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ORIGINAL PAPER

Permeability and selectivity prediction of poly (4-methyl 1-pentane) membrane modified by nanoparticles in gas separation through artificial intelligent systems

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ABSTRACT

In this work, the effects of operative parameters on CH_4, CO_2, O_2, and N_2 membrane gas separation for poly (4-methyl-1-pentane) (PMP) membrane modified by adding nanoparticles of TiO_2, ZnO, and Al_2O_3 are assessed and investigated. The operative parameters were type and percentage of nanoparticles, and cross membrane pressure. The membrane permeability and selectivity were selected as the responses and indexes of separation process performance. To design the experimental layout, design of experiment methodology (DoE) techniques were used. Further, the separation process was modeled and simulated using artificial intelligence (AI) methods. So, a robust black-box model based on radial basis function (RBF) network was developed and trained with the ability for predicting the performance of membrane process. The developed model could simulate the process and predict the permeability with R^2-validation of 0.9. Finally, it was found that addition of nanoparticles and increasing the operative pressure had positive effects on membrane performance. Maximum permeability values for O_2, N_2, CO_2 and CH_4 were 181.58, 52.09, 550.85, and 54.26, respectively. The maximum values of validation-R^2 of optimum structure for CO_2/N_2 and CO_2/CH_4 selectivity were 0.8697 and 0.7028, respectively. **Polyolefins J (2020) 7: 91-98**

Keywords: Poly (4-methyl 1-pentane); AI; membrane gas separation; nanoparticle.

INTRODUCTION

Gas separation process is usually performed using conventional methods such as absorption, adsorption and cryogenic distillation. Nowadays, novel technologies such as membrane process are applied for gas separation [1-4]. Since reducing the pollution, power consumption, and investment costs are of interest, using membrane technology in different industries such as natural gas sweetening is increasing [5]. In recent years, this technology obtained a deep improvement compared to the other gas separation methods [6]. There are several applications of gas separation in different industries [4, 7]. It is worthwhile noting that lower power consumption and operating cost, compact structure, ease of maintenance as well as environmentally friendly issues have increased the use of this technology in various fields of science and engineering [8,

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9].

There are several attempts to increase the performance of membrane separation processes, both permeability and selectivity. Hassanajili et al. assessed the effect of adding metal nanoparticles to polyester membranes on the separation of CH_4 and CO_2. They reported that by increasing the silica content, the permeability increases. This could be due to the separation of the molecular chain that resulted in increasing the free volume of the polymer network [10]. Further, they studied n-C_4H_{10}/CH_4 separation performance by mixed component of poly (4-methyl-1-pentane) (PMP) and silica particles. They reported that adding the silica component to the PMP polymer matrix could increase the selectivity of n-C_4H_{10}/CH_4 from 13 to 26. Similarly, gas permeability would increase from about 3 to 4 times compared to pure PMP [11].

Abedini et al. studied the separation-purification of hydrogen using PMP mixed matrix membranes embedded by MIL53 ($C_8H_5AlO_5$) particles. They reported that increasing the MIL53 particle in PMP matrix leads to an increase in hydrogen solubility while CO_2 solubility decreases, significantly. Also, every increase in pressure and the embedding of nanoparticles result in enhancement of the CO_2/H_2 selectivity and CO_2 permeability [12]. In another research, Abedini et al assessed the effect of adding functionalized NH_2-MIL45 particles on the CO_2/CH_4 separation performance of PMP. They found that any increase in particle loading leads to increase of the CO_2 permeability and CO_2/CH_4 selectivity [13]. PMP has the best permeability for pure hydrocarbons [14]. So, this substance is selected to make membranes for gas separation processes.

Pechaf et al worked on a composite polymer membrane made from polyimide and zeolite. They made a membrane consisted of polyimide and 20 wt% zeolite to analyze the permeability of different gases. They reported that in this process, the CH_4 and CO_2 permeability would increase, but an adverse effect was observed for N_2 and O_2. These differences in permeability could be explained by the changes in the permeability coefficient [15].

