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ORIGINAL PAPER

Optimization of parameters affecting separation of gas mixture of O_2, N_2, CO_2 and CH_4 by PMP membrane modified with TiO_2, ZnO and Al_2O_3 nanoparticles

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ABSTRACT

The application of membranes in various industries is one of the most urgent needs to reduce energy consumption and environmental pollutants as well as low investment costs in the process of separation. In this investigation, the optimization of effective parameters for separation of gas mixture of CH_4, CO_2, O_2 and N_2 is studied by modified poly(4-methyl-1-pentane) (PMP) membrane including nanoparticles (TiO_2, ZnO, Al_2O_3). Design expert software was used and prevailing data on membrane modeling were categorized according to the process variables such as permeability, selectivity, composition and percentage of nanoparticle, and gas pressure difference. In order to validate the model, the results predicted by the model were compared with the experimental data. Good agreement was observed between the predicted and experimental data, and it was found that nanoparticles have a considerable effect on the results. In the case of gas permeability, the best results were obtained for the nanoparticles of alumina (15 wt%) at the pressure of 3 bar. However, titanium dioxide nanoparticle (10 wt%) at the pressure of 9 bar showed the best results for gas selectivity. The optimum point for both permeability and selectivity was obtained for the membrane containing 10 wt% titanium dioxide at 5 bar. **Polyolefins J (2020) 7: 13-24**

Keywords: Poly(4-methyl 1-pentane), Permeability, Selectivity, Titanium dioxide, Aluminum oxide.

INTRODUCTION

In recent years, gas separation is progressively performed by separation methods such as absorption, adsorption, and cryogenic distillation by novel technologies like membrane systems [1-4]. Industries continually are looking for a new method to reduce environmental pollution, reduce energy consumption and lower investment costs, so the approach has changed to use membranes in industries such as natural gas sweetening [5]. Over the past decade, this technology showed an immense growth compared to the conventional gas separation processes [6]. The matter of gas separation has been verified in several professions and many applications [7,8]. The advantages of membrane separation processes such as lower energy requirements,

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compact structure, lower operating and maintenance cost, ease of processing and also the least impact on the environment cause to gain interest in various industries [9,10]. Hassanajili et al. studied the efficacy of metal nanoparticles on the separation of CH_4 and CO_2 pure gases for two nanocomposite membranes of polyesters. The net gas permeability test illustrates that the permeability improves along with the rising silica content. This might be related to the increase in the free volume of the polymer network caused by the separation of the molecular chain [11]. Also, they investigated the property of mixed component of PMP and silica particles in the separation of n-C_4H_{10}/CH_4. Results of their research showed that pure PMP membrane has different gas permeability properties compared to PMP/silica compound. Adding the silica in the PMP polymer matrix resulted in gas permeability and selectivity of n-C_4H_{10}/CH_4 enhancement. Selectivity of n-C_4H_{10}/CH_4 was 13 for the pure PMP and the selectivity for the PMP filled with 45 wt% silica increased to 26. Furthermore, the permeability of n-C_4H_{10} increased about 3 to 4 times compared to the pure PMP [12]. Abedini et al. investigated the separation and purification of hydrogen with embedding MIL53 particles on PMP mixed matrix membranes (MMMs). Their results showed that solubility of hydrogen compared to CO_2 decreased significantly with increasing the MIL53 particle in PMP matrix. Increasing of feed pressure and the embedding of nanoparticles increase the CO_2/H_2 selectivity and permeability of CO_2 [13].

The result of functionalized NH_2-MIL45 particles on the features of PMP in the separation of CO_2/CH_4 was investigated separately in another research by Abedini et al. According to these results, by increasing particle loading in the polymer matrix, an enhancement occurred in the permeability of CO_2. Moreover, CO_2/CH_4 selectivity was enhanced considerably [14]. In fact, among the known polymers in gas separation processes, PMP has the superior permeability of pure hydrocarbons [15] and therefore PMP is introduced as a proper material to fabricate dense homogeneous membranes for gas separation. Pechaf et al [16] have studied the combination of polyimide and zeolite as a polymer membrane. For this object, they prepared a mixed network membrane made up of polyimide and 20 wt% zeolite and then analyzed the permeability data for gases including O_2, CO_2, N_2, and CH_4. The permeability of N_2 and O_2 gases decreased, but it increased for CH_4 and CO_2. This change in permeability is strongly influenced by the changes in the permeability coefficient. Matteucci et al studied the permeability of CH_4, N_2 and CO_2 by adding TiO_2 nanoparticles to poly (1-trimethylsilyl-1-propyne) (PTMSP). Results showed that permeability of these gases increased more than 4 times in comparison with the pure polymer [17]. Also, they studied the effect of TiO_2 nanoparticles on 1, 2-polybutadiene (PB) in another research. Obtained results showed that in a membrane containing 27 vol.% TiO_2 nanoparticles, permeability coefficients of CO_2, CH_4, N_2 ,and H_2 gases increased 3 times in comparison with the pure polymer. Furthermore, the solubility coefficient of the gases increased by adding the nanoparticles to the polymer, while the permeability coefficients decreased by addition of the nanoparticles [18].

Statistical modeling has been utilized as a method to evaluate the effect of various variables including adding nanoparticles zinc oxide (ZnO), aluminum oxide (Al_2O_3), titanium dioxide (TiO_2) to PMP membrane on both structural characteristics of the membranes and performance of the polymeric membranes. Furthermore, a statistical method was employed in a previous work to research and optimize permeability and selectivity on the polymer membranes for the gas separation [19]. Experimental data for permeability and selectivity of different gases for several polymer membranes are summarized in Table1.

