Est. 1984

ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2015, Vol. 31, No. (2):
Pg. 1091-1098

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[1-16]. In general, mechanical separation processes for separating gaseous or liquid streams use membrane technology[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[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 [70-77]:

$$J = \frac{m}{A\,t} \qquad \text{...(1)}$$

where J is the total flux (kg/m^2 h), m is the permeate weight (kg), A is the effective membrane surface area (m^2) 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 1: Effect of nano silica adding on separation performance of polyamide membranes

Di-ethylene glycol concentration at the outlet (wt. %)		Di-ethylene glycol
With Nano-silica	Without Nano-silica	concentration in the feed stream (wt. %)
64.34	49.27	40
75.90	67.01	50
99.95	95.18	60
83.51	73.65	60
98.32	93.62	70
99.52	95.03	80

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.

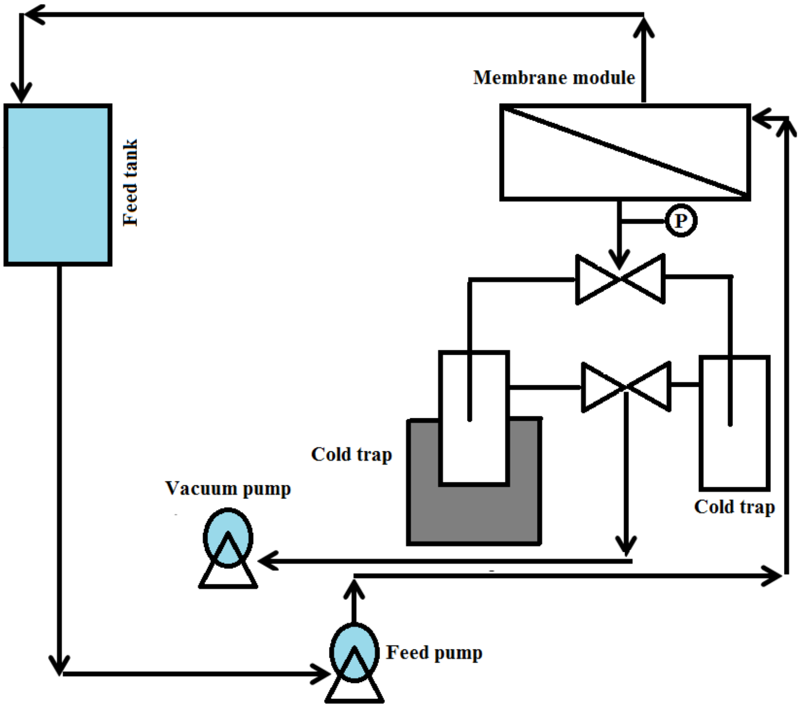

Fig. 1: Experimental setup used for pervaporation separation of water from 2-propa ethylene glycol and di-ethylene glycol

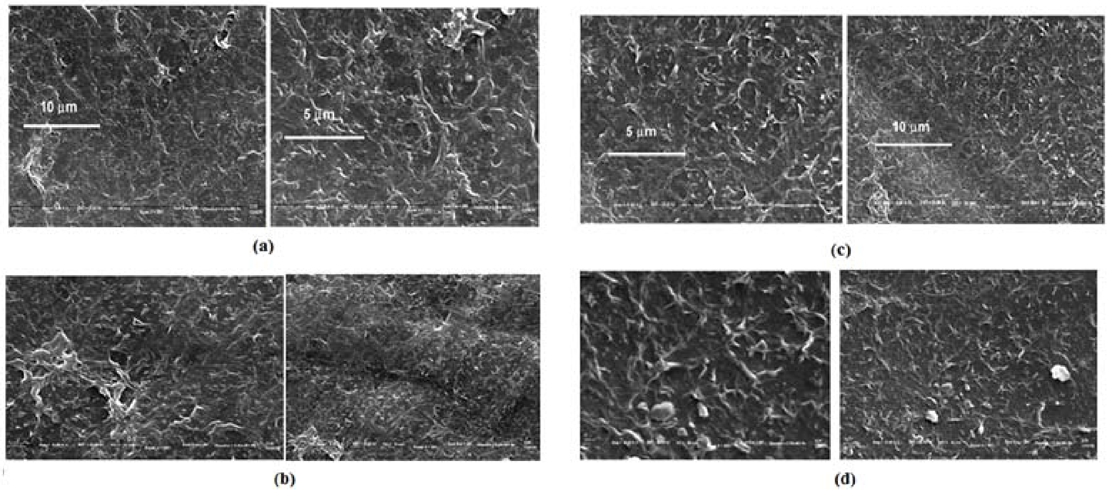

Fig. 2: SEM images of synthesized membranes at different nano silica loadings. a: pure polyamide; b: 0.5 wt. % nano silica; c: 1 wt. % nano silica; d: 2 wt. % nano silica