Matteucci et al studied the effect of adding TiO_2 nanoparticles to poly (1-trimethylsilyl-1-propyne) on the permeability of membranes. They found that adding this nanoparticle would increase the permeability up to 4 times [16]. In another study, these researchers investigated the effect of adding TiO_2 nanoparticles to 1, 2-polybutadiene (PB). They reported an increase in permeability up to 3 times for the membrane containing 27 vol.% TiO_2 nanoparticles in comparison with pure membrane. It is found that by addition of the nanoparticles to the polymer, the solubility coefficient would increase but the permeability coefficients decrease [17].

The simulation tools developed based on artificial intelligence (AI) prepare a suitable environment to model the membrane separation processes. These models are used in various fields of science and engineering to explain the input-output relations [18-20]. The capability in describing the non-linear input-output relations makes this an interesting alternative in comparison with conventional methods.

Investigating the previous researches shows that the addition of nanoparticle ZnO, Al_2O_3, and TiO_2 to PMP membrane has considerable positive effects on membrane performance. So, the main aim of this work is to assess the effects of addition of these nanoparticles to PMP membrane on advancement of the gas permeation and separation performance in the mixed matrix membranes.

In the work of Alihosseini et al., the addition of nanoparticle to PMP is deeply investigated through design of experiment (DoE) methodology, and the results were well documented. They utilized a statistical modeling method termed as response surface methodology (RSM) to assess the effect of adding nanoparticles including zinc oxide (ZnO), aluminum oxide (Al_2O_3) and titanium dioxide (TiO_2) to PMP membrane on characteristics properties [21]. There are different works in different fields of science that have used DoE methods for experimental design layout, analysis and optimization of the process [22-25].

In this study, AI algorithms were used to model the performance of membrane gas separation using the data and results of Alihosseini's work [21]. Next, the influences of several operative parameters including type of nano particle, percentage of nano particle and pressure on the performance of membrane gas separation processes were investigated. The membrane permeability and selectivity were selected as the responses and indexes of process performance.

To simulate the process using AI, a robust black-box model based on radial basis function (RBF) network was developed and trained with the ability for predicting the performance of membrane process. This model has the ability for forecasting the membrane permeability and selectivity by changing the operative parameters of the process over a determined range of values without doing conventional excess runs. The operative parameters were type and percentage of added nanoparticles, and pressure gradient on the both side of membrane module.

EXPERIMENTAL

Materials

Low molecular weight PMP (purchased from Sigma Aldrich) was used as the background phase. The additive nanoparticles such as ZnO, Al_2O_3, and TiO_2 were prepared from Aldrich Chemical Company (Milwaukee, USA). The average size of nanoparticles was in the range of 20-30 nm. Further, the percentage of these nanoparticles was in the range of 5 to 15%.

Assessment

The performance of conventional (pure) and improved membrane was investigated by membrane permeability and selectivity. The permeability of pure gases such as N_2, O_2, CH_4, and CO_2 was measured both for a pure and an improved membrane. The membrane permeability is calculated as follows:

$$\overline{y} = \frac{\sum_{i=1}^{n} y_{i,tar.}}{n} \tag{1}$$

$$Permeability = \frac{ql}{(p_1 - p_2)A} \tag{2}$$

Where, q and l are the flow rate of permeate gas and membrane thickness, respectively; p_1 and p_2 are pressure values in two sides of the membrane, and A is the active area of the membrane. The selectivity of the gas pairs was calculated by dividing the ratio of the gas permeability.

For gas A and B, the membrane selectivity is calculated as follows:

$$S_{AB} = \frac{P_A}{P_B} \tag{3}$$

Where, P_A and P_B are the permeability of gas A and B, respectively.

Artificial neural network (ANN)

Artificial neural network (ANN) is a useful tool for pattern recognition, data clustering and fitting problems that was developed on the basis of natural nervous system of human kind. This network consists of some independent processing elements called neurons. These neurons are connected each other by series of assigned weights. It is worthwhile noting that the prediction performance of a network is dependent on the structure and learning process strategies.

