₂ over N₂. The statistical approaches were ANOVA analysis, factorial design and fitted model equations to compute the complex interaction between the independent process factors [18]. Thus, the approachability of these membranes for the dissociation of industrially significant CO₂ and N₂ could be investigated and the transport mechanism through each membrane type could be explained thoroughly by mechanistic clarification on deviations from single gas permeability assessment of the membranes.

This research aimed to synthesize and investigate the flat sheet mixed-matrix membrane of polysulfone (PSF) and zeolite for CO₂ and N₂ gas separation by screening different concentration of mixture. The membranes were fabricated and characterized for their permeability and selectivity. In order to investigate permeability of CO₂ and selectivity of CO₂ over N₂, this current study is aimed at illustrating the interaction between concentration of PSF, zeolite and NMP in diagnostic analysis using Design of Expert (DOE). Final regression models obtained from DOE are expected to be able to predict the optimum mixture concentration parameters in producing high permeability of CO₂.

2. Experimental

2.1. Chemicals

The polymeric material used for the membrane preparation was analytical grade polysulfone, PSF, which was purchased from Sigma Aldrich. The polymer has a weight-averaged molecular weight of 35,000 and melt index of about 6.5 g/10 min. Analytical grade N-Methyl-2-pyrrolidone, NMP was used as solvent with purity of 99.5% were sourced from Sigma-Aldrich. It has the chemical formula of C₅H₉NO and boiling point is 202°C per liter. The filler material was molecular sieve, 4Å with particle size of 8 - 12 mesh was purchased from Aldrich. They were dried at 80°C for 24 hours before using in membrane preparation. Nitrogen and carbon dioxide with purity 99% were obtained from Air Products Malaysia SdnBhd for gas permeation.

2.2. Sample Preparation

The mixed matrix membrane was prepared by immersion precipitation method. The zeolite was prepared from 10 to 30 W/V% and dissolved in the NMP varied from 75 to 100 cm³. The mixture was then mixed homogeneously in the shaker at 200 rpm and 25°C for three hours. Polysulfone was weighed from 10 to 30 W/V% and added into mixture solution. In order to yield homogenous solution, mechanical stirrer was set at 300 rpm to agitate the mixture for another three hours at room temperature. The dope solution was settled in a storage vessel and degassed by using ultrasonic bath to withdraw any trace of bubbles generated by mechanical stirrer [19]. The glass plate was prepared for casting by using glass rod. The sample membranes were ready for the permeability and selectivity testing for CO₂ and N₂ separation.

2.3. Single Gas Permeation Test for CO₂/N₂ Separation

Permeability and selectivity of membrane were characterized by gas permeation equipment. The test module

containing membrane with the diameter of approximately 6 cm each was prepared. The pure gas permeation study was measured based on the gas solubility, CO₂ gas must be the last gas to be measured due to its encouragement of membrane plasticization [20]. Thus, the modules were connected to the gas permeation apparatus manufactured by ABA Manufacturing SdnBhd using purified nitrogen at two barg. The gas permeation rate from the permeate side was measured at room temperature (25°C ± 5°C) using soap-bubble meter manufactured by Dwyer. The procedures of conducting permeation test were repeated by using the carbon dioxide as the replacement of test gas at the pressure of 2 bar.

2.4. Screening Study of Membrane for CO₂/N₂ Separation

The permeability and selectivity of membrane were screening by using Design of Experiment (DOE) software, version 7.1. Three variables were investigated in the study, coded as concentration of zeolite (X₁), concentration of PSF (X₂) and concentration of NMP (X₃) in the software. The result of gas content of nitrogen and carbon dioxide diffused through membrane housed in a Single Gas Permeation Test was analyzed as response which coded as Y in the software. All experiments were set in random order to reduce the influence of unexplainable variability in the observed responses due to insignificant aspects. Mathematical models containing the notable terms were developed for each response parameter using the multiple linear regression analysis (MLRA) and analysis of variance (ANOVA).

3. Results and Discussion

3.1. Gas Performance Analysis

The permeability of CO₂, permeability of N₂ and selectivity of CO₂/N₂ were performed based on the single gas permeation measurement. In this study, single gas permeation measurements for N₂ and CO₂ gasses were performed for all fabricated membranes. At least three samples from eight different casting solutions for each of the membrane formulation were used with vary concentration of PSF, zeolite and NMP. The complete eight numbers of experiment design matrix and the output responses were shown in **Table 1**.