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

1. Barati, F., *et al*., CFD simulation and modeling of membrane-assisted separation of organic compounds from wastewater. *Chemical Engineering and Technology*, **2014**, *37*(1): p. 81-86.
2. Daraei, A., *et al*., Modeling and transport analysis of silver extraction in porous membrane extractors by computational methods. *Transactions of the Indian Institute of Metals*, **2014**, *67(2)*: p. 223-227.
3. Fadaei, F., *et al*., Mass transfer simulation of ion separation by nanofiltration considering electrical and dielectrical effects. *Desalination,* **2012**, *284*: p. 316-323.
4. Fadaei, F., S. Shirazian, and S.N. Ashrafizadeh, Mass transfer modeling of ion transport through nanoporous media. *Desalination*, **2011**, *281(1):* p. 325-333.
5. Fadaei, F., S. Shirazian, and S.N. Ashrafizadeh, Mass transfer simulation of solvent extraction in hollow-fiber membrane contactors. *Desalination*, **2011**, *275(1-3)*: p. 126-132.
6. Fasihi, M., *et al*., Computational fluid dynamics simulation of transport phenomena in ceramic membranes for SO_2 separation. Mathematical and Computer Modelling, **2012**, *56(11-12)*: p. 278-286.
7. Ghadiri, M., *et al*., Simulation of membrane distillation for purifying water containing 1,1,1-trichloroethane. Chemical Engineering and Technology, **2014**, *37(3)*: p. 543-550.
8. Ghadiri, M., M. Asadollahzadeh, and A. Hemmati, CFD simulation for separation of ion from wastewater in a membrane contactor. *Journal of Water Process Engineering*, **2015**, *6*, 144-150.
9. Ghadiri, M. and S.N. Ashrafizadeh, Mass transfer in molybdenum extraction from aqueous solutions using nanoporous membranes. *Chemical Engineering and Technology,* **2014**, *37(4)*: p. 597-604.
10. Ghadiri, M., S. Fakhri, and S. Shirazian, Modeling and CFD simulation of water desalination using nanoporous membrane contactors. *Industrial and Engineering Chemistry Research*, **2013**, *52(9)*: 3490-3498.
11. Ghadiri, M., S. Fakhri, and S. Shirazian, Modeling of water transport through nanopores of membranes in direct-contact membrane distillation process. *Polymer Engineering and Science*, **2014**, *54(3)*: p. 660-666.
12. Ghadiri, M., *et al*., Computational simulation for transport of priority organic pollutants through nanoporous membranes. *Chemical Engineering and Technology,* **2013**, *36(3):* 507-512.
13. Ghadiri, M., A. Marjani, and S. Shirazian, Mathematical modeling and simulation of CO_2 stripping from monoethanolamine solution using nano porous membrane contactors. *International Journal of Greenhouse Gas Control,* **2013**, *13*: p. 1-8.
14. Ghadiri, M., M. Parvini, and M.G. Darehnaei, Simulation of zinc extraction from aqueous solutions using polymeric hollow-fibers. *Polymer Engineering and Science*, **2014**, *54(10)*: 2222-2227.
15. Ghadiri, M. and S. Shirazian, Computational simulation of mass transfer in extraction of alkali metals by means of nanoporous membrane extractors. *Chemical Engineering*

and Processing: Process Intensification, **2013**, *69*: p. 57-62.