Radial basis function (RBF) is a neural network that is categorized in feed-forward types. Networks with RBF structure consists of three layers. The first layer (input layer) is the entrance of network that obtains the input values and transfers these values into the next hidden layer. The transferring process is done using transfer functions. In other words, transfer function is assigned to each neuron in the hidden layer for determination of the value of outputs. There are different types of transfer functions. Multilayer neural networks usually use sigmoid, linear, and log-sigmoid as transfer function. According to the neuron inputs, these functions generate output values in the range of 0 to 1.

Faster learning procedure as well as simpler changes in hidden layers in comparison with multi-layer perceptron are the advantages of RBF [26]. The structure of RBF is characterized through determination of mean squared error goal, spread constant, maximum neuron numbers, and number of neurons that adding between displays. To increase the performance of the RBF model, input and output data are normalized by the following equation:

$$X_N = 0.9 \times \frac{X - X_{min}}{X_{max} - X_{min}} + 0.05 \tag{4}$$

Where, X_N is the normalized operative parameter, X is the operative parameter and X_{min} and X_{max} are the values of high and low levels of X, respectively.

In training any feed-forward net, the usual performance function is mean square error (MSE). MSE is defined as follow:

$$MSE = \frac{\sum_{i=1}^{n}(y_{i,pred.} - y_{i,tar.})^2}{n} \qquad (5)$$

Note, the capability of the network in data prediction is assessed by the determination coefficient (R^2). This index could be calculated as follows:

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(y_{i,tar.} - y_{i,pred.})^2}{\sum_{i=2}^{n}(y_{i,tar.} - \overline{y})^2} \qquad (6)$$

$$\overline{y} = \frac{\sum_{i=1}^{n} y_{i,tar.}}{n} \qquad (7)$$

Where, $y_{pred.}$ and $y_{tar.}$ are predicted and target outputs, respectively. Moreover, n is the number of data.

The probable error in developing a neural network model is the occurrence of over-fitting. Over-fitting is a situation that the trained model is able to predict the target of the training dataset in a manner that the determination coefficient is approaching 1, but the capability of this network in data prediction of test dataset is not acceptable. Decreasing the probability of over-fitting is of interest. Increasing the size of the training dataset (numbers of data) could be an effective option in preventing over-fitting. In this study, leave-one-out method was used for training the network, which is an effective method in decreasing the probability of occurrence of this situation.

In leave-one-out training method, data is classified into two datasets (training and validation datasets). Training and validation sets contain N-1 and 1 data, respectively. Accordingly, first network would be created and trained. This procedure will be repeated N times in a way that each data will be fallen in validation group during the N times partitioning.

Finally, N neural networks will be created in a way that each network will be developed and trained, independently. So, the predicted target values are hybrid of outputs of N networks.

Low molecular weight PMP (purchased from Sigma Aldrich) was used as the background phase. The additive nanoparticles such as ZnO, Al_2O_3, and TiO_2 were prepared from Aldrich Chemical Company (Milwaukee, USA). The average size of nanoparticles was in the range of 20-30 nm. Further, the percentage of these nanoparticles was in the range of 5 to 15%.

RESULTS AND DISCUSSION

To evaluate the effect of membrane modification with nanoparticles and operative parameters on membrane performance, DoE was used to develop the layout of experiments. The obtained data was analyzed statistically and analysis of variance (ANOVA) tables were assessed for permeability and selectivity of each pair of gases. Further, these experimental data were used to develop an artificial neural network as a prediction model.

In previous work, several permeability and selectivity models for different gasses were developed for different nanoparticle additives by using statistical methods [21]. In current work, authors focused on developing an advanced neural network model and subsequent related optimization.

Model Development

Permeability

In this work, for networks that deal with permeability values, maximum number of neurons is set at 20 and number of neurons to add between displays is set at 1. Accordingly, several networks with different structures were investigated for permeability of oxygen, nitrogen, carbon dioxide, and methane. Each network was trained through leave-one-out method as explained previously. The preciseness of artificial network was assessed by determination coefficient (R^2) of validation dataset. Through assessing the different structures of networks, it is found that the model developed for prediction the permeability of oxygen has the best forecasting performance with spread constant of 2.148. In Table 1, the average values of R^2 of validation dataset of optimum structures of RBF with optimum mean squared error goal are shown, while the spread constant is 2.148.