According to the above-mentioned parameters that can affect the membrane properties and the problems involved in high-performance membranes, the main objective of this study is to investigate the percentage of ZnO, Al_2O_3 and TiO_2 nanoparticles added to PMP membrane for evaluating the effect of nanoparticle type and its percentage on improvement of the gas permeation and separation performance in the mixed matrix membranes. Moreover, another aim of this study is to use the design expert software to identify the influences of the experimental variables to reach optimal conditions for high-performance mixed matrix membranes (MMMs) made from PMP membrane. The permeability and selectivity of CH_4, N_2, O_2, and

Table 1. Experimental data for permeability and selectivity of different gases for several polymer membranes.

Ref	years	Filler	Particle size/nm	Pore Size/nm	Loding/wt%	Polymer	Feed gas	Operation Conditions	CO_2 permeability x10[14]/ Mol.M.M[-2].S[-1] Pa[-1]	CO_2/N_2 selectivity	CO_2/CH_4 selectivity	CO_2/H_2 selectivity
20	2012	PANI	Thickness:40-60	-	17	PVAM	CO_2/N_2 (20:8 V/V)	25°C, 0/11Mpa in	40.20	120	-	-
21	2013	ZIF-8	<80	-	20	6FDA-Dure	CO_2/CH_4 (50:50 Mol/Mol	humidified stated	24.39	-	19.61	-
22	2015	PANI nanorod	Diameter: 30	-	17	Ne/DABA	CO_2/N_2 (15.85 V/V)	state	53.67	240	-	-
23	2014	MEL-S_3	Length:160	0.91	30	(9/1)	Pure gas	35 °C, 0/2 Mpa	12.64	-	-	24.96
24	2014	ZIF-8	100	-	5,10,15,20,25,30,35	PVAM	Pure gas	25°C, 0/11Mpa in	12.23-43.11	29.6-32.3	8.1-9.0	-
25	2014	MW-NH_2-MI	-	-	8,15,25,	PMP	CO_2/CH_4 (1:1)	humidified stated	~0.18~0.28	-	~24~29.0	-
26	2015	L-I01 (AL)	~1000	-	8,15	Pebax	CO_2/CH_4 (1:1)	state	~0.35, 0.32	-	35,~36	-
27	2015	CU-BTC-S_1	13000	-	10	PSF		30 °C, 0.8 Mpa	~2.85	~18.5	~23.5	~1.0
28	2015	CU-BTC-S_2	6000	-	10	Matrimid	Pure gas	25 °C, 0.2 Mpa	~2.88	~23.5	~28.5	~1.0
29	2015	NH_2-MIL-125 (Ti)	Lenth1000	-	40,20,30	PPO	Pure gas	35°C, 0.3 Mpa	0.62-1.34	-	28.3-29.2	-
30	2015	H-ZIF-8	Width: 500	0.96	10,20,30	PPO	$CO_2:CH_4$Mol/Mol	30 °C	5-70-20.87	-	12.2-11.2	-
31	2015	Sod-ZMOF	721±36	1.54	5,10,20	PSF	Pure gas	30 °C	0.23-0.46	-	36.6-43.4	-
32	2015	Inorganic/ CSM-	2000~20000	-	30	PVC-g-POE	$CO_2:CH_4$	30°C, 0.3 Mpa	1.32	38.1	-	-
33	2015	18.4	~520±140	-	20	M	CO_2/N_2	35 °C	0.28	61.24	20	-
34	2015	PEGSS	350-420	-	5,10,15,20	Matrimid	Pure gas	(50:50 35°C, 0.4 Mpa)	29.82-67.87	36-85	5,10,15,20	-
35	2016	CANs	900	0.6	5, 10, 15, 20	Matrimid	Pure gas	35°C, 0.9 Mpa (50:50,	9.56-9.39	43-52	5,10,15,20	-
36	2016	NHs	~250	-	10	Matrimid	Pure gas	V/V)	4.68	61.1	-	-
37	2016	Uio-66	60-80	-	16.67	Pebax	CO_2/N_2 (50:50 V/V)	30°C, 0.1Mpa	334.06	20.27	16.67	-
38	2016	HCP	0.6	1.08	6	Matrimid	Pure gas	25°C, 0.2 Mpa	8.30	47.6	6	-
		ZIF-8@G0-6	55	-	10,15,20	Pebax	Pure gas	30°C, 0.2 Mpa in	314.90-712.51	21.2-28.7	14.3-19.2	-
		MoF-74	-	-	15,30		Pure gas	humidifeid stated state	0.60,0.90	-	44.37	-
		MIL-25	10000-15000		15,30	PIM-1	$CO_2:CH_4$ (Mol/Mol)	25°C, 0.3	0.57-1.68	-	50,37	-
		NH_2-MIL-25	1500-2000			Pebax	$CO_2:CH_4$ (Mol/Mol)	Mpahamidified stated				
			<1500-2000			PIM-I		state				
						Matrimid		25°C, 0.2 Mpa				
						Matrimid		25°C, 0.1Mpa				
								25 °C, 0.2 Mpa				
								(50:50, 0.9Mpa)				
								(50:50, 0.9Mpa)				

CO_2 gases have been studied in order to investigate the specifications in the employed PMP membrane by nanoparticles. These experiments were also optimized and modeled for the industrial applications in gas separation.

