Investigation the Effect of Nanocomposite Material on Permeation Flux of Polyerthersulfone Membrane using a Mathematical Approach

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ABSTRACT Integrally skinned asymmetric membranes based on nanocomposite polyethersulfone were prepared by the phase separation process using the supercritical CO_2 as a nonsolvent for the polymer solution. In present study, the effects of temperature and nanoparticle on selectivity performance and permeability of gases has been investigated. It is shown that the presence of silica nanoparticles not only disrupts the original polymer chain packing but also alters the chemical affinities of penetrants in polyethersulfone matrices. Because, in the presence of hydrophilic silica, CO_2 affinity filler, hydrogen-bond interactions between the oxygen atoms of carbon dioxide and the hydrogen atoms of hydroxyl group on the nanosilica surface would take place at the interface and thus solubility and consequently permeability towards CO_2 are higher in comparison with CH_4 for the membranes. Furthermore, in present study, a novel mathematical approach has been proposed to develop a model for permeation flux and selectivity performance of the membrane using Support Vector Machine.

SVM is employed to develop model to estimate process output variables of a nanocomposite membrane including permeation flux and selectivity performance. Model development that consists of training, optimization and test was performed using randomly selected 80%, 10%, and 10% of available data respectively. Test results from the SVM based model showed to be in better agreement with operating experimental data compared to other developed mathematical model. The minimum calculated squared correlation coefficient for estimated process variables is 0.99. Based on the results of this case study SVM proved that it can be a reliable accurate estimation method.

KEYWORDS Nanocomposite material • polyerthersulfone membrane • silica nanoparticles • Support Vector Machine (SVM).

1. INTRODUCTION

Support Vector Machine introduced first by Vapnik, is a supervised learning method with associated learning algorithm that analyzes data and recognizes patterns of input/output data. In recent years, ANN has been demonstrated to be a substitute for deterministic modeling and estimation methods with good potentials to be explored.

SVM is based on the structural risk minimization principle from computational learning theory. It is one of the most sophisticated non-parametric supervised classifiers available today, with many different configurations depending on kernel function used to generate transform function that maps input space into output space. Commonly, several functions including linear, polynomial, Radial Basis Function (RBF) and multilayer perceptron are used as the kernel function in SVM. By the use of kernels necessary computations are performed directly in the input space .Although, it is mostly considered as a linear algorithm in a high dimensional feature space, it does not necessitate the practical input/output mapping problem to be a high dimensional space problem. A brief discussion on mathematical basis of SVM is presented here that helps understanding the way SVM works and the features that render it superiority over other learning algorithms.

2. Mathematical Model

Pattern recognition or classification can be performed by SVM in a data set consisting of N data point $\{x_k, y_k\}$ $k = 1,2, \ldots, N$ where x_k is a p-dimensional vector and y_k can take one of the two values, either +1 or -1 (i.e., $y_k \epsilon \{+1, -1\}$ indicating the class to which the point x_k belongs. In their basic form, they learn a linear hyperplane that separates a set of positive samples from a set of negative samples with maximum margin. Consider Figure 1 which shows two possible separating hyperplanes and their associated margins. Both hyperplanes can correctly classify all the given data. However, we expect the hyperplane with the larger margin to be more accurate in classifying new data than the hyperplane with the smaller margin. This is the reason that SVM searches for the hyperplane with the largest margin.

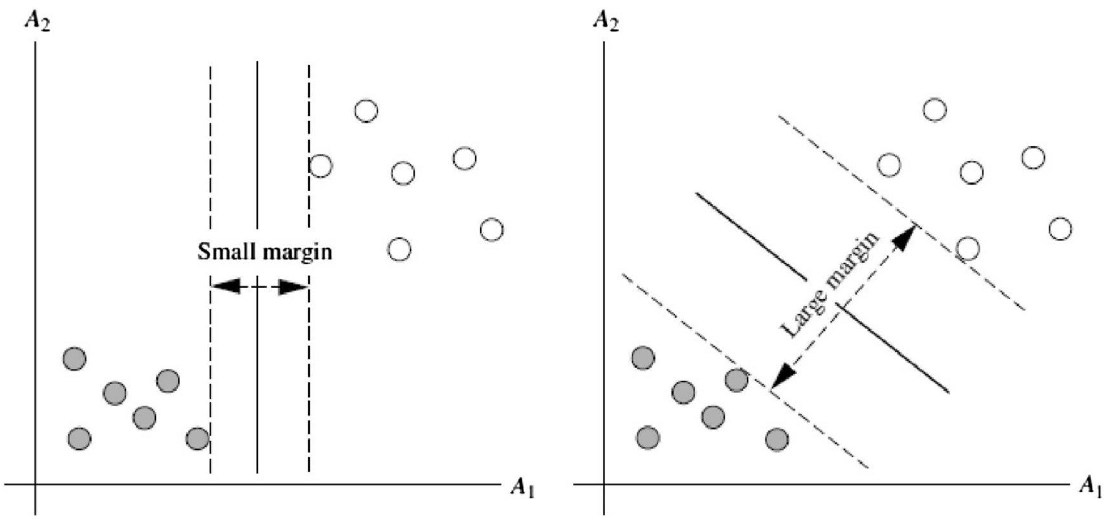

Figure 1. Support Vector Machine Classifier.

