

# DESALINATION OF AQUEOUS SOLUTIONS BY LTA AND MFI ZEOLITE MEMBRANES USING PERVAPORATION METHOD

A. Malekpour<sup>1\*</sup>, A. Samadi-Maybodi<sup>2</sup> and M. R. Sadati<sup>2</sup>

<sup>1</sup>Department of Chemistry, University of Isfahan, Phone: +98 311 7932714,  
Fax: +98 311 6689732, Isfahan 81746-73441 Iran.  
E-mail: a.malekpour@sci.ui.ac.ir

<sup>2</sup>Department of Chemistry, Faculty of Basic Science, Mazandaran University, Babolsar, Iran.

(Submitted: October 8, 2010 ; Revised: February 22, 2011 ; Accepted: May 17, 2011)

**Abstract** - LTA and MFI zeolite membranes were hydrothermally grown on the surface of an  $\alpha$ -alumina porous support. The synthesized membranes were used for removal of cationic and anionic species from aqueous solutions by the pervaporation method. The perfection of the membranes was improved by employing the multi-stage synthesis method. The membranes were characterized by XRD, SEM and IR methods. The membranes were initially evaluated by the pervaporation separation of water from aqueous 2-propanol mixtures. The separation factors obtained were 7081 and 105 for NaA and ZSM-5 membranes, respectively. The ability of membranes for desalination of some aqueous solutions containing I<sup>-</sup>, Cs<sup>+</sup> and Sr<sup>2+</sup> ions was examined in various conditions. These ionic species were chosen because of their importance in the nuclear sciences. Both membranes effectively removed (more than 99 wt%) I<sup>-</sup>, Cs<sup>+</sup> and Sr<sup>2+</sup> from their single-salt solutions (0.001 mol dm<sup>-3</sup>) over a temperature range of 298–338 K. The effects of parameters such as time and temperature on the separation factors and fluxes were investigated. This work shows that, due to their excellent chemical, thermal and mechanical stability, the zeolitic membranes are useful for desalination of aqueous solutions and treating saline wastewaters by pervaporation. Therefore, this method has the ability to desalinate harsh environment solutions involving strong solvent and radioactive components.

**Keywords:** Desalination; Zeolite membranes; Pervaporation (PV); Ion rejection; Wastewater treatment.

## INTRODUCTION

Zeolites are inorganic crystalline structures with uniform-sized pores of molecular dimensions. These inorganic materials have been used extensively as catalysts and adsorbents. More recently, continuous polycrystalline zeolite layers have been deposited on porous supports and used as zeolite membranes (Bowen et al., 2004). A zeolite membrane is a porous layer that can separate mixtures by adsorption and diffusion differences and, in some cases, by molecular sieving. The first reported zeolite membranes were prepared by Suzuki (Suzuki, 1987)

and more than 12 zeolite structures have been prepared as membranes (Bowen et al., 2003).

The use of natural zeolites for environmental applications, especially for nuclear wastewaters and hazardous industrial wastes, is gaining new research interest, mainly due to their properties and significant worldwide occurrence (Kazemian, 1999; Panayotova, 2001; Petruzzelli et al., 1999; Wang et al., 2000). Different liquid wastes may be produced continuously or discontinuously and may vary considerably in volume, quality and chemical composition. A wide range of treatment methods has been used in industry to treat wastes. During the past

---

\*To whom correspondence should be addressed

5–10 years, membrane technology has been gradually introduced into nuclear power plants for treatment of low-level liquid radioactive wastes (LRWs). These processes are used for reduction of the discharge of radioactivity to the environment and to decrease solid waste from existing effluent treatment facilities (IAEA, 2004). Most research on zeolites in the nuclear waste field, based on the literature, has focused on the removal of cationic species such as cesium and strontium from nuclear wastewaters (Abusafa and Yucel, 2002, Dyer and Aggarwal, 1995).

Desalination is a novel application of zeolitic membranes for the treatment of hazardous wastes (Duke et al., 2007), although other inorganic membranes have been used to concentrate radioactive solutions by reverse osmosis and membrane distillation (Chmielewski et al., 2001; Zakrzewska-Trznadel et al., 2001).