EXPERIMENTAL

Methodology

PMP with low molecular weight (Sigma Aldrich) was used as the membrane in the background phase, while the nanoparticles ZnO, Al_2O_3, TiO_2 added to PMP membrane as mineral modifiers were purchased from Aldrich Chemical Company (Milwaukee, USA). The average size of the used nanoparticles was 20-30 nm, while they have been used in various contents from 5-15%. The permeability of pure gases including N_2, O_2, CH_4, and CO_2 was measured in a pure membrane and PMP membrane modified with the nanoparticles. Eq. (1) is used to calculate gas permeability:

$$P = \frac{ql}{(P_1 - P_2)A} \quad (1)$$

where P is the gas permeability, q is the flow rate of permeate gas, l is the membrane thickness, P_1-P_2 is the pressure drop in the membrane, and A is the permeation area. The selectivity of the gas pairs was calculated by dividing the ratio of the gas permeability. Eq 2 is used to evaluate the ratio of selectivity of gas A to gas B.

$$S_{A/B} = \frac{P_A}{P_B} \quad (2)$$

Where $S_{A/B}$ is selectivity, P_A is gas A permeability and P_B is gas B permeability.

Statistical analysis and design expert

The design expert software (Version 7.0.0, 2005) has been used for evaluation of the equation coefficients and data regression analysis. Design expert is a software for designing of experiments, modeling, evaluating the effects of different variables and finding the optimized conditions to get a response. For this object, design expert has been applied for designing of the experiments and statistical analysis, in order to prepare an effective model. For the purpose of statistical calculations, experimental variables of Y_{actual} in the frame of Y_{coded} have been coded on the basis of the following equation:

$$Y_{coded} = \frac{Y_{actual} - \bar{Y}}{\Delta Y} \quad (3)$$

Y_{coded} is the coded (dimensionless) amount of the variables (Y_{actual}), $\bar{Y}$ is the average amount (Y_{actual}) and "ΔY" gives the difference between $\bar{Y}$ and Y_{actual}.

Eq. 4 is the response as a function of variables with multiple regression applications using the least square method.

$$F = A_0 + A_1Y_1 + A_2Y_2 + A_3Y_3 + A_4Y_4 + A_{12}Y_1Y_2 + A_{13}Y_1Y_3 + \ldots \quad (4)$$

This ploynominal equation is necessary for the purpose of modeling because the encoding method enables execution of the same. In this research, for modeling of the gas selectivity and permeability in the PMP-modified membranes a general function with optimization design was used, since the independent variables are identified as:

Y_1= type of polymer,
Y_2= percentage of polymer
Y_3= type of nanoparticle
Y_4 = percentage of nanoparticle

Interactions and combinations of the domain variables are some of the important advantages of experimental design method in comparison to the classic statistical approach. In addition, components selectivity of CO_2/CH_4 $S_{(CO_2/CH_4)}$, N_2/CH_4 $S_{(O_2/N_2)}$, O_2/N_2 $S_{(O_2/N_2)}$, and CO_2/N_2 $S_{(CO_2/N_2)}$ and components permeability of O_2 (P_{O_2}), CH_4 (P_{CH_4}), CO_2 (P_{CO_2}), and N_2 (P_{N_2}) were taken as the responses of the function. Table 2 shows four important variables that applied in this analysis with their levels and relevant types and also the variables of PMP polymer and nanoparticle type in dimensionless form (constant and definite). Also, standard analysis has been done for analyzing the model and curve production. The most appropriate polynominal model has been selected with significant amounts ($p<0.05$), with use of design expert software obtained the R^2, CV and appointed multiple correlation coefficient (appointed R^2).

RESULTS AND DISCUSSION

To evaluate polymer modification with nanoparticles, design expert software is used and the results of the model, as well as permeability, selectivity and then optimization of operational conditions, are discussed.
Permeability results for different gasses
The permeability models for different gasses using design expert software are as following:
a) Permeability models for TiO_2 nanoparticles as a function of nanoparticle percentage and gas pressure.

$$P_{O_2} = 6.41 - 1.91X_4 - 0.013P - 5.32\times10^{-3} P\times X_4 + 0.018X_3 - 7.83\times10^{-3} P^2 - 0.01\times X_4^2 - 0.016\times X_4\times P$$

$$P_{N_2} = 106.55 + 19.27X_4 - 1.07P\times X_4 - 1.24X_4 - 0.3P^2 - 1.52\times10^{-3} X_4^2 - 2.91X_4\times P$$

$$P_{CO_2} = 127.39 - 112.4X_4 + 0.8P - 1.06\times P\times X_4 - 0.093P^2 - 0.087X_4^2 - 1.83X_4\times P$$

$$P_{CH_4} = 29.82 - 8.3X_4 + 0.13P - 0.4X_4 - 4.57\times10^{-3}\times X_4 - 0.1X_4^2 + 0.36P^2 - 0.11P\times X_4$$

b) Permeability models for Al_2O_3 nanoparticles as a function of nanoparticle percentage and gas pressure.

$$P_{O_2} = 604 + 1.08X_4 + 0.013P - 5.32\times10^{-3}\times P\times X_4 + 0.018X_3 - 7.83\times10^{-3}\times P^2 - 0.01X_4^2 - 0.016\times X_4\times P$$

$$P_{N_2} = 106.55 + 31.38X_4 - 1.07P\times 3.019\times P\times X_4 - 1.24X_4 - 0.3P^2 - 1.52\times10^{-3}\times X_4^2 - 2.91\times X_4\times P$$

Table 2. Variables types and their levels of factorial experiments design matrix.