A separating hyperplane can be written as $w.x - b = 0$ [1, 2], where w is the normal vector to the hyperplane and b represents the offset of the hyperplane from origin that is referred to as bias. The offset along the vector w from the origin can be determined by $b/_{||w||}$. As shown in Figure 2, for the cases that the training data are linearly separable, two hyperplanes can separate the data in a way that there are no data points between them. Obviously these hyperplanes can be described as:

$$w.x - b = 1 \tag{2}$$

$$w.x - b = -1 \tag{3}$$

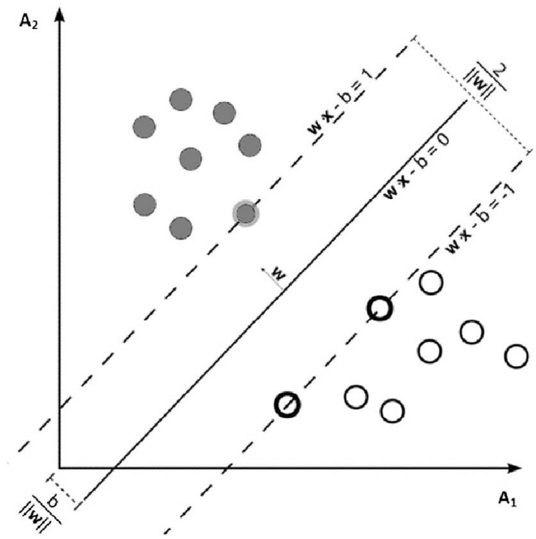

Figure 2. Hyperplane Definition**.**

By using geometry, one can show that distance between these two hyperplanes is $^2/_{||w||}$, so the problem of ||w|| minimization is required to maximize hyperplane margin. It is also required to prevent data points from falling into the margin, and other necessary constraints are imposed as:

w.x_k–b ≥ 1	For x_k of the first class	(4)
w.x_k–b ≤ –1	For x_k of the second class	(5)

That can be rewritten as:

$$y_i(w.x_k - b) \geq 1 \qquad \text{For } all \quad 1 \leq k \leq N \tag{6}$$

Constraint minimization of ||w|| is thus required to develop an ideal classifier. Such minimization problem is difficult to solve, however it is possible to substitute 0.5 $||w||^2$ instead of ||w|| in problem. It was shown that, minimization problem can be formulated as:

$$\min_{w,b} \max_{a \geq 0} \left\{ \frac{1}{2} ||w||^2 - \sum_{i=1}^{N} a_i \left(y_i(wx - b) - 1 \right) \right\} \tag{7}$$

where α_i is Lagrangian multiplier that helps in finding the local minimum or maximum of a function. The problem of Eq. 7 can be solved by standard quadratic programming techniques that results in finding normal vector to the hyperplane as presented in Eq. 8:

$$w = \sum_{k=1}^{n} a_i \, y_i x_i \tag{8}$$

Input/output support vector machine model with the general form of $y = f(x)$ takes the form of Eq.9 in feature space:

$$f(x) = \sum_{k=1}^{N} a_i \, . K(x, x_k) + b \tag{9}$$

where $f(x)$ represents output vector and $K(x, x_k)$ is the kernel function calculated from the inner product of the two vectors x and x_k in the feasible region built by the inner product of the vectors $\Phi(x)$ and $\Phi(x_k)$ as follows:

$$K(x, x_k) = \Phi(x)^{\,r} . \, \Phi(x_k) \tag{10}$$

Among choices for Kernel function the Radial Basis Function (RBF) Kernel that is used extensively has been applied in this work that is presented in Eq. 11,

$$K(x, x_k) = \exp\left(\frac{-||x_k - x||^2}{\sigma^2}\right) \tag{11}$$

where σ is kernel parameter to be determined by an external optimization algorithm during the internal SVM calculations. Bias, b, is usually determined by using primal constraints as:

$$b = -\left(\frac{1}{2}\right)\left[\max_{\{i, y_i=-1\}}\left(\sum_{j\epsilon\{SV\}}^{m} y_i a_i \, K(x_i, x_j)\right)\right] + \min_{\{i, y_i=-1\}}\left(\sum_{j\epsilon\{SV\}}^{m} y_i a_i \, K(x_i, x_j)\right) \tag{12}$$