The proportion differentiation between the permeability data for the whole design matrix was below 5% based on gas permeation performed on three samples. However, it was in the range of 5.1% - 8.4% for the selectivity of CO₂/N₂. Thus, the membrane preparation and testing methods were confirmed to be reproducible in this research. The single gas permeation was tested at the pressure of 2 bar. From the **Table 1**, the permeability of CO₂ through the membrane was in higher range from 9.873 to 11.641 GPU. The solubility coefficient of CO₂ was greater at a lower operating pressure [20]. The solubility coefficient was a significant element in gas carrier mechanism through a polymeric dense layer because the increasing of gas solubility promoted a greater permeation rate. Thus, low pressure was preferable in single gas permeation test [9] [20]. From **Table 1**, gas component permeation obtained was lower than the values reported in the previous research for PSF membrane [12]. The

Table 1. Experimental design matrix and response results.

Specimen	Concentration Variables			Experimental Result		
	X ₁ (W/V%)	X ₂ (W/V%)	X ₃ (cm ³)	Y ₁ (GPU)	Y ₂ (GPU)	Y ₃
1	10	10	75	11.641	9.978	1.164
2	10	10	100	11.093	6.371	1.222
3	30	10	100	10.535	8.271	1.261
4	10	30	75	9.873	6.571	1.397
5	30	30	75	10.838	8.980	1.238
6	30	30	100	10.654	8.771	1.211
7	30	10	75	11.429	9.476	1.224
8	10	30	100	11.641	9.978	1.184

X₁, concentration of PSF; X₂, concentration of Zeolite; X₃, concentration of NMP; Y₁, permeability of CO₂; Y₂, permeability of N₂; Y₃, selectivity of CO₂/N₂.

difference may be due to the lengthy evaporation time in the research, thus it fabricated thicker dense top layer structure which influenced the permeability of CO₂.

3.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectra were used to investigate the interactions between polymers and zeolite particles. In this respect following the samples with higher permeability of CO₂ with 11.641 GPU was determined to reveal the significant morphology of membrane polymerization based on the fabrication of polymer concentration. **Figure 1** characterized that the FTIR spectra of PSF membrane with higher permeability of CO₂. The peak at 3596.17 cm⁻¹ corresponds to O-H bound in zeolite. This peak expressed the existence of an interaction between polymer and zeolite. In high zeolite loadings, the peak intensity increased and the bounds between two phases become durable. However, this interaction was not strong enough to eliminate the void spaces between the polymer matrix and zeolite [22]. The spectra showed two intense bands associated with aromatic -CH vibration at approximately 3859.91 cm⁻¹ and 3748.70 cm⁻¹.

The FTIR bands at 1013.36 cm⁻¹ and 1295.62 cm⁻¹ on the PSF spectrum corresponded to ether diaryl C-O-C stretch and anhydride C-O stretch groups respectively. Peak at 1000 - 1100 cm⁻¹ was related to O = S = O bound of polysulfone. This bound revealed the existence of polysulfone [22]. The band located at 1322 cm⁻¹ was associated with sulfone S = O vibration of the membrane. The band observed at 1680.16 cm⁻¹ was assigned to the aromatic carbon double bond vibration which indicates the bonds were not disrupted and still remained in the polymerisation structure. The disappearance of aromatic C-H bond and CH₃ alkene bend with 3000 cm⁻¹ and 1375 cm⁻¹ respectively in the spectra. It reflects the completion of polymerisation reaction. **Table 2** summarized the characteristics adsorption of membrane sample with selectivity of CO₂/N₂ of 1.222.

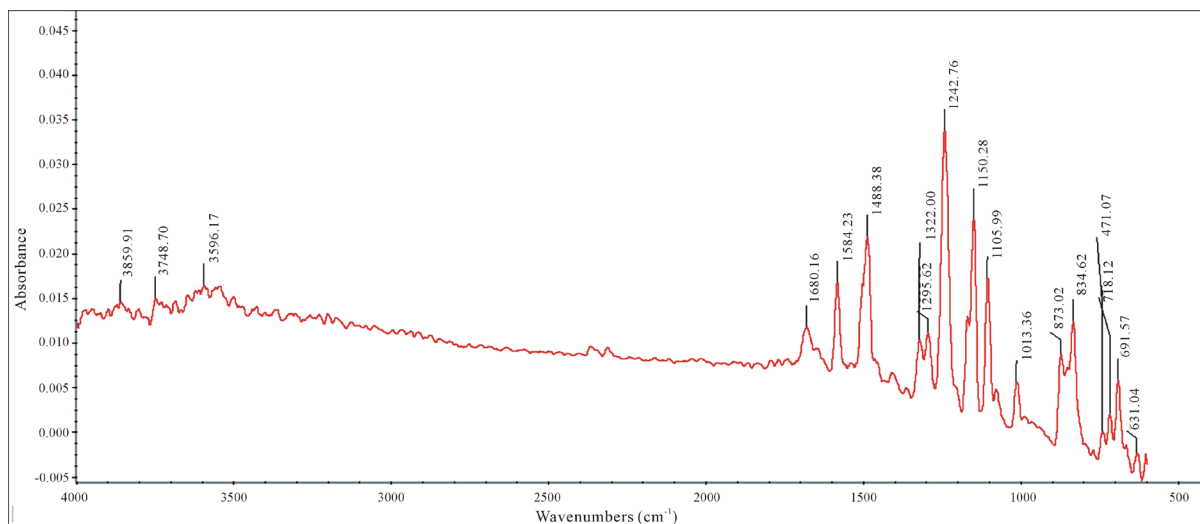


Figure 1. FTIR spectra of polysulfone based membrane with higher permeability of CO₂ and higher selectivity of CO₂/N₂.

Table 2. Functional group of membrane sample with selectivity of CO₂/N₂ of 1.222 in comparison of characteristics adsorption [29].

Functional Group	Sample	Characteristics Adsorption [29]
Sulfone S=O	1322	1300
Aromatic carbon double bond C=C	1680.16	1600 or 1475
Aromatic carbon hydrogen bond C-H	3859.91	3000 - 3020
Ether Diaryl C-O-C stretch	1013.36	1000 - 1300
Anhydride C-O stretch	1295.62	1300
O-H bound in Zeolite	3596.17	3200 - 3600

3.3. ANOVA Analysis

The models expressed by the variables of amount of polysulfone (Y_1), amount of zeolite (Y_2) and concentration of NMP (Y_3) as a function of permeability of CO_2 gas (A), permeability of N_2 gas (B) and selectivity of CO_2 over N_2 . Based on the statistical point of view, there were two analysis involved to assess the model like test of significance of factors (SOF) and R-squared (R^2) test. **Table 3** exhibited the result of the test of SOF and interactions for the Y_1 , Y_2 , and Y_3 after discarding the significant factors with $\text{Prob} > F$ was less than 0.05. In other words, it reflected that the statistical proof with the valid result ($P < 0.5$). The elements of lack of fit and pure error were ignored in the fitted models. The models were analysed to have great (>0.70) determination coefficient of R^2 indicating that the variation in the response could be justified by the mathematical model. **Table 3** revealed the original R^2 , adjusted R^2 and predicted R^2 for the models after eliminating the insignificant terms. For each of the models, the predicted R^2 for permeability of N_2 was in an acceptable concurrence with the adjusted R^2 because they were within 0.2 with one another. The mathematical models were also investigated for its conviction by correlated with the experimental data and the predicted data provided by the models. The data was observed in **Table 3**.

The data proved that the model provided an accurate description of the experimental data, indicating the connection between the variables and output data. The results demonstrated that there were tendencies in the linear regression fit, and the model explains the experimental range studied adequately. The fitted regression equation showed good fit of the models and was successful in capturing the correlation between the three concentration variables. From all these validity tests, the model was found to be adequate for predicting the optimized production of polysulfone based mixed matrix membrane within the range of the preparation mixture concentration studied.

3.4. Empirical Model Analysis

This empirical model was well-fitted to the experimental results, as the great value of R^2 of 0.9 gave a convinced justification to the reliability of regression models for membrane's permeability of carbon dioxide, as shown in **Table 3**. The model equations were analysed by F-test ANOVA which indicated that these regressions were statistically significant at 95% confidence level. The P-value for the permeability of CO_2 , permeability of N_2 and selectivity of CO_2/N_2 model were less than 0.5 expressing that LOF for the mathematical models were significant. This problem has been previously reported [23]. This condition arised when the model was well fitted to the data but the measurement method was very accurate and complex. The models generated for the permeability of CO_2 and N_2 and selectivity of CO_2/N_2 by discarding the insignificant effects which was obtained after performing eight experiments, were listed in **Table 4**.

It reflected the single concentration variable has low effect, however the mixture concentration interaction was capable to bring the better selectivity of CO_2 over N_2 with F value of 0.012 if compared with concentration of PSF and zeolite. At F value of zeolite of 0.006, it was considered as minor effects on the selectivity of CO_2/N_2 . At high zeolite loadings of 30%, the size of interfacial voids was usually greater than gas molecular

Table 3. ANOVA and R-squared (R^2) statistics for the fitted models.