Many papers in the field of application of zeolitic membranes have been reported (Okamoto et al., 2001; Pera-Titus et al., 2006; Pina et al., 2004). Pervaporation (PV) is a membrane separation technology in which a liquid feed mixture contacts the feed side of a selective membrane; the other side of the membrane is typically under vacuum to provide vapor permeate (Tuan et al., 2002). The potential of using zeolitic materials for membrane-based solvent separations like PV has only been realized in recent years (Shah et al., 2000). A zeolite membrane might be used for water PV since it shows not only molecular sieve effects, but also good thermal, chemical and mechanical stabilities (Ahn et al., 2006). Kumakiri et al. (2000) first applied the zeolite membranes in the reverse osmosis process. Their results showed 0.44 rejection from 10wt% ethanol water mixtures. Li et al. (2001; 2007) investigated the application of MFI zeolite membranes for removal of ions from aqueous solutions via reverse osmosis. They reported an experimental study of the reverse osmosis desalination of aqueous solutions using alumina-supported MFI-type zeolite membranes. In their work, high rejection values were obtained for a concentrated solution containing different types of cations (Li et al., 2007; 2004).

This study demonstrates the hydrothermal synthesis of zeolite A and ZSM-5 membranes on porous  $\alpha$ -alumina supports and evaluates their performance for removal of  $I^-$ ,  $Cs^+$  and  $Sr^{2+}$  ions from simulated wastewaters by the pervaporation (PV) method. The effects of time and temperature on the process were also investigated and discussed.

## EXPERIMENTAL

### Materials

A porous  $\alpha$ -alumina disc 20 mm diameter, with 1.2 mm thickness, 150 nm pore radius and about 30% porosity was prepared by the Materials and Energy Research Center (MERC) in Iran and was used as support for the membrane preparation. All chemicals, silicic acid (Merck, technical grade,  $SiO_2:0.5 H_2O$ ), sodium aluminate (Riedel-de Haen,  $Al_2O_3: 54\%$ ,  $Na_2O: 41\%$ ), sodium hydroxide (Merck, 99%), tetrapropylammonium hydroxide (Fluka, 20 wt% in water), and 2-propanol (Merck, 99.9%), cesium nitrate (Merck 99), strontium nitrate (Merck) and sodium iodide (Merck) were analytical grade and used without further purification. Zeolite A and ZSM-5 for seeding were provided by Merck and Aldrich, respectively.

### Membrane synthesis

The surface of the support was polished using 800 grade sandpaper on both sides and washed thoroughly with deionized water in an ultrasonic cleaner for 10 min to remove the loose particles created during polishing. A stable aqueous suspension of zeolite seed crystals ( $3g\ dm^{-3}$ ) was used to deposit the seeds on the surface of the porous supports through the dip-coating method.

Thin zeolite membrane layers were grown hydrothermally on the external surface of the supports. NaOH (0.723 g) was dissolved in  $0.08\ dm^3$  of distilled water. The solution was divided into two equal volumes and kept in polypropylene bottles. Aluminate solution was prepared by adding 6.212 g of sodium aluminate to one part of the NaOH solution. Silicate solution was prepared by adding 6.952 g of sodium silicate to another part of the NaOH solution. Homogenized gel was formed by mixing the silicate solution and aluminate solution. NaA zeolite is represented by the following molar ratio:  $1.926\ SiO_2:Al_2O_3:3.165\ Na_2O:128\ H_2O$ . The crystallization of the NaA zeolite membrane was carried out under autogenous pressure at 373 K for 3 h.

ZSM-5 zeolite membrane was prepared with a molar ratio of  $3.25\ Na_2O: 2TPAOH: Al_2O_3: 30\ SiO_2: 958\ H_2O$  (Thompson, 1982). The seeded support was placed vertically with a Teflon holder in a polyethylene autoclave to avoid any precipitation of zeolite crystals onto the support during the membrane synthesis. The synthesis solution was carefully added to a Teflon-lined stainless steel autoclave. For synthesis of the ZSM-5 zeolite

membrane, the autoclave was placed in an oven and heated to 453 K for 40 h. After hydrothermal treatment, the ZSM-5 zeolite membrane was calcined at 800 K for 3 h to burn out the template TPAOH.

The as-synthesized zeolite membranes were washed several times with deionized water until the pH value of the washings became neutral, then dried in air at 373 K for 24 h. In order to improve the quality of the NaA and ZSM-5 zeolite membranes, repeated synthesis (which is called multi-stage synthesis) was adopted. More continuous zeolitic layers of NaA and ZSM-5 zeolites form on the support after a three-stage synthesis and the perfection of the zeolite membranes is improved.

### Characterization

The structure of the as-synthesized membranes was determined by a Bruker D8-Advanced X-ray diffractometer (XRD) equipped with a Cu-K $\alpha$  radiation source ( $\lambda = 1.54056 \text{ \AA}$ ), employing a stepwise scanning with a step size of 0.05 in the ( $2\theta$ ) range from 5 to 90°.

The morphology and the thickness of the membranes were examined by scanning electron microscopy (SEM). SEM micrographs were obtained with a Philips XL30 microscope operated at 20 kV. The integrity and quality of the alumina-supported ZSM-5 and NaA membranes were further investigated through pervaporation measurements with 90 wt% 2-propanol in water.

### PV Experiments

PV experiments were performed by using an in-house designed apparatus shown in Fig. 1. The effective area of the membrane in contact with the

feed stream was  $3.14 \times 10^{-4} \text{ m}^2$ . The vacuum on the downstream side of the apparatus was maintained by using a vacuum pump (Alcatel, France). The test membrane was allowed to equilibrate for about half an hour in contact with the feed mixture before performing the PV experiment. After attaining the steady state, permeate was collected in the trap immersed in liquid nitrogen on the downstream side at a fixed time interval (1h). The experiments were carried out at 298, 323 and 338 K. After each desalination process, the permeate side of the support was flushed with deionized water to remove permeated salt.

Membrane performance in the PV experiments was evaluated by calculating the total flux ( $J$ ), the separation factor ( $\alpha$ ) for separation of water–alcohol mixtures and the rejection factor ( $R_i$ ) for desalination from ionic solutions. These parameters were calculated, respectively, using the following equations:

$$J = W/At \quad (1)$$

$$\alpha_{w/o} = (y_w/y_o)/(x_w/x_o) \quad (2)$$

$$R_i = \left[ \frac{(C_i)_F - (C_i)_P}{(C_i)_F} \right] \times 100 \quad (3)$$

where  $W$  is the mass of permeate (kg);  $A$  is the effective membrane area ( $\text{m}^2$ );  $t$  is the permeation time (h);  $x$  and  $y$  are the weight fractions of the components in the feed and the permeate, respectively. Subscripts  $W$  and  $O$  refer to water and organic liquid components and  $(C_i)_F$  and  $(C_i)_P$  are ion concentrations in the feed and permeate solutions, respectively.

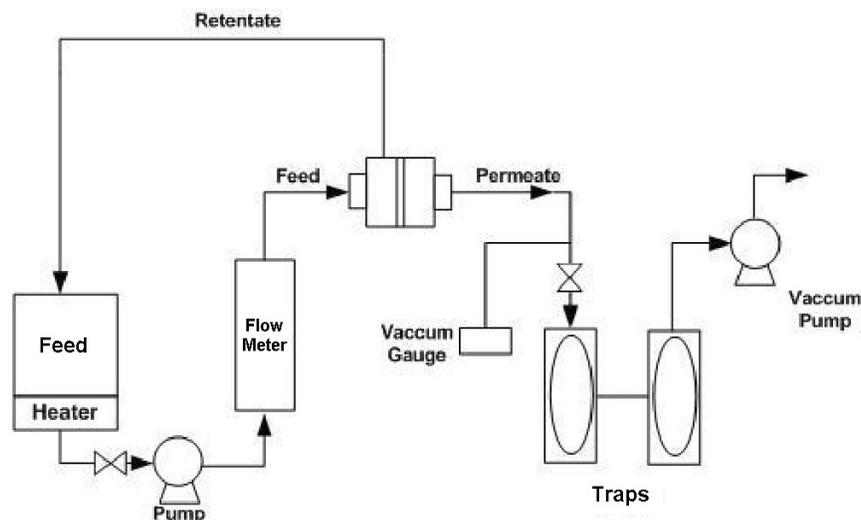


Figure 1: Experimental set up for pervaporation processes

A mixture of distilled water and 2-propanol were used as the feed solution in a 10/90 ratio; the amounts of 2-propanol were estimated by gas chromatography (GC) (Back Science Model 910 with FID detector). For desalination experiments, aqueous solutions containing  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> of the ionic species were used. Flame atomic absorption (FAA) (Varian Model Plus 20) was used for elemental analysis. The concentration of I<sup>-</sup> was measured with an ion selective electrode (Orion Model 53-94).

## RESULTS AND DISCUSSION

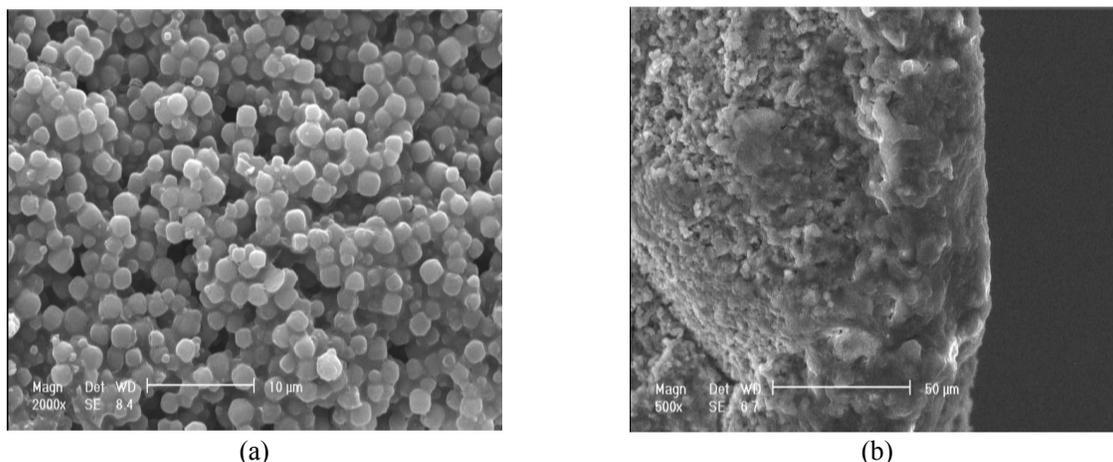
Comparison of the X-ray peaks and relative intensities with the standard NaA zeolite pattern shows that pure zeolite with the LTA-type structure is the only crystalline phase present in this sample, in agreement with our previous work (Malekpour et al., 2008).

Fig. 2 displays the SEM images of the NaA zeolite membranes from the top and a side view. After 3 h of hydrothermal treatment, the surface of the seeded support was completely covered with a continuous crystalline layer. The film thickness, obtained from the SEM cross-section, is about 15  $\mu$ m with 1-3  $\mu$ m diameter particles and was almost the same at different areas. No defects and no holes between the NaA crystals were observed.

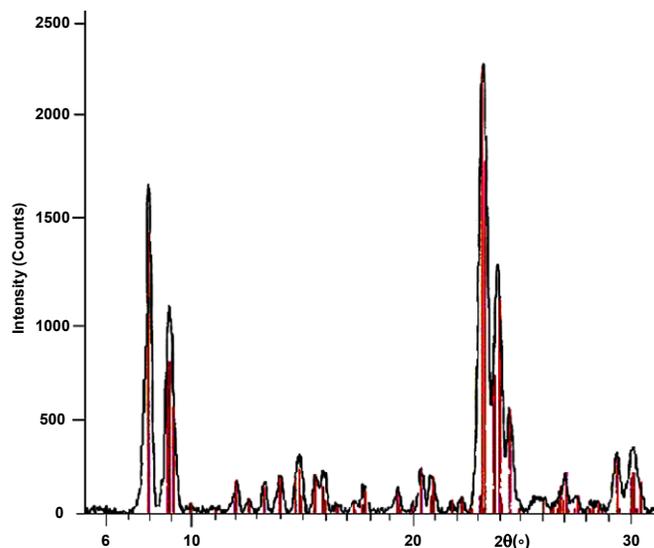
Fig. 3 shows the X-ray diffraction pattern of the ZSM-5 zeolite membranes synthesized under hydrothermal heating compared with standard ZSM-5 zeolite crystals. It can be seen that, after 40 h, the typical diffraction peaks of ZSM-5 crystals appeared, suggesting the formation of pure ZSM-5 crystals on the surface of the substrate.

SEM images of the synthesized membranes from the top and side view are shown in Fig. 4. Based on these images, after 40 h of hydrothermal treatment, the support was completely covered with 2–3  $\mu$ m diameter spherical ZSM-5 crystals to a thickness of about 10  $\mu$ m, the crystals being well compacted together on the surface of the support.

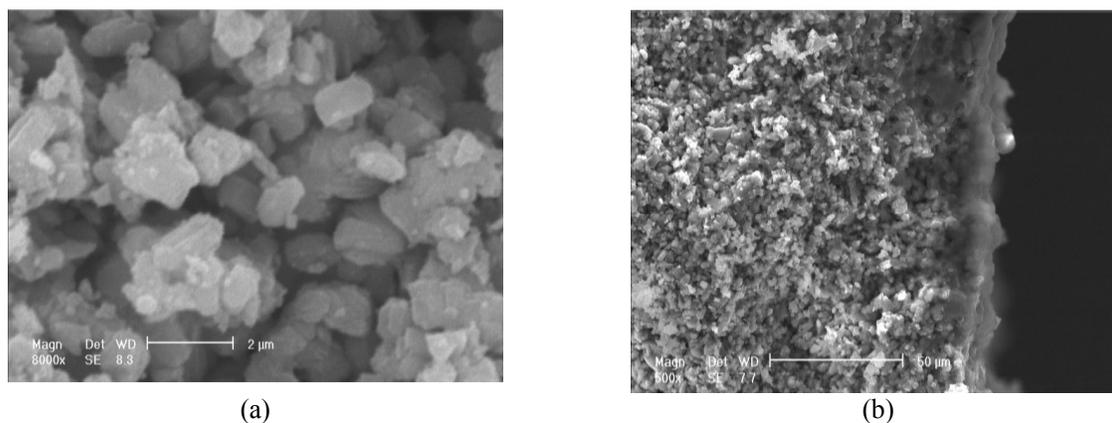
Initial experiments were performed to evaluate the quality of the membranes. For this propose, water removal from 2-propanol was achieved using the PV method. Pervaporation studies with a NaA membrane have been previously reported for water removal from highly concentrated 2-propanol solutions. Related results showed that NaA and ZSM-5 membranes achieved a very high separation factor and good permeation flux for removal of water (Abdollahi et al., 2007; Malekpour et al., 2008). Table 1 shows the separation factors and fluxes obtained in the pervaporation of 90 wt% 2-propanol–water solutions by as-synthesized membranes. Based on these data, NaA membranes show higher fluxes than ZSM-5 at similar feed concentrations and temperature. This is because the ZSM-5 zeolite membrane has a higher Si/Al ratio and is more hydrophobic than the NaA zeolite membrane. As the Si/Al ratio increases, the membrane becomes more hydrophobic and, consequently, the water adsorption on the membrane surface decreases. Although ZSM-5 pore diameters are larger than those of zeolite A, the separation factors for NaA membranes are higher than those for ZSM-5 membranes, probably because of pore diameters (about 4 Å) that are more efficient and more specific for water molecules. The results obtained show that the as-synthesized membranes are defect free and of high quality.



**Figure 2:** SEM images of NaA zeolite membrane after a three stage synthesis: (a) top; (b) cross section



**Figure 3:** XRD pattern of the ZSM-5 zeolite membrane on an alumina support.



**Figure 4:** SEM images of ZSM-5 zeolite membrane after a three stage synthesis: (a) top; (b) cross section

**Table 1: Fluxes and separation factors for pervaporation of water from 90 wt% 2-propanol/water through Zeolitic membranes**

Membrane	Flux ( $\text{mol m}^{-2} \text{h}^{-1}$ )	Separation factor ( $\alpha$ )	Temperature (K)
NaA	5.71	7081	298
ZSM-5	1.12	105	298

Figs. 5 and 6 show the variation of the water fluxes and ion rejections versus PV operation time for different ionic solutions. It is obvious that ions are effectively rejected from the membranes of NaA and ZSM-5 and that only water molecules are allowed to pass through the membranes. For all of the solutions, the water fluxes decreased while the ion rejections increased with time. The decrease of the water flux and the enhancement of ion rejection with time can be related to the hydration of the ions in solution and the surface of the membrane pores, which hinders the entry of water molecules and ions. Ion exchange of the investigated cations with sodium

cations can also affect the amounts of permeation. On the other hand, this behavior might be attributed to partial fouling of the membrane channels after passing salt solutions and closing the intra-crystalline pores (due to salt precipitation). After blocking of the non-zeolite pores, only zeolitic pores are responsible for water permeation, while ionic species cannot pass across these narrow channels. In the other words, the anions cannot move across the membrane channels because of the negative charge of the zeolite framework, so the cationic species also cannot move through the membrane channels (to keep charge neutrality).