16. Ghadiri, M., S. Shirazian, and S.N. Ashrafizadeh, Mass Transfer Simulation of Gold Extraction in Membrane Extractors. *Chemical Engineering and Technology*, **2012**, *35*(12): p. 2177-2182.
17. Hemmati, M., *et al.*, Phenol removal from wastewater by means of nanoporous membrane contactors. *Journal of Industrial and Engineering Chemistry*, **2015**, *21:* . 1410-1416.
18. Hoshyargar, V., *et al.*, Prediction of flow behavior of crude oil-in-water emulsion through the pipe by using rheological properties. *Oriental Journal of Chemistry,* **2012**, *28(1):* p. 109-113.
19. Khansary, M.A., A.H. Sani, and S. Shirazian, Mathematical-thermodynamic solubility model developed by the application of discrete Volterra functional series theory. *Fluid Phase Equilibria,* **2015**, *385*: p. 205-211.
20. Kohnehshahri, R.K., *et al.*, Modeling and numerical simulation of catalytic reforming reactors. *Oriental Journal of Chemistry,* **2011**, *27(4):* 1351-1355.
21. Marjani, A., P. Mohammadi, and S. Shirazian, Preparation and characterization of poly (vinyl alcohol) membrane for pervaporation separation of water-organic mixtures. *Oriental Journal of Chemistry,* **2012**, *28(1):* p. 97-102.
22. Marjani, A., M. Rezakazemi, and S. Shirazian, Vapor pressure prediction using group contribution method. *Oriental Journal of Chemistry,* **2011**, *27(4)*: 1331-1335.
23. Marjani, A., M. Rezakazemi, and S. Shirazian, Simulation of methanol production process and determination of optimum conditions. *Oriental Journal of Chemistry,* **2012**, *28(1):* p. 145-151.
24. Marjani, A., Y. Shirazi, and S. Shirazian, Investigation on the best conditions for purification of multiwall carbon nanotubes. *Asian Journal of Chemistry*, 2011, *23(7):* p. 3205-3207.
25. Marjani, A. and S. Shirazian, CFD simulation of dense gas extraction through polymeric membranes. *World Academy of Science, Engineering and Technology,* **2010**, *37*: p. 1043-1047.
26. Marjani, A. and S. Shirazian, Simulation of heavy metal extraction in membrane contactors using computational fluid dynamics. *Desalination*, **2011**, *281*(1): 422-428.
27. Marjani, A. and S. Shirazian, Hydrodynamic investigations on heavy metal extraction in membrane extractors. *Oriental Journal of Chemistry*, **2011**, *27(4):* p. 1311-1316.
28. Marjani, A. and S. Shirazian, Computational fluid dynamics simulation of ammonia removal from wastewaters by membrane. *Asian Journal of Chemistry,* **2011**, *23(7):* p. 3299-3300.
29. Marjani, A. and S. Shirazian, Investigation on copper extraction using numerical simulation. *Asian Journal of Chemistry,* 2011. 23(7): p. 3289-3290.
30. Marjani, A. and S. Shirazian, Investigation on numerical simulation of acetone and ethanol separation from water by using membrane. *Asian Journal of Chemistry*, **2011**, *23(7)*: p. 3293-3294.
31. Marjani, A. and S. Shirazian, CFD simulation of mass transfer in membrane evaporators for concentration of aqueous solutions. *Oriental Journal of Chemistry,* **2012**, *28(1):* p. 83-87.
32. Marjani, A. and S. Shirazian, Modeling of organic mixtures separation in dense membranes using finite element method (FEM). *Oriental Journal of Chemistry,* **2012**. *28(1)*: p. 41-46.
33. Marjani, A. and S. Shirazian, Theoretical studies on copper extraction by means of polymeric membrane contactors. *Oriental Journal of Chemistry*, **2012**, *28(1)*: p. 23-28.
34. Marjani, A. and S. Shirazian, Application of CFD Techniques for Prediction of NH_3 transport through porous membranes. *Oriental Journal of Chemistry,* **2012**, *28(1):* p. 67-72.
35. Marjani, A. and S. Shirazian, Mathematical modeling and CFD simulation of hydrocarbon purification using membrane technology. *Oriental Journal of Chemistry,* **2012**, *28(1)*: p. 123-129.
36. Marjani, A., *et al.*, Mathematical modeling of gas separation in flat-sheet membrane contactors. *Oriental Journal of Chemistry,*

2012, *28(1):* p. 13-18.