In Figure 1, the permeability predicted by optimized RBF has been scattered vs. data generated for different gases. As is shown, acceptable distribution around the line y=x proves the agreement between the data generated by developed neural network model and experimental data. This developed model can be used to predict the permeability only in the determined range of operative parameters.

Table 1. Maximum R^2 of validation dataset for different gases.

Gas	Maximum validation-R^2	Optimum mean squared error goal
oxygen	0.9188	0.0155
nitrogen	0.9078	0.0141
CO_2	0.8956	0.0155
CH_4	0.9176	0.0238

In Figure 2 the difference between experimental data and data predicted by RBF termed residuals has been scattered vs. predicted data by RBF. Random distribution of residuals is of interest.

In Table 2, the maximum values of permeability for different gases that were predicted using the developed models have been presented. As the table shows, maximum values of permeability for O_2, N_2, CO_2 and CH_4 are equal to 181.58, 52.09, 550.85, and 54.26, respectively. This observation shows that addition of AL_2O_3 is more effective than addition of TiO_2 and ZnO nanoparticles. For O_2, N_2, and CO_2, the optimum volume percentage of AL_2O_3 nanoparticle is 15%; but for CH_4, this value is 12.41%. Further, the optimum operative pressure for O_2, N_2, and CO_2, is 25 bar; but for CH_4, this value is 21.83 bar.

In Figure 3, the 3-D surfaces of permeability of PMP for oxygen vs. pressure and concentration of

Table 2. Maximum values of permeability of different gases for modified PMP.

Gas	Maximum permeability value	Corresponding conditions		
		Type of nano particle	Nanoparticle percentage	Operative pressure
O_2	181.58	AL_2O_3	15	25
N_2	52.09	AL_2O_3	15	25
CO_2	550.85	AL_2O_3	15	25
CH_4	54.26	AL_2O_3	12.41	21.83

nanoparticles have been plotted for three types of nanoparticles. Note that the values of permeability were generated using the optimum developed model. As shown, by increasing the pressure and percentage of nanoparticles, permeability of oxygen gas increases. At constant pressure across the membrane, increasing the nanoparticle content leads to increase the gas permeability. It is clear that at high percentage values of nanoparticles, increasing the pressure results in increase of permeability; but this routine effect is not observed at low values of nanoparticle percentages.

Selectivity

In Table 3, the variation of network performances in term of selectivity for different structures of RBF (mean squared error goal) for two pairs of gases (CO_2/N_2 and

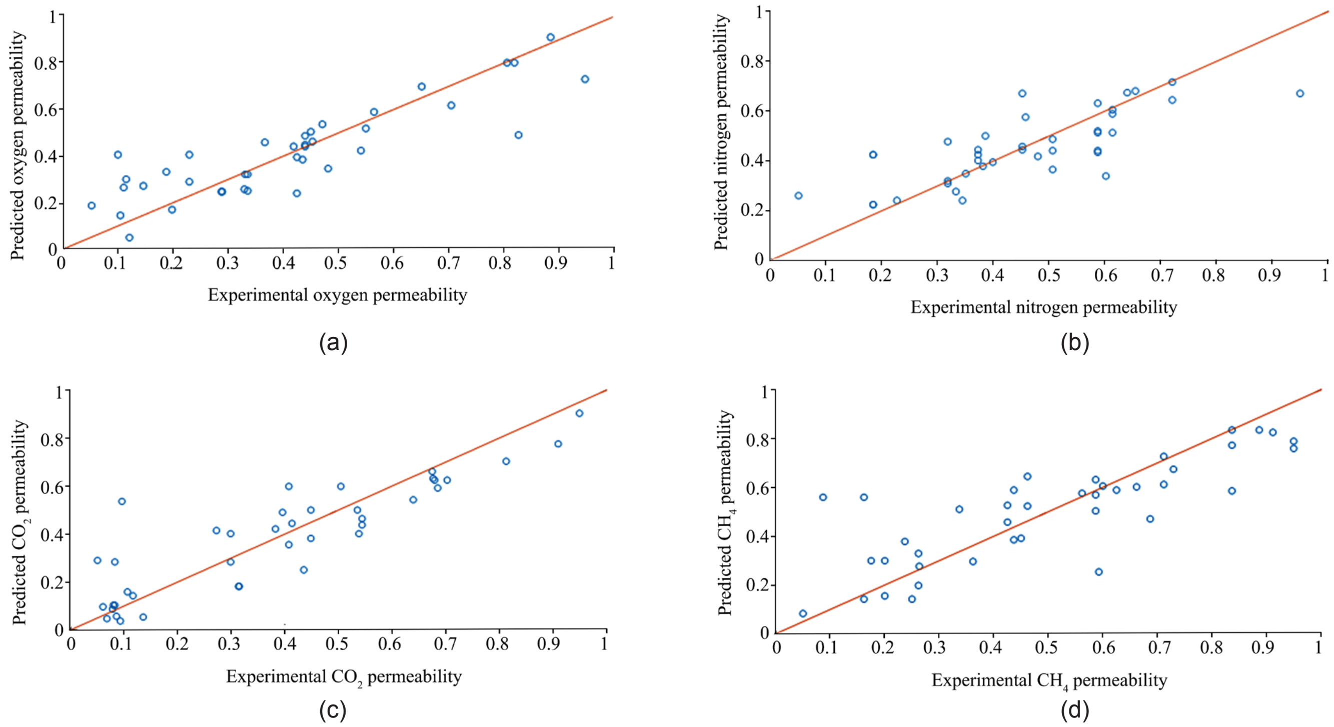

Figure 1. Permeability data predicted by optimized RBF vs. experimental data for (a) oxygen, (b) nitrogen, (c) carbon dioxide, and (d) methane.

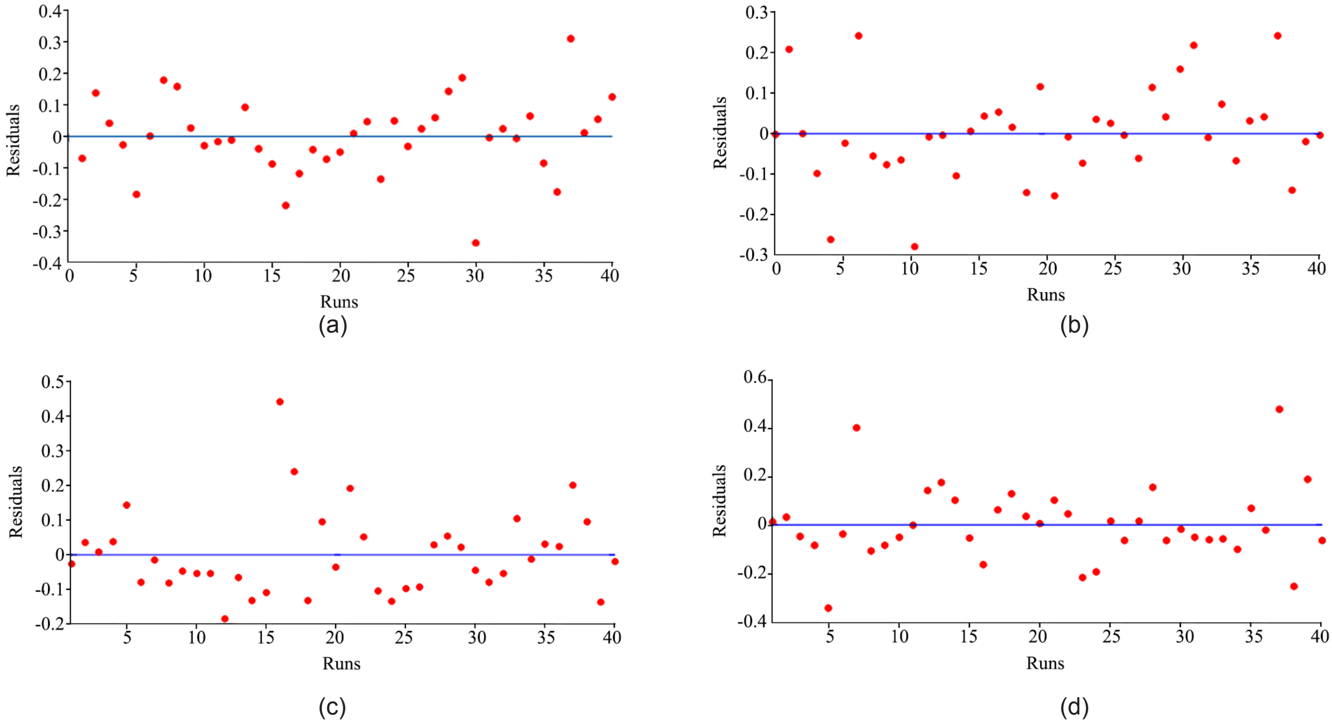

Figure 2. Residual vs. run numbers for (a) oxygen, (b) nitrogen, (c) carbon dioxide, and (d) methane.

Table 3. Validation-R^2 for different mean squared error goals for selectivity.

Mean squared error goal		0.01	0.013	0.017	0.02	0.023	0.027	0.03	0.033	0.037	0.04
Validation-R^2	CO_2/N_2	0.8697	0.8422	0.8175	0.8078	0.6967	0.6596	0.6863	0.6861	0.6861	0.6861
	CO_2/CH_4	0.7028	0.6714	0.6494	0.6494	0.6494	0.6494	0.6494	0.6494	0.6494	0.6494

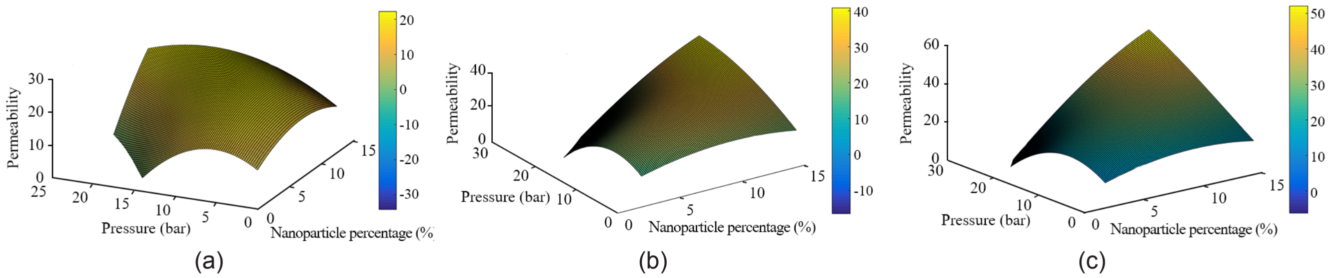

Figure 3. Predicted nitrogen permeability for (a) TiO_2, (b) ZnO, and (c) AL_2O_3.

CO_2/CH_4) has been shown while the value of spread constant is fixed at 2.148. It is found that the prediction preciseness of RBF for permeability is higher than that for selectivity. As shown, the maximum values of validation-R^2 of optimum structure for CO_2/N_2 and CO_2/CH_4 are 0.8697 and 0.7028, respectively.

CONCLUSION

In this study, artificial neural network models based on the radial basis function (RBF) were developed to predict the performance of PMP membrane modified by different nanoparticles including TiO_2, Al_2O_3 and ZnO. The permeability and selectivity of membrane were used to assess the performance of membrane separation process. Moreover, the neural networks were validated by leave-one-out validation methodology. Several networks with different structures were investigated for permeability of oxygen, nitrogen, carbon dioxide, and methane. The developed model could simulate the process and predict the permeability with R^2-validation of

0.9. Through assessing the different structures of networks, it was found that the model developed for prediction of oxygen permeability has the best forecasting performance with spread constant of 2.148. In addition, by increasing the concentration of added nanoparticles, membrane permeability advanced. It was demonstrated that the prediction preciseness of RBF for permeability was higher than that for selectivity. It was revealed that the addition of AL_2O_3 has better result in comparison with the addition of other nanoparticles. For O_2, N_2, and CO_2, the optimum value of volume percentage of nanoparticle was 15%; but for CH_4, this value was 12.41%. Further, for O_2, N_2, and CO_2, the pressure of 25 bar led to optimum result; but for CH_4, this value was 21.83 bar.

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