Lagrangian multipliers, a_i, can be calculated by solving following quadratic programming problem:

$$\omega(a) = \sum_{i=1}^{N} a_i - \frac{1}{2}\sum_{i,j=1}^{N} a_i a_j y_i y_j K(x_i, x_j) \tag{13}$$

Subject to constraints $0 \leq a_i \leq \gamma$, $i = 1, \ldots, N$, where γ is regularization parameter and controls the tradeoff between complexity of the support vector machine model and the number of non-separable points. This compact formulation of quadratic optimization has been proved to have a unique solution. In conclusion, the SVM takes the form of the constrained optimization problem of Eq. 14 in order to obtain the optimum value of γ

$$\min_{\omega, \beta, \xi_i \xi_i^*} \frac{1}{2} ||\omega||^2 + \gamma . \sum_{i=1}^{N} (\xi_i, \xi_i^*) \tag{14}$$

Subject to

$$\begin{array}{ll} y_i - \omega^T x_i - b \leq \varepsilon + \xi_i & t = 1, \ldots, N \\ \omega^T x_i + b - y_i \leq \varepsilon + \xi_i^* & t = 1, \ldots, N \\ \xi \geq 0 & t = 1, \ldots, N \\ \xi_i \geq 0 & t = 1, \ldots, N \end{array}$$

where ε is the precision threshold and ξ_i, ξ_i^* represent the slack variables with nonnegative values to ensure feasible constraints. The first term in Eq. 14 represents model complexity while the second term represents the model accuracy or error tolerance. The Mean Square Error (MSE) and Mean Absolute Error (MAE) as defined by Eqs. 15 and 16 are used to calculate prediction error of the developed SVM model.

$$\text{MSE} = \frac{\sum_{i=1}^{n}(O_i - T_i)^2}{n} \tag{15}$$

$$\text{MAE} = \frac{1}{n}\sum_{i=1}^{n}|O_i - T_i| \tag{16}$$

where O_i is the simulation results of SVM model, T_i represents real time plant data of the natural gas sweetening plant and n denotes the number of the data used for model evaluation.

3. Results and Discussion

The Figurs 3, 4 show the effect of nanoparticle on the CO_2 permeation of an integrally skinned asymmetric polyethersulfone membrane formed at T=45˚C, P=100 bar, DMAc/PES mass ratio of 2.5 and the depressurization rate of 1.83 bar/min. The incorporation of silica nanoparticle in the membranes results in further increase in permeability towards CO_2 compared to CH_4 and thus increases the membrane selectivity. It is believed that the presence of silica nanoparticles not only disrupts the original polymer chain packing but also alters the chemical affinities of penetrants in polyethersulfone matrices. Because, in the presence of hydrophilic silica, CO_2 affinity filler, hydrogen-bond interactions between the oxygen atoms of carbon dioxide and the hydrogen atoms of hydroxyl group on the nanosilica surface would take place at the interface and thus solubility and consequently permeability towards CO_2 are higher in comparison with CH_4 for the membranes.

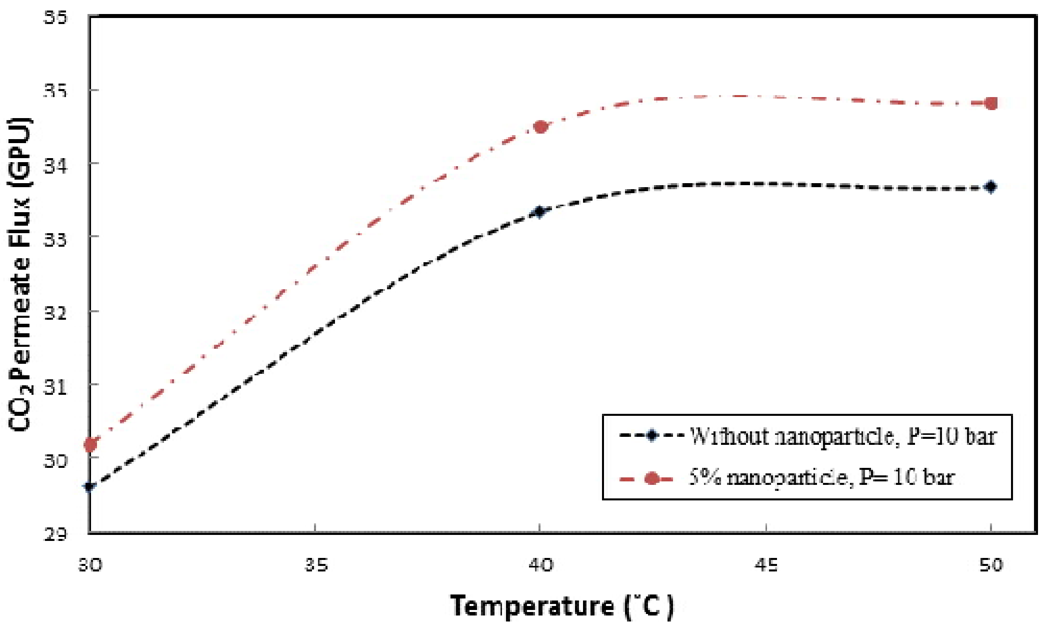

Figure 3. Effect of silica nanoparticle on the CO_2 permeation of the integrally skinned polyethersulfone membrane.

