Polyamide/nano Mixed Matrix Membranes for Pervaporation Dehydration Ethylene Glycols

OMID SABZEVARI, AZAM MARJANI* and AMIRMOHAMMAD DARIPOUR

Department of Chemistry, Islamic Azad University, Arak Branch, Arak, Iran
*Corresponding author E-mail: a-marjani@iau-arak.ac.ir

http://dx.doi.org/10.13005/ojc/310260

(Received: April 30, 2015; Accepted: June 15, 2015)

ABSTRACT

In this study, nano silica was successfully incorporated into the polyamide solution to prepare polyamide/nano silica mixed matrix membranes (MMMs). The prepared MMMs were characterized by scanning electron microscopy (SEM). The prepared MMMs were used to separate mixtures of Ethylene glycols/water at 25 °C in the pervaporation (PV) process. The different nano silica loadings in polyamide polymer, such as 0.5, 1 and 2 wt%, have been tried and nano silica with 0.5 wt% loading shows the best PV performance. As a result, the 0.5 wt% nano silica in polyamide membrane leads to increases in permeation, but, decrease in the separation factor. Separation factor decreases significantly at higher loadings of nano silica due to the agglomeration of nano-particles in the polyamide matrix.

Key words: Mix matrix membrane, Nano-silica, Polyamides, ethylene glycol; Separation.

INTRODUCTION

Membrane technology covers all engineering approaches for the transport of substances between two fractions with the help of permeable membranes\textsuperscript{1-16}. In general, mechanical separation processes for separating gaseous or liquid streams use membrane technology\textsuperscript{17-30}.

Among membrane processes, pervaporation systems are developed in many applications such as alcohols and ethylene glycols dehydration. Currently, hydrolysis of ethylene oxide is the commercially method for production of ethylene glycol (EG), where a large amount of water is consumed in the hydrolysis reaction to increase the conversion. The excess water requires to be removed for ethylene glycol purification. Although ethylene glycol and water do not form an azeotrope over the entire composition range, separation of ethylene glycol/water mixtures by evaporation or distillation is still energy intensive because of the high boiling point of ethylene glycols. Therefore, pervaporation system can be appropriate alternative for purification of ethylene glycols\textsuperscript{31-69}.

The main goal of this study is in synthesis of nano mixed matrix membranes for purification
and separation of ethylene glycols. The membrane is made of polyamide incorporated with nano-silica particles. The membranes were used in separation of ethylene glycols from ethylene glycol/water mixtures using pervaporation.

**EXPERIMENTAL**

**Materials**

Ultramid® Polyamide: PA 6 (Nylon 6, BASF), deionized water, nano silica, ethylene glycols (Merck, 99%), and dimethyl acetamide (Merck, 99%) were used in the all experiments. All chemicals used were analytical grade reagents and were used as received without further purifications.

**Membrane preparation**

The polyamide/nano silica MMMs were prepared via solution casting and solvent evaporation technique. Polyamide powder (12 wt. %) was dissolved in dimethyl acetamide by stirring and the solution was filtered to remove insoluble impurities. Afterwards, the nano silica nano particles were added into the previously prepared polyamide solution. The solution was then stirred for 60 min vigorously and then exposed to ultrasonication for 30 min. The solution was cast on the onto a clean glass plate. The polymer casting solution was dried in ambient temperature for 24 h and then MMMs peeled from the glass. The prepared mixed matrix membranes were evaluated in a PV separation system which is shown in Fig. 1. The permeate samples collected in the cold trap were analyzed after weighted, using gas chromatography with a flame ionization detector for confirmation. Total permeation flux (J) was determined using the following Equation 1:

\[
J = \frac{m}{At}
\]

where J is the total flux (kg/m² h), m is the permeate weight (kg), A is the effective membrane surface area (m²) and t is the PV time (h).

**RESULTS AND DISCUSSION**

**SEM characterization**

The synthesized membranes were characterized using scanning electron microscopy (SEM) to observe the dispersion of nano silica in the polymer matrix. Fig. 2 illustrates SEM images of synthesized membranes at different nano silica loadings ranging from 0.5 to 2 wt. %. As can be seen, the porosity of the membrane without nano silica is low, on the other word this membrane is dense. As shown, the membrane with 0.5 wt. % nano silica loading shows the best nano silica dispersion. Increasing nano silica loading results in coagulation of particles in polymer matrix and non-uniform dispersion of nano silica which in turn reduce the separation performance of mix matrix membranes.

**Effect of nano silica**

Separation performance of polyamide (PA) membranes in the case of pure and nano mixed matrix were evaluated to investigate the effect of nano silica on mixed matrix membrane performance. Table 1 depicts the influence of nano silica adding to polyamide on concentration of ethylene glycols in permeate side. The nano silica loading was 0.5 wt. % which reveals the best

<table>
<thead>
<tr>
<th>Di-ethylene glycol concentration at the outlet (wt. %)</th>
<th>Di-ethylene glycol concentration in the feed stream (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With Nano-silica</td>
<td>Without Nano-silica</td>
</tr>
<tr>
<td>64.34</td>
<td>49.27</td>
</tr>
<tr>
<td>75.90</td>
<td>67.01</td>
</tr>
<tr>
<td>99.95</td>
<td>95.18</td>
</tr>
<tr>
<td>83.51</td>
<td>73.65</td>
</tr>
<tr>
<td>98.32</td>
<td>93.62</td>
</tr>
<tr>
<td>99.52</td>
<td>95.03</td>
</tr>
</tbody>
</table>
dispersion from SEM observations which it can be seen in Fig. 2. As it can be seen from Table 1, adding nano silica to polymer matrix increases the concentration of ethylene glycols in permeate significantly. The latter means that adding nano silica increases both separation factor and permeation flux of ethylene glycols. This could be attributed to the increasing chemical bound between ethylene glycols and nano silica which increase sorption of ethylene glycols in the mixed matrix membrane.

Fig. 1: Experimental setup used for pervaporation separation of water from 2-propanol ethylene glycol and di-ethylene glycol

Fig. 2: SEM images of synthesized membranes at different nano silica loadings. a: pure polyamide; b: 0.5 wt. % nano silica; c: 1 wt. % nano silica; d: 2 wt. % nano silica
CONCLUSION

In the current study, polyamide/nano silica MMMs prepared for PV dehydration of ethylene glycols. Silica nano particles, with sizes smaller than 100 nm, were dispersed in the matrix of polyamide directly with a loading ranging from 0.5 to 2 wt%. SEM observation confirmed that the agglomeration of nano silica was observed only in the higher contents of nano silica. Permeation values of the polyamide/nano silica MMMs membranes were higher than that of the neat polyamide membrane, which indicates better PV efficiency for the separation of water and ethylene glycols after the incorporation of nano silica nano particles into the polyamide membranes.

REFERENCES

15. Ghadiri, M. and S. Shirazian, Computational simulation of mass transfer in extraction of alkali metals by means of nanoporous membrane extractors. Chemical Engineering


54. Shirazian, S. and S.N. Ashrafizadeh, Mass transfer simulation of caffeine extraction by subcritical CO$_2$ in a hollow-fiber membrane contactor. *Solvent Extraction and Ion


74. Sohrabi, M.R., et al., Simulation studies on