Variable	Level		
	Type	Actual	Coded
Type of polymer	X_1	PMP	{ 1 }
Percentage of polymer	X_2	3%	{ 1 }
Type of nanoparticle	X_3	TiO_2 AL_2O_3 ZnO	{ 0 } { 1 } {- 1 }
Percentage of nanoparticle	X_4	5 10 15	1 0 -1

$$P_{CO_2} = 127.39 - 65.35X_4 + 0.8P - 1.06\times P\times X_4 - 2.7\ X_4 - 0.093\times P^2 - 0.87\times X_4^2 - 1.83\times X_4\times P$$

$$P_{CH_4} = 29.82 - 0.21X_4 + 0.13\times P - 0.4\times X_4 - 4.57\times10^{-3}\times X_4\times - 0.1\times X_4^2 + 0.36P^2 - 0.11\times X_4\times P$$

c) Permeability models for ZnO nanoparticles as a function of nanoparticle percentage and gas pressure.

$$P_{O_2} = 6.4 + 1.93X_4 + 0.013P - 3.321\times10^{-3} P\times X_4 + 0.018X_3 - 7.83\times10^{-3} P^2 - 0.01X_4 - 0.016X_4\times P$$

$$P_{N_2} = 106.55 + 24.05X_4 - 1.07P - 3.19P\times X_4 - 1.24X_4 - 0.3P^2 - 1.52\times10^{-3}\times X_4^2 - 2.91\times X_4\times P$$

$$P_{CO_2} = 127.39 - 51.27X_4 + 0.8P - 1.06P\times X_4 - 2.7\ X_4 - 0.093P^2 - 0.87X_4^2 - 1.83X_4\times P$$

$$P_{CH_4} = 29.82 - 0.15X_4 + 0.13P - 0.4X_4 - 4.57\times10^{-3} P\times X_4 - 0.1X_4^2 + 0.36P^2 - 0.11X_4\times P$$

Table 3 shows the model data of different conditions and response of the gases to the different amounts of variables; the permeability of the pure gases show that with increasing the volume fraction of added nanoparticles, gases permeability increases. However, gas permeability is depended on the amount of nanoparticles, because some effective parameters of the gases such as solubility and molecular size are different from each other. In such a way, the permeability of the gas molecules with smaller kinetics diameter has been greater than that of the larger molecules, because the permeability is the dominant parameter in the polymeric membranes and synthetic network. It can be seen that the addition of nanoparticles to the membrane has increased the gas permeability since it is known as an effective factor in the improvement of membrane permeability.

As the table shows, maximum values of permeability for O_2, N_2, CO_2 and CH_4 are equal to 92.5, 30, 350 and 48 barrer, respectively, in PMP membrane modified with 15 % of Al_2O_3 at the pressure of 9 bar. Figures 1 and 2 show combined effects of the percentage of nanoparticle and pressure on CO_2 and O_2 permeability.

As shown in these figures, by increasing the pressure and percentage of nanoparticles, permeability is increased in the PMP membrane. Moreover, the

Table 3. Membrane permeability and gas separation under different conditions.

Number	Nano particle	Nano%	Pressure (bar)	O_2	N_2	CO_2	CH_4
1	TiO_2	5	9	19.5	16.2	31	22.07
2	TiO_2	5	3	13	5	22	13.5
4	TiO_2	5	5	18	15	28.50	19.55
3	ZnO	8	3	48.5	26	140.50	35
5	ZnO	2.5	3	48.5	25.55	100	35.25
6	ZnO	8	5	50	26	200	36.50
7	Al_2O_3	8	3	30	10	110	18
8	TiO_2	8	2	18.55	15.55	49.55	21.55
9	Al_2O_3	15	9	92.5	30	350	48
10	TiO_2	8	9	27	22	34	29
11	Al_2O_3	10	9	86.25	38.57	250	45
12	Al_2O_3	2.5	5	40	15	160	21
13	Al_2O_3	2.5	9	43	17.33	165	25
14	Al_2O_3	2.5	3	35.52	16	115	19.55
15	Al_2O_3	15	5	75.25	20	299.52	40.68
16	Al_2O_3	8	9	98.50	25	34.8	49.55
17	Al_2O_3	5	5	59.66	17	18.01	30
18	Al_2O_3	2.5	3	35.67	11.57	115.50	18.50
19	ZnO	2.5	9	39.50	25	145.50	28.50
20	ZnO	5	9	49.55	20.22	197	35.55
21	ZnO	15	3	50	25	150	28.55
22	ZnO	10	5	50	26	165	35
23	ZnO	5	5	54	25	200	39
24	ZnO	15	9	70.25	27	335	49.52
25	ZnO	8	9	60.55	27.55	235.52	40
26	ZnO	10	9	62	30	252	45
27	TiO_2	15	25	30	21	42.55	34
28	TiO_2	15	20	26	17.50	39	29
29	TiO_2	15	3	19	10	30	22
30	ZnO	15	4	87	15	249	35
31	Al_2O_3	10	9	85	20	259	47
32	Al_2O_3	10	3	48	20	150	38
33	ZnO	5	3	39.55	17	110	29.52
34	ZnO	15	5	53	25	248.52	40
35	ZnO	2.5	5	40	17	152	22
36	TiO_2	2.5	9	18.55	10	29	18
37	Al_2O_3	8	3	17.52	10	30	15
39	Al_2O_3	15	3	51.25	22	185.55	45
40	Al_2O_3	10	4	51	22	198	30
41	TiO_2	10	5	22	18	25	26

nanoparticles in contrast to the pressure also show higher values. This means that at constant pressure, increasing the nanoparticle content can increase the gas permeability. If the percentage of specific nanoparticle increases, with the increase of gas permeability, the pressure in the PMP membrane also shows a relative increase.