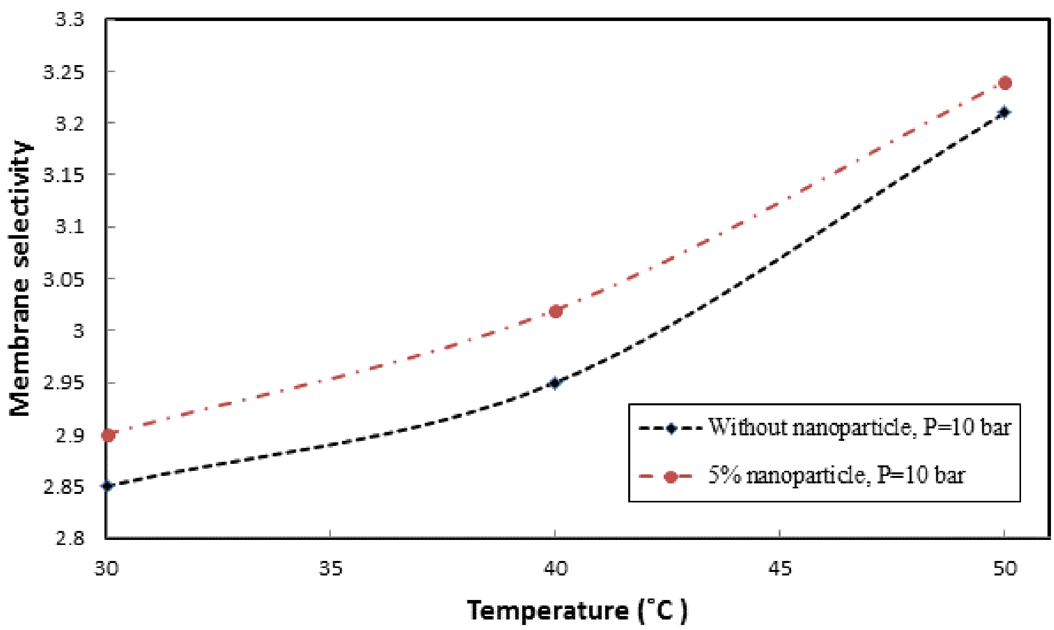

Figure 4. Effect of silica nanoparticle on membrane selectivity of the integrally skinned polyethersulfone membrane.

The operating plant data collected over the span of one year is used in this case study. The data has been normalized between -1 and +1 to prevent truncation error due to wide ranges of numerical values for input/output variables to be included in the SVM model. Since the model development is based on normalizing data, it is necessary to map input data to normalized space accordingly. Normalized model output should also be mapped into the space of real values for output variable to be compared to operating plant data. To develop input/output model the calculation procedure of section 3 that is programmed in Matlab environment is executed on an Intel dualcore2.40 GHz processor accompanied by 4G RAM that it took around 12 hours to get convergence. Convergence indicates that optimum model is achieved; however, it does not guarantee accuracy of model predictions. To ensure model reliability the input variables of test data subset are entered to the developed model and model predictions are validated against experimental data and are also compared with ANN model prediction where available. The ANN based model is of feed-forward back propagation type and was developed using the same training data that is used in this research work.

4. Conclusion

The effects of experimental operating conditions such as the temperature and the presence of silica nanoparticles in the structure of dense nanocomposite layers were investigated. It was found that, it is possible to induce a very-controlled asymmetry in a dense film and pore sizes by changing the temperature and pressure. Also, presence of silica nanoparticle proved to increase the permeability of CO_2 and thus the membrane selectivity. Also this study demonstrates the applicability of SVM to develop accurate input/output model of the operational variables of ananocomposite membrane. The kernel parameters for developed model are determined and model predictions are compared with those obtained from another mathematical model. Beside the general advantages that are cited for SVM over ANN as an input/output modeling tool, the predicted data in this study showed better performance of support vector machine over artificial neural networks in terms of accuracy. The numerical values of AAD% calculated showed a minimum 12% improvement gained by SVM over ANN that is of great importance if the predicted data are to be used for monitoring and/or control purposes. This study reveals some the application potentials of SVM as a modeling tool in oil and gas industries that requires much more attention to be fully understood.

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