37. Miramini, S.A., *et al*., CFD simulation of acetone separation from an aqueous solution using supercritical fluid in a hollow-fiber membrane contactor. *Chemical Engineering and Processing: Process Intensification,* **2013**, *72*: p. 130-136.
38. Moghadassi, A., *et al*., Gas separation properties of hollow-fiber membranes of polypropylene and polycarbonate by melt-spinning method. *Asian Journal of Chemistry,* **2011**, *23(5)*: p. 1922-1924.
39. Mohammadi, M., *et al*., Separation of greenhouse gases from gas mixtures using nanoporous polymeric membranes. *Polymer Engineering and Science*, **2015**, *55(5)*: p. 975-980.
40. Moradi, S., *et al*., 3 dimensional hydrodynamic analysis of concentric draft tube airlift reactors with different tube diameters. *Mathematical and Computer Modelling*, **2013**, *57(5-6)*: p. 1184-1189.
41. Nosratinia, F., M. Ghadiri, and H. Ghahremani, Mathematical modeling and numerical simulation of ammonia removal from wastewaters using membrane contactors. *Journal of Industrial and Engineering Chemistry*, **2014**, *20(5)*: p. 2958-2963.
42. Nosratinia, F., H. Ghahremani, and S. Shirazian, Preparation and characterization of nanoporous ceramic membranes for separation of water from ethanol. *Desalination and Water Treatment*, **2015**, *54*(6): p. 1550-1555.
43. Pishnamazi, M., *et al*., Mathematical modeling and numerical simulation of wastewater treatment unit using CFD. *Oriental Journal of Chemistry*, **2012**, 28(1): p. 51-58.
44. Ranjbar, M., *et al*., Computational Fluid Dynamics Simulation of Mass Transfer in the Separation of Fermentation Products Using Nanoporous Membranes. *Chemical Engineering and Technology*, **2013**, *36(*5): p. 728-732.
45. Razavi, S.M.R., A. Marjani, and S. Shirazian, CO_2 Capture from Gas Mixtures by Alkanol Amine Solutions in Porous Membranes. *Transport in Porous Media,* **2014**, *106(2):* p. 323-338.
46. Razavi, S.M.R., *et al*., CFD simulation of CO_2 capture from gas mixtures in nanoporous membranes by solution of 2-amino-2-methyl-1-propanol and piperazine. *International Journal of Greenhouse Gas Control*, **2013**, *15*: p. 142-149.
47. Razavi, S.M.R., S. Shirazian, and M.S. Najafabadi, Investigations on the ability of Di-Isopropanol amine solution for removal of CO_2 from natural gas in porous polymeric membranes. *Polymer Engineering and Science,* **2015**, *55(3):* p. 598-603.
48. Rezakazemi, M., *et al*., Numerical modeling and optimization of wastewater treatment using porous polymeric membranes. *Polymer Engineering and Science*, **2013**, *53(6)*: p. 1272-1278.
49. Rezakazemi, M., *et al*., Transient computational fluid dynamics modeling of pervaporation separation of aromatic/aliphatic hydrocarbon mixtures using polymer composite membrane. Polymer *Engineering and Science, **2013***, *53(7)*: p. 1494-1501.
50. Rezakazemi, M., A. Marjani, and S. Shirazian, Development of a group contribution method based on UNIFAC groups for the estimation of vapor pressures of pure hydrocarbon compounds. *Chemical Engineering and Technology*, **2013**, *36(3):* 483-491.
51. Rezakazemi, M., *et al*., CFD simulation of natural gas sweetening in a gas-liquid hollow-fiber membrane contactor. *Chemical Engineering Journal,* **2011**. *168(3)*: 1217-1226.
52. Rezakazemi, M., *et al*., CFD simulation of water removal from water/ethylene glycol mixtures by pervaporation. *Chemical Engineering Journal*, **2011**. 168(1): p. 60-67.
53. Rezakazemi, M., S. Shirazian, and S.N. Ashrafizadeh, Simulation of ammonia removal from industrial wastewater streams by means of a hollow-fiber membrane contactor. *Desalination,* **2012**, *285*: p. 383-392.
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

Exchange, **2010**, *28(2)*: p. 267-286.