Source	SS	DF	MS	F-Value	Prob > F	Insignificant factors included		
						R^2	Adjusted R^2	Predicted R^2
(a) Y_1 Model Residual	0.43 0.03	6 1	0.072 0.026	2.79	0.042	0.9436	0.6052	2.6095
Coefficient of variation (CV):				2.7%				
(b) Y_2 Model Residual	0.03 0.01	6 1	0.0056 0.0058	0.97	0.037	0.8536	0.6246	8.3675
Coefficient of variation (CV):				3.39%				
(c) Y_3 Model Residual	0.01 0.01	6 1	0.0045 0.0009	0.51	0.048	0.752	0.7362	14.8737
Coefficient of variation (CV):				2.51%				

Y_1 , permeability of CO_2 ; Y_2 , permeability of N_2 ; Y_3 , selectivity of CO_2/N_2 ; SS, sum of squares; DF, degree of freedom and MS, mean square. *Significant at "Prob > F" less than 0.05.

Table 4. ANOVA for the regression model equation and coefficients of permeability of CO₂, permeability of N₂ and selectivity of CO₂/N₂.

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Value	Prob > F
Permeability of CO ₂					
A-Zeolite	0.0620	1	0.057	0.78	0.046
B-PSf	0.0720	1	0.057	0.79	0.045
C-NMP	0.0110	1	0.057	0.71	0.043
AB	0.0340	1	0.057	0.69	0.045
AC	0.1500	1	0.057	0.87	0.037
BC	0.1400	1	0.057	0.58	0.046
Permeability of N ₂					
A-Zeolite	0.0170	1	0.027	0.36	0.032
B-PSf	0.0200	1	0.027	0.36	0.032
C-NMP	0.0053	1	0.027	0.35	0.034
AB	0.014	1	0.027	0.33	0.035
AC	0.033	1	0.027	0.37	0.031
BC	0.046	1	0.027	0.29	0.039
Selectivity of CO ₂ /N ₂					
A-Zeolite	0.00528	1	0.0053	0.006	0.045
B-PSf	0.00496	1	0.0049	0.005	0.045
C-NMP	0.01081	1	0.0108	0.012	0.043
AB	0.02080	1	0.0208	0.023	0.040
AC	0.01154	1	0.0115	1.290	0.046
BC	0.01510	1	0.0151	1.690	0.042

A, concentration of zeolite; B, concentration of PSf; C, concentration of NMP.

diameter thus gas molecules were able to penetrate into these voids with lower diffusion resistance instead of selective pores of zeolite. This led the molecular sieve role of zeolite pores less adequate [24]. As the result, the rate of permeability growth for larger molecules, N₂ was lower than smaller molecules, CO₂ and this in turn caused to faster selectivity CO₂/N₂ increasing in **Table 4**.

The function of interaction between concentration of PSF and NMP (BC) had considerable effect on the selectivity of CO₂/N₂, NMP presented a high degree of polarity and hydrogen bonding which was able to overcome the solvent volatility [25]. Hence, the outermost surface of the membrane fabricated with high polymer concentration as a more volatile solvent was discharged during the evaporation process. The more solvent evaporated, the thicker the concentrated polymer region which then caused to a thicker selective skin and a minimization in permeation rate [26]. Thus, affinity between PSF and NMP potentially led the permeability of CO₂ and N₂ as well as selectivity of CO₂/N₂. Association of NMP and PSF can increase with increasing polymer concentration. Increasing in solvent-polymer interaction can result decreasing of the coagulation value [25]. Thus, those effects encouraged delay demixing.

The concentration of zeolite and PSF had the significant effect on the selectivity of CO₂ over N₂ due to the F value with 0.023, however the interaction had higher permeability of CO₂ with the F value of 0.69. The cause of low selectivity was adverse association between the zeolite and the polymer influencing to a great free volume within the membrane [27]. During casting, the PSF was detached from the Zeolite 4's surface causing micro-cavities throughout the membrane. Although it enhanced the permeability of CO₂, but it limited the sieving

mechanism which resulted low selectivity of CO₂ over N₂. For mixed matrix membranes to perform effectively, it is required to functionalize molecular sieves to have great interaction between the polymeric phase and sieves.

3.5. Verification on Statistical Models and Diagnostic Statistic

Responses surface methodology has the gain of observing the interaction effect among independent variables. The model was able to easily investigate the influences of binary combination of combining two independent factors. From **Figure 2**, it revealed the variable interaction for all responses. The non-parallel curvatures indicated that there was an interaction between the element of zeolite (A) and PSF (B) in **Figure 2**. Based on the model, the maximum operating condition of the membrane stretching was predicted around the region of higher concentration of PSF and zeolite. The range of screening PSF and zeolite concentration implied from 22.30 to 27.45 W/V% for the better selectivity of CO₂/N₂.

From **Figure 3(a)**, it displayed the normal probability of the residuals, to prove whether the standard deviations between the actual and the predicted response values do obey the normal distribution [28]. The general impact from the graph demonstrated that the underlying errors were distributed normally as the residuals fall on the side of straight line, and thus, there was no severe evidence of non-normality of the experimental results. The plot of the residuals versus predicted response for the response was presented from **Figure 3(b)**. All points of experimental runs were scattered randomly within the constant range of residuals across the graph within the horizontal lines at point of ± 1.50 . This indicated that the model proposed was adequate and the constant variance assumption was confirmed.

Reliability and adequacy of empirical model from respective responses was confirmed when the actual values obtained from experimental results were compared to the estimated values from regression models from **Figure 3(c)**. Points above the diagonal line were those which were over-estimated and vice versa. The graph shown from **Figure 3(c)**, it generally implied that all experiment design points were distributed along the diagonal line. Responses from the experimental results were well-fitted in acceptable variance range when collated to the predicted values from respective empirical models. This proved that error occurred was due to uncontrollable experimental error could be disregarded. Thus, regression models obtained from DOE can be further used as a predictor for the screening of membrane concentration variables in order to produce a high selectivity of CO₂/N₂.

3.6. Model Equations Based on Screening Effect

In general, all concentration factors had first-order effect. The linear model was performed on membrane permeability of CO₂ and N₂ as well as selectivity of CO₂/N₂. Three of the mixture concentration factors had significant model terms, which were A: concentration of zeolite, B: concentration of PSF and C: concentration of NMP. The model equations were assessed by F-test ANOVA analysis which expressed that these regressions were statistically significant at 95% confidence level. **Table 5** showed the ANOVA for the regression model

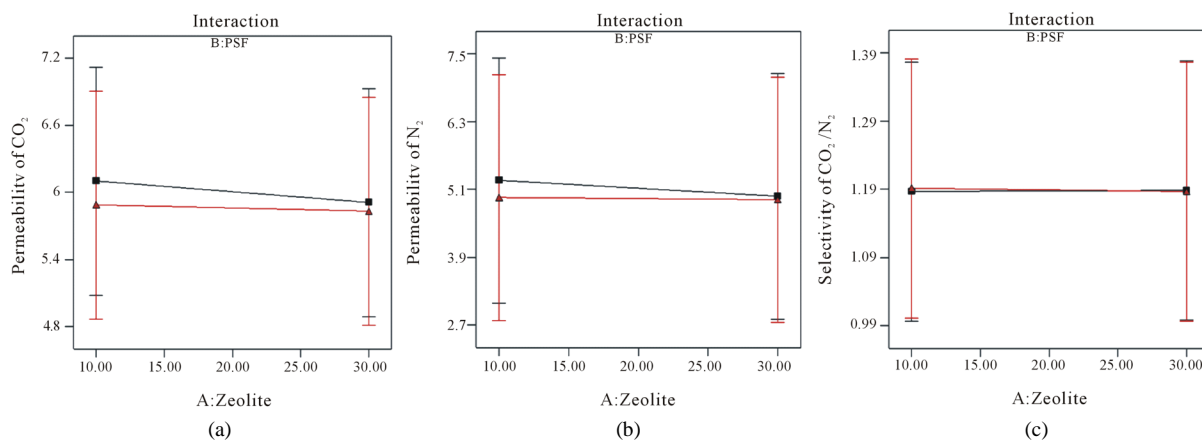


Figure 2. Interaction via concentration of PSf and zeolite for (a) permeability of CO₂; (b) permeability of N₂ and (c) selectivity of CO₂/N₂.

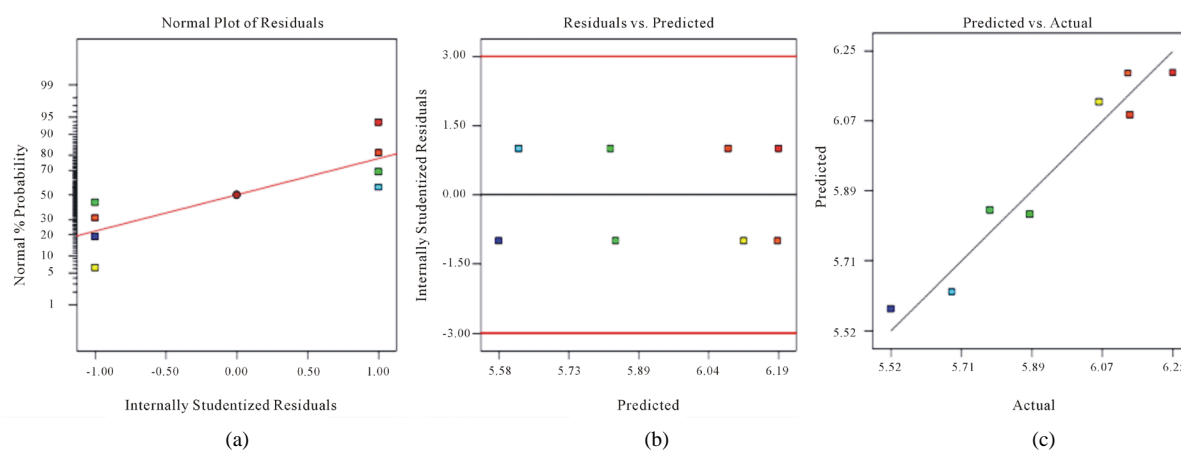


Figure 3. (a) Normal probability plot of residual; (b) Plot of residual versus predicted response and (c) Predicted vs. actual values plot.

Table 5. The model equations for permeability of CO₂, permeability of N₂ and selectivity of CO₂/N₂.

Response	Equation
Permeability of CO ₂	$Y_1 = 5.93 - 0.062A - 0.072B + 0.011C + 0.034AB - 0.15AC + 0.14BC - 0.057ABC$
Permeability of N ₂	$Y_2 = 2.24 - 0.017A - 0.02B - 0.00527C + 0.014AB - 0.033AC + 0.046BC - 0.027ABC$
Selectivity of CO ₂ /N ₂	$Y_3 = -12.63 + 1.37A - 0.38B + 3.38C + 8.88AB - 3.88AC - 3.13BC + 5.13ABC$

Y₁, permeability of CO₂; Y₂, permeability of N₂; Y₃, selectivity of CO₂/N₂; A, concentration of zeolite; B, concentration of PSf; C, concentration of NMP.

equations and coefficients for permeability of carbon dioxide.

4. Conclusion

The polysulfone-zeolite based mixed matrix membranes were fabricated in order to investigate the effect of polymer concentration on the permeability of CO₂ and N₂ as well as selectivity of CO₂/N₂. The polymer mixtures were miscible and formed completely homogenous matrix. In accordance to our expectation, FTIR results revealed that the intensity at 3596.17 cm⁻¹ described the existence of an interaction between polymer and zeolite. Maximum permeability of CO₂ and selectivity of CO₂/N₂ of the membrane were observed at 11.641 GPU and 1.397 respectively. The DOE results revealed that these matrix membranes were affected by the interaction of PSF and NMP to offer higher permeability and acceptance selectivity using ANOVA analysis. The range of screening PSF and zeolite concentration was from 22.30 to 27.45 W/V% for the better selectivity of CO₂/N₂. The model regression equations were developed in Table 5 for screening the permeability of CO₂ and N₂ as well as selectivity of CO₂/N₂ based on the effect of polymer concentration.

Acknowledgements

Thank you for UMP Grant (RDU 130310) for support this research.

References

- [1] Moaddeb, M. and Koros, W.J. (1997) Gas Transport Properties of Thin Polymeric Membranes in the Presence of Silicon Dioxide Particles. *Journal of Membrane Science*, **125**, 143-163. [http://dx.doi.org/10.1016/S0376-7388\(96\)00251-7](http://dx.doi.org/10.1016/S0376-7388(96)00251-7)
- [2] Suer, M., Bac, N. and Yilmaz, L. (1994) Gas Permeation Characteristics of Polymer-Zeolite Mixed Matrix Membranes. *Journal of Membrane Science*, **91**, 77-86. [http://dx.doi.org/10.1016/0376-7388\(94\)00018-2](http://dx.doi.org/10.1016/0376-7388(94)00018-2)
- [3] Hacarlioglu, P., Toppare, L. and Yilmaz, L. (2003) Polycarbonate-Polypyrrole Mixed Matrix Gas Separation Membranes. *Journal of Membrane Science*, **225**, 51-62. [http://dx.doi.org/10.1016/S0376-7388\(03\)00342-9](http://dx.doi.org/10.1016/S0376-7388(03)00342-9)
- [4] Duval, J., Kemperman, A., Folkers, B., Desgrandchamps, G. and Smolders, C. (1994) Preparation of Zeolite Filled

- Gassy Polymer Membranes. *Journal of Applied Polymer Science*, **54**, 409-418. <http://dx.doi.org/10.1002/app.1994.070540401>
- [5] Vu, D., Koros, W. and Miller, S. (2003) Mixed Matrix Membranes Using Carbon Molecular Sieves I. Preparation and Experimental Results. *Journal of Membrane Science*, **211**, 311-334. [http://dx.doi.org/10.1016/S0376-7388\(02\)00429-5](http://dx.doi.org/10.1016/S0376-7388(02)00429-5)
- [6] Mahajan, R. and Koros, W. (2002) Mixed Matrix Membrane Materials with Glassy Polymers. Part II. *Polymer Engineering and Science*, **42**, 1432-1440. <http://dx.doi.org/10.1002/pen.11042>
- [7] Huang, Z., Li, Y., Wen, R., Toeh, M. and Kulprathipanja, S. (2006) Enhanced Gas Separation Properties by Using Nanostructured PES-Zeolite 4A Mixed Matrix Membranes. *Journal of Applied Polymer Science*, **101**, 3800-3805. <http://dx.doi.org/10.1002/app.24041>
- [8] Moore, T. and Koros, W. (2005) Non-Ideal Effects in Organic-Inorganic Materials for Gas Separation Membranes. *Journal of Molecular Structure*, **739**, 87-98. <http://dx.doi.org/10.1016/j.molstruc.2004.05.043>
- [9] Li, Y., Chung, T., Cao, C. and Kulprathipanja, S. (2005) The Effects of Polymer Chain Rigidification, Zeolite Pore Size and Pore Blockage on Polyethersulfone (PES)-Zeolite 4A Mixed Matric Membranes. *Journal of Membrane Science*, **260**, 45-55. <http://dx.doi.org/10.1016/j.memsci.2005.03.019>
- [10] Ritter, J. and Ebner, A. (2007) State-Of-The-Art Adsorption and Membrane Separation Processes for Hydrogen Production in the Chemical and Petrochemical Industries. *Separation Science and Technology*, **42**, 1123-1193. <http://dx.doi.org/10.1080/01496390701242194>
- [11] Bos, A., Punt, I., Wessling, M. and Strathmann, H. (1998) Plasticization-Resistant Glassy Polyimide Membranes for CO₂/CH₄ Separations. *Separation and Purification Technology*, **14**, 27-39. [http://dx.doi.org/10.1016/S1383-5866\(98\)00057-4](http://dx.doi.org/10.1016/S1383-5866(98)00057-4)
- [12] Aroon, M., Ismail, A., Montazer-Rahmati, M. and Matsuura, T. (2010) Morphology and Permeation Properties of Polysulfone Membranes for Gas Separation: Effects of Non-Solvent Additives and Co-Solvent. *Separation and Purification Technology*, **72**, 194-202. <http://dx.doi.org/10.1016/j.seppur.2010.02.009>
- [13] Sridhar, S., Aminabhavi, T. and Ramakrishna, M. (2007) Separation of Binary Mixtures of Carbon Dioxide and Methane through Sulfonated Polycarbonate Membranes. *Journal of Applied Polymer Science*, **105**, 1749-1756. <http://dx.doi.org/10.1002/app.24628>
- [14] Chan, W. and Tsao, S. (2003) Fabrication of Nanofiltration Membranes with Tunable Separation Characteristics Using Methods of Uniform Design and Regression Analysis. *Chemometrics and Intelligent Laboratory Systems*, **65**, 241-256. [http://dx.doi.org/10.1016/S0169-7439\(02\)00141-7](http://dx.doi.org/10.1016/S0169-7439(02)00141-7)
- [15] Gulden, D., Hacarlioglu, P., Toppare, L. and Yilmaz, L. (2001) Effect of Preparation Parameters on the Performance of Conductive Composite Gas Separation Membranes. *Journal of Membrane Science*, **182**, 29-39. [http://dx.doi.org/10.1016/S0376-7388\(00\)00551-2](http://dx.doi.org/10.1016/S0376-7388(00)00551-2)
- [16] Ismail, A., Rahim, R. and Rahman, W. (2008) Characterization of Polyethersulfone/Matrimid®5218 Miscible Blend Mixed Matrix Membranes for O₂/N₂ Gas Separation. *Separation and Purification Technology*, **63**, 200-206. <http://dx.doi.org/10.1016/j.seppur.2008.05.007>
- [17] Jia, M., Peinemann, K. and Behling, R. (1997) Molecular Sieving Effect of the Zeolite-Filled Silicone Rubber Membranes in Gas Permeation. *Journal of Membrane Science*, **57**, 289-292. [http://dx.doi.org/10.1016/S0376-7388\(00\)80684-5](http://dx.doi.org/10.1016/S0376-7388(00)80684-5)
- [18] Montgomery, D. (2001) Design and Analysis of Experiments. John Wiley & Sons, Hoboken.
- [19] Norida, R., Ismail, A. and Abdul Rahman, W. (2004) The Dope Solution Was Placed in a Storage Bottle and Degassed by Using Ultrasonic Bath to Remove Any Trace of Bubbles. *Proceedings of 2nd Reg. Sym. & Workshop of Membr.Sci & Tech.*, 45-54.
- [20] Pal, P., Sikder, J., Roy, S. and Giorno, L. (2009) Process Intensification in Lactic Acid Production: A Review of Membrane Based Processes. *Chemical Engineering and Processing*, **48**, 1549-1559. <http://dx.doi.org/10.1016/j.cep.2009.09.003>
- [21] Ahn, J., Chung, W., Pinnau, I. and Guiver, M. (2008) Polysulfone/Silica Nanoparticle Mixed-Matrix Membranes for Gas Separation. *Journal of Membrane Science*, **314**, 123-133. <http://dx.doi.org/10.1016/j.memsci.2008.01.031>
- [22] Al-Juaied, M. and Koros, W. (2006) Performance of Natural Gas Membranes in the Presence of Heavy Hydrocarbons. *Journal of Membrane Science*, **274**, 227-243. <http://dx.doi.org/10.1016/j.memsci.2005.08.013>
- [23] Marcos, J., Fonseca, L., Ramalho, M. and Cabral, J. (2002) Application of Surface Response Analysis to the Optimization of Penicillin Acylase Purification in Aqueous Two-Phase System. *Enzyme and Microbial Technology*, **31**, 1006-1014. [http://dx.doi.org/10.1016/S0141-0229\(02\)00230-2](http://dx.doi.org/10.1016/S0141-0229(02)00230-2)
- [24] Clarizia, G., Algieri, C., Regina, A. and Drioli, E. (2008) Zeolite-Based Composite PEEK-WC Membranes: Gas Transport and Surface Properties. *Microporous and Mesoporous Materials*, **115**, 67-74. <http://dx.doi.org/10.1016/j.micromeso.2008.01.048>

- [25] Julian, H. and Wenten, I. (2012) Polysulfone Membranes for CO₂/CH₄ Separation: State of the Art. *IOSR Journal of Engineering*, **2**, 484-495. <http://dx.doi.org/10.9790/3021-0203484495>
- [26] Scervini, M. (2009) Thermoelectric Materials for Thermocouples. Department of Material Science and Metallurgy, University of Cambridge, Cambridge.
- [27] Huntzinger, D. and Eatmon, T. (2009) A Life-Cycle Assessment of Portland Cement Manufacturing: Comparing the Traditional Process with Alternative Technologies. *Journal of Cleaner Production*, **17**, 668-675. <http://dx.doi.org/10.1016/j.jclepro.2008.04.007>
- [28] LeVan, M. (1995) Pressure Swing Adsorption: Equilibrium Theory for Purification and Enrichment. *Industrial and Engineering Chemistry Research*, **34**, 2655-2660. <http://dx.doi.org/10.1021/ie00047a014>
- [29] Silverstein, R., Bassler, G. and Morrill, T. (1981) Spectrometric Identification of Organic Compounds. 4th Edition, John Wiley and Sons, New York.

Symbols

P : permeability GPU
 A : effective membrane area cm²
 T : temperature °C
 T_g : glass transition temperature °C
 M : molecular weight of the gas
 x_i : mole fraction of gas component i in the feed side
 y_i : mole fraction of gas component i in the permeate side
 Δp : trans membrane pressure difference Bar
 ρ : density of the gas

Greek Letters

δ : membrane thickness μm
 α : selectivity

Subscripts

DOE: Design of experiment
DPE: Diphenyl ether
FTIR: Fourier transform infrared
GC: Gas chromatograph
MMM: Mixed matrix membrane
NMP: N-methyl-2-pyrrolidone
PSf: Polysulfone