Figure 3 illustrates the combined effects of percentage of the nanoparticle and precursor on CO_2/CH_4 selectivity with the average material (actual factor). As shown in Figure 3, by increasing the pressure and nanoparticle content, selectivity increases in the PMP membrane. Similar to permeability in selectivity, nanoparticles in contrast to the pressure shows higher values as well. This means that at constant pressure, increasing of the nanoparticle content causes to increase the value of gas selectivity. If the percentage of specific nanoparticle increases with the increase of gas selectivity, the pressure in the PMP membrane again shows a relative increase. The results of both permeation and selectivity of PMP/nanoparticle show that addition of nanoparticle can enhance gas permeability and selectivity for PMP.

Figures 4 to 7 illustrate an adaption between the data obtained from the experimental data and gas permeation models for different gases (O_2, N_2, CO_2 and

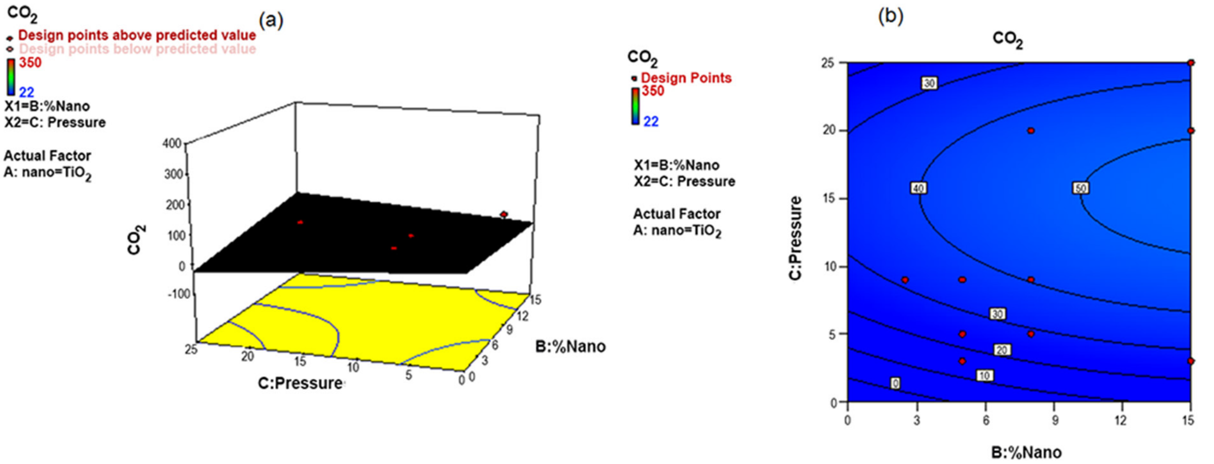

Figure 1. Effects of combined pressure and nanoparticle percentage on CO_2 permeability (a) surface plot and (b) contour plot.

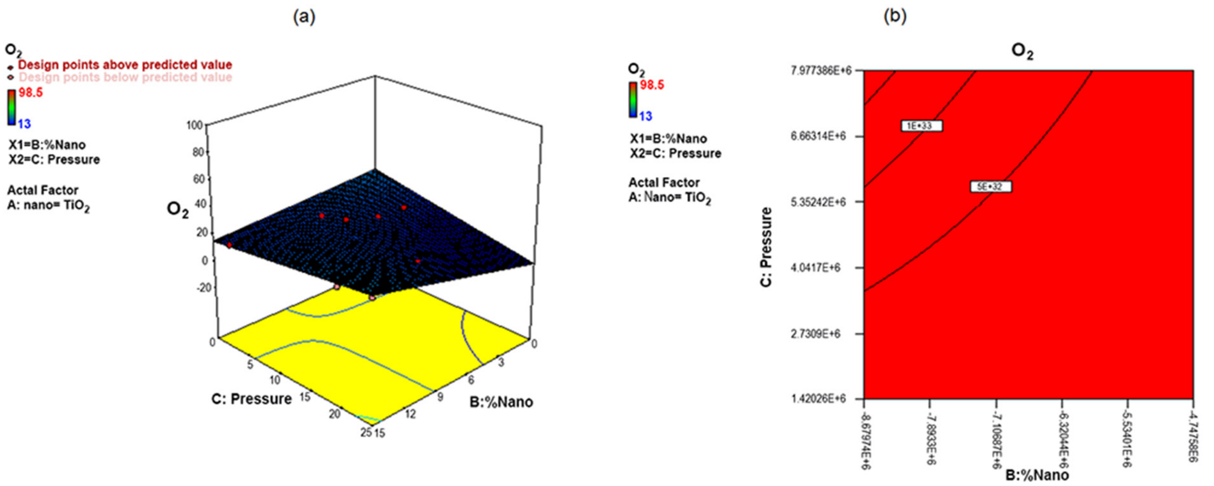

Figure 2. Effects of combined pressure and nanoparticle percentage on O_2 permeability; (a) surface plot and (b) contour plot.

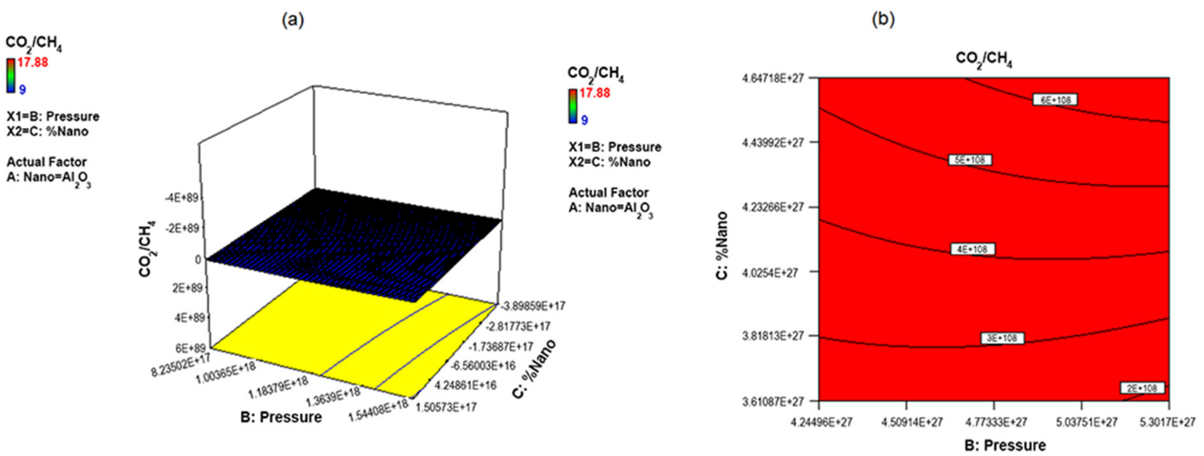

Figure 3. The combined effects of percentage of nanoparticle and precursor on CO_2/CH_4 selectivity with average material (actual factor); (a) surface plot and (b) contour plot.

CH_4), and a good agreement between the models and experimental data can be seen. These figures show a good conformity between the data obtained from the experimental amounts and those estimated from the gas transport models for both permeability and selectivity of gasses in the optimized condition.

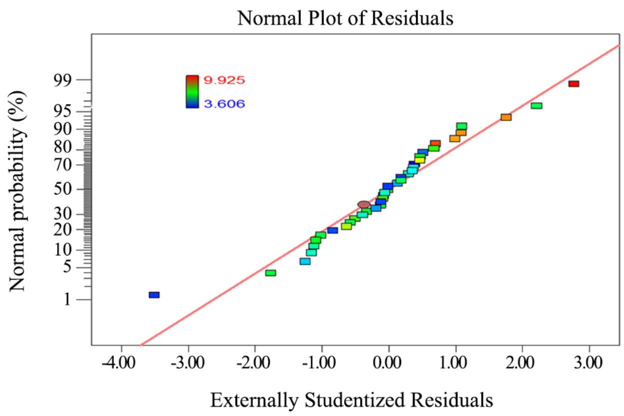

Figure 4. Comparison between observed and estimated responses for O_2.

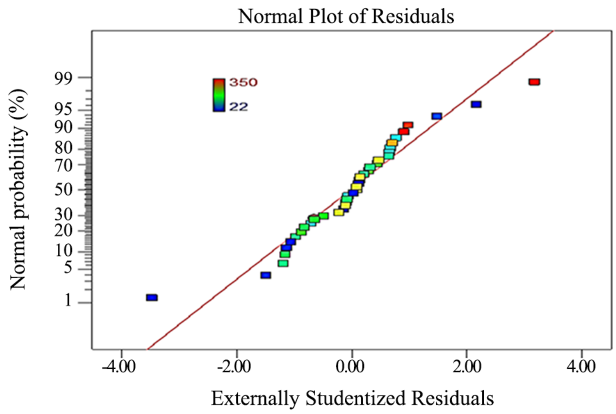

Figure 6. Comparison between observed and estimated responses for CO_2.

Selectivity results for different gases

The selectivity models for different gases using design expert software are as following:

a) Selectivity models for TiO_2 nanoparticles as a function of nanoparticle percentage and gas pressure.

$$S_{\frac{O_2}{N_2}} = 18.8 - 0.41P - 0.048X_4 + 0.088P \times X_4 + 0.04P^2 - 3.39 \times 10^{-3} X_4^2 - 0.00621P^2 \times X_4$$

$$S_{\frac{CO_2}{N_2}} = 34.97 + 3.61P - 2.19X_4 + 0.95P \times X_4 + 0.002P^2 - 0.011X_4^2 - 0.06P^2 \times X_4$$

$$S_{\frac{CO_2}{CH_4}} = 48.63 - 0.12P - 3.54X_4 + 1.15P \times X_4 + 0.0088P^2 - 0.32X_4^2 - 0.003P^2 \times X_4$$

b) Selectivity models for Al_2O_3 +nanoparticles as a function of nanoparticle percentage and gas pressure.

$$S_{\frac{O_2}{N_2}} = 6.7 - 0.046P - 0.048X_4 + 0.088P \times X_4 + 0.0026P^2 - 0.0039X_4^2 - 0.0062P^2 \times X_4$$

$$S_{\frac{CO_2}{N_2}} = 23.37 + 0.11P - 2019X_4 + 0.958P \times X_4 + 0.0020P^2 - 0.011X_4^2 - 0.06P^2 \times X_4$$

$$S_{\frac{CO_2}{CH_4}} = 34.64 - 0.31P - 3.54X_4 + 2.15P \times X_4 + 0.00881P^2 - 0.011X_4^2 - 0.06P^2 \times X_4$$

c) Selectivity models for ZnO nanoparticles as a function of nanoparticle percentage and gas pressure.

$$S_{\frac{CO_2}{CH_4}} = 21.02 - 0.12P - 3.54X_4 + 2.15P \times X_4 + 0.0088P^2 - 0.32X_4^2 - 0.003P^2 \times X_4$$

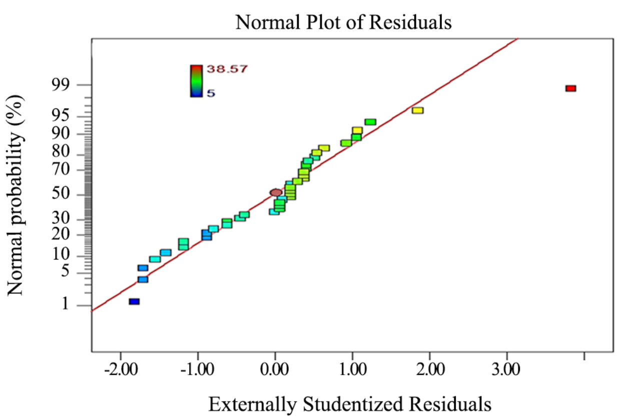

Figure 5. Comparison between observed and estimated responses for N_2.

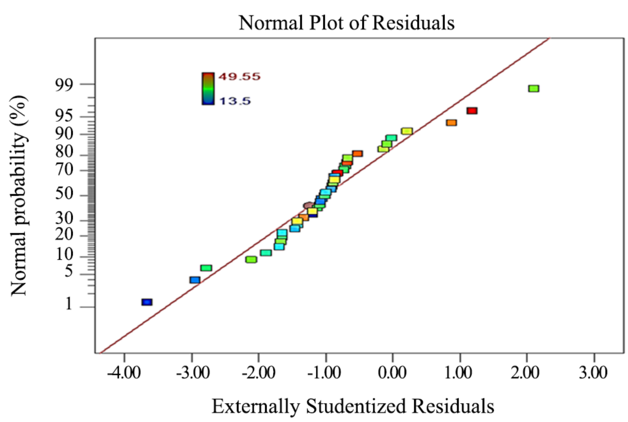

Figure 7. Comparison between observed and estimated responses for CH_4.

Table 4. Effect of the different variables (percentage and type of nanoparticles, pressure) on gas selectivity of the modified PMP membrane.

Number	Pressure (bar)	Nano (%wt)	Nano Type	$CO2/N_2$ (-)	$CO2/CH_4$ (-)	O_2/N_2 (-)	Number	Pressure (bar)	Nano (%wt)	Nano Type	$CO2/N_2$ (-)	$CO2/CH_4$ (-)	O_2/N_2 (-)
1	3	10	TiO_2	46.7	16.83	19.2	**35**	7	30	Al_2O_3	57	15	12
2	4	10	TiO_2	50	17.12	19.53	**36**	7	10	Al_2O_3	36	10.2	8.5
3	5	10	TiO_2	67.7	21.26	19.96	**37**	7	15	Al_2O_3	45	15	9.85
4	7	10	TiO_2	77.7	22.21	20	**38**	7	0	ZnO	25	9.2	7.2
5	8	10	TiO_2	79.95	23	20.2	**39**	7	2.5	ZnO	26	10	8.85
6	9	10	TiO_2	80.2	33.98	20.6	**40**	7	5	ZnO	26.75	9.2	7.2
7	3	0	ZnO	24.9	8.5	6.75	**41**	7	8	ZnO	33.92	10.2	7.98
8	3	2.5	ZnO	24.93	8.88	6.2	**42**	7	10	ZnO	34.95	11.2	8.95
9	3	5	ZnO	24.97	8.95	7.2	**43**	7	15	ZnO	39.2	12.56	9.97
10	3	8	ZnO	24.97	9.8	6.9	**44**	3	0	Al_2O_3	25.2	10	7.2
11	3	8	ZnO	25.55	8.4	6.98	**45**	9	20	Al_2O_3	50	12.3	9.85
12	3	10	ZnO	25.52	9.2	8.2	**46**	9	5	Al_2O_3	29	9.2	7.7
13	3	15	ZnO	27.3	10.3	9.2	**47**	9	30	Al_2O_3	57	15	10.2
14	4	0	ZnO	24.4	9.5	7.3	**48**	9	10	Al_2O_3	35	12.3	8.99
15	4	2.5	ZnO	25.2	9.3	7.4	**49**	9	15	Al_2O_3	44.2	14	9.2
16	4	5	ZnO	25	9	7.9	**50**	9	0	ZnO	24.98	9.50	7.3
17	4	8	ZnO	28.2	9.4	8.5	**51**	9	2.5	ZnO	27.2	9.92	77
18	4	10	ZnO	29.2	10	8.85	**52**	9	5	ZnO	26.2	9.9	7.8
19	4	15	ZnO	30.2	11.1	9.2	**53**	9	8	ZnO	31	10.95	8.95
20	5	0	Al_2O_3	24.2	9.2	7.2	**54**	9	10	ZnO	36	11.95	8.2
21	5	20	Al_2O_3	40	12	10.2	**55**	9	15	ZnO	40	11	9.2
22	5	5	Al_2O_3	27.2	9.85	7.5	**56**	10	0	Al_2O_3	24.59	8.5	6.3
23	5	30	Al_2O_3	45	10.2	10.2	**57**	10	20	Al_2O_3	45	12.3	10.2
24	10	5	Al_2O_3	30	10.2	8.5	**58**	10	5	Al_2O_3	29.7	8.7	6.9
25	5	15	Al_2O_3	36	12.3	9.5	**59**	10	30	Al_2O_3	54.2	12.5	10.3
26	5	0	ZnO	24.98	8.95	7.2	**60**	10	10	Al_2O_3	33.55	9.88	6.8
27	5	2.5	ZnO	25.2	9.4	7.3	**61**	10	15	Al_2O_3	41.2	12.2	9.8
28	5	5	ZnO	25	9.95	7.5	**62**	10	0	ZnO	24.2	9.95	7.82
29	5	8	ZnO	29.92	10.2	8.2	**63**	10	2.5	ZnO	26.2	8.2	8.4
30	5	10	ZnO	31.2	9.8	7.98	**64**	10	5	ZnO	27.2	9.2	8.3
31	5	15	ZnO	34.95	11.2	9.56	**65**	10	8	ZnO	31	10.2	8.4
32	7	5	Al_2O_3	25.4	10.3	7.5	**66**	10	10	ZnO	35	11	8.9
33	7	20	Al_2O_3	48	12	10.2	**67**	10	15	ZnO	39.98	11.2	9.9
34	7	5	Al_2O_3	28.2	10.3	8.2							

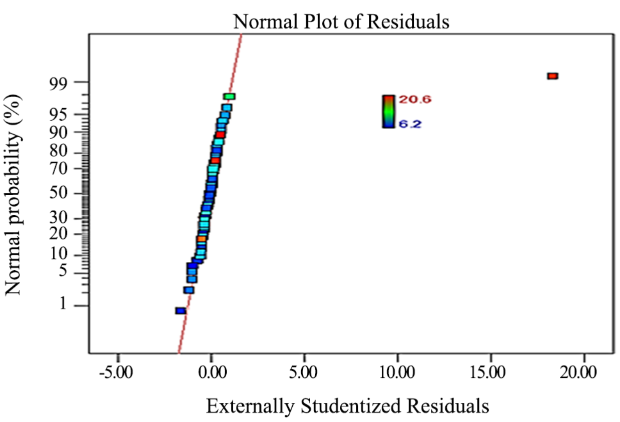

Figure 8.Comparison between observed and estimated responses for O_2/N_2 selectivity.

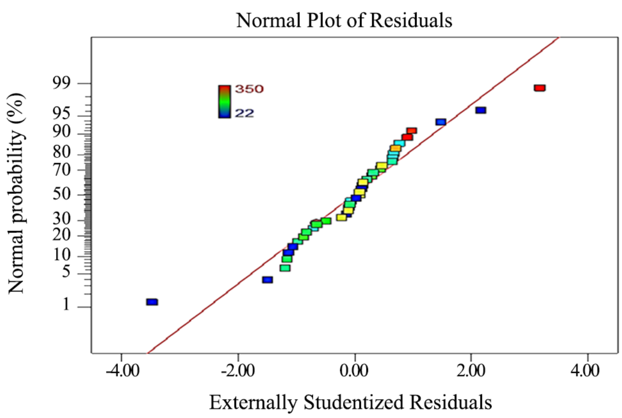

Figure 9.Comparison between observed and estimated responses for CO_2/N_2 selectivity.

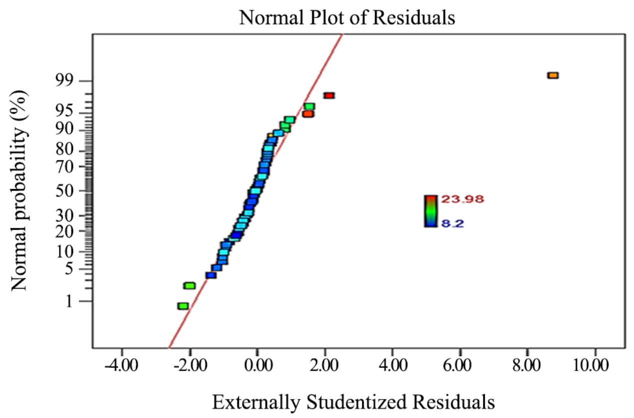

Figure 10.Comparison between observed and estimated responses for CO_2/CH_4 selectivity.

$$S_{\frac{O_2}{N_2}} = 4.2 + 0.935P - 0.048X_4 + 0.088P \times X_4 - 0.064P^2 - 0.00339X_4^2 - 0.0\ 62P^2 \times X_4$$

$$S_{\frac{CO_2}{N_2}} = 25.62 - 0.31P - 2.19X_4 + 0.95P \times X_4 + 0.00202P^2 - 0.011X_4^2 - 0.06P^2 \times X_4$$

Table 4 shows the model data and response of the different gas selectivity to the different amounts of variables (pressure and type and content of nanoparticle). It can be seen that the addition of the nanoparticles to the membrane has increased the gas selectivity since it is known as an effective factor in the improvement of the membrane selectivity. As the table shows, in PMP membrane modified by 10% TiO_2 at the pressure of 9 bar, the maximum values of selectivity for CO_2/N_2, CO_2/CH_4 and O_2/N_2 are 80.2, 23.98 and 20.6 barrer, respectively.

Figures 8, 9 and 10 illustrate a fine conformity between the data obtained from the experimental values and those estimated from the gas selectivity models for O_2/N_2, CO_2/N_2 and CO_2/CH_4 selectivity, respectively. It can be seen that between the models and experimental data is a good agreement.

CONCLUSIONS

In this study, the effects of incorporation of selected nanoparticles such as TiO_2, Al_2O_3 and ZnO on the efficiency of PMP membranes were investigated. To this purpose, different variables such as operating gas pressure, type and concentration of nanoparticle were applied as the main controller parameters to evaluate the gas transportation properties throughout PMP. Experimental design, modeling and improvement of the gas separation procedure have been fulfilled. Design expert software was used and prevailing data on membrane modeling and the results were categorized according to process variables such as permeability, selectivity, composition of nanoparticle percentage and gas pressure. In PMP membrane modified by 15 wt% Al_2O_3 at the pressure of 9 bar, maximum values of permeability for O_2, N_2, CO_2 and CH_4 were equal to 92.5, 30, 350 and 48 barrer, respectively. TiO_2 nanoparticles were found to be the best nanoparticle in selectivity, so that maximum values of selectivity for CO_2/N_2, CO_2/CH_4 and O_2/N_2 were, respectively, equal to 80.2, 23.98 and 20.6 in PMP membrane modified by 10 wt% TiO_2 at the pressure of 9 bar.

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