55. Shirazian, S. and S.N. Ashrafizadeh, Mass transfer simulation of carbon dioxide absorption in a hollow-fiber membrane contactor. *Separation Science and Technology*, **2010**, *45(4)*: 515-524.
56. Shirazian, S. and S.N. Ashrafizadeh, Near-critical extraction of the fermentation products by membrane contactors: A mass transfer simulation. *Industrial and Engineering Chemistry Research,* **2011**, *50(4)*: 2245-2253.
57. Shirazian, S. and S.N. Ashrafizadeh, 3D Modeling and Simulation of Mass Transfer in Vapor Transport through Porous Membranes. *Chemical Engineering and Technology,* **2013**, *36(1):* p. 177-185.
58. Shirazian, S. and S.N. Ashrafizadeh, Optimum conditions for the synthesis of CHA-Type zeolite membranes applicable to the purification of natural gas. *Industrial and Engineering Chemistry Research*, **2014**. *53(31):* 12435-12444.
59. Shirazian, S. and S.N. Ashrafizadeh, Synthesis of substrate-modified LTA zeolite membranes for dehydration of natural gas. *Fuel,* **2015**, *148*: p. 112-119.
60. Shirazian, S. and S.N. Ashrafizadeh, Investigations on permeation of water vapor through synthesized nanoporous zeolite membranes; A mass transfer model. RSC Advances, **2015**, *5(39)*: 30719-30726.
61. Shirazian, S. and S.N. Ashrafizadeh, LTA and ion-exchanged LTA zeolite membranes for dehydration of natural gas. *Journal of Industrial and Engineering Chemistry,* **2015**, *22*: p. 132-137.
62. Shirazian, S., F. Fadaei, and S.N. Ashrafizadeh, Modeling of Thallium Extraction in a Hollow-Fiber Membrane Contactor. *Solvent Extraction and Ion Exchange*, **2012**, *30(5):* p. 490-506.
63. Shirazian, S., A. Marjani, and F. Fadaei, Supercritical extraction of organic solutes from aqueous solutions by means of membrane contactors: CFD simulation. *Desalination,* **2011**, 277(1-3): p. 135-140.
64. Shirazian, S., A. Marjani, and M. Rezakazemi, Separation of CO_2 by single and mixed aqueous amine solvents in membrane contactors: Fluid flow and mass transfer modeling. *Engineering with Computers,* **2012**, *28(2)*: p. 189-198.
65. Shirazian, S., A. Marjanm, and F. Azizmohammadi, Prediction of SO_2 transport across ceramic membranes using finite element method (FEM). *Oriental Journal of Chemistry*, **2011**, *27(2)*: p. 485-490.
66. Shirazian, S., A. Moghadassi, and S. Moradi, Numerical simulation of mass transfer in gas-liquid hollow fiber membrane contactors for laminar flow conditions. *Simulation Modelling Practice and Theory*, **2009**, *17(4):* p. 708-718.
67. Shirazian, S., S.G. Parto, and S.N. Ashrafizadeh, Effect of water content of synthetic hydrogel on dehydration performance of nanoporous LTA zeolite membranes. *International Journal of Applied Ceramic Technology,* **2014**, *11(5)*: p. 793-803.
68. Shirazian, S., *et al*., Implementation of the Finite Element Method for Simulation of Mass Transfer in Membrane Contactors. *Chemical Engineering and Technology,* **2012**, *35(6)*: p. 1077-1084.
69. Shirazian, S., *et al*., Hydrodynamics and mass transfer simulation of wastewater treatment in membrane reactors. *Desalination,* **2012**, *286*: p. 290-295.
70. Shirazian, S., *et al*., Development of a mass transfer model for simulation of sulfur dioxide removal in ceramic membrane contactors. *Asia-Pacific Journal of Chemical Engineering*, **2012**, *7(6)*: p. 828-834.
71. Sohrabi, M.R., *et al*., Theoretical studies on membrane-based gas separation using Computational Fluid Dynamics (CFD) of mass transfer. *Journal of the Chemical Society of Pakistan*, **2011**, *33(4)*: p. 464-473.
72. Sohrabi, M.R., *et al*., Preparation and simulation of polycarbonate hollow-fiber membrane for gas separation. *Asian Journal of Chemistry*, **2011**, 23(1): p. 302-304.
73. Sohrabi, M.R., *et al*., Mathematical modeling and numerical simulation of CO_2 transport through hollow-fiber membranes. *Applied Mathematical Modelling***, 2011**, *35(1):* p. 174-188.
74. Sohrabi, M.R., *et al*., Simulation studies on

H_2S absorption in potassium carbonate aqueous solution using a membrane module. *Asian Journal of Chemistry,* **2011**, *23(9)*: p. 4227-4228.

75. Sohrabi, M.R., *et al*., Simulation of ethanol and acetone extraction from aqueous solutions in membrane contactors. *Asian Journal of Chemistry*, **2011**, *23(9)*: p. 4229-4230.

76. Tahvildari, K., *et al*., Numerical simulation studies on heat and mass transfer using vacuum membrane distillation. *Polymer Engineering and Science*, **2014**, *54(11)*: p. 2553-2559.

77. Valavi, M., *et al*., Calculation of the density and activity of water in ATPS systems for separation of biomolecules. *Journal of Solution Chemistry,* **2013**, *42(7):* 1423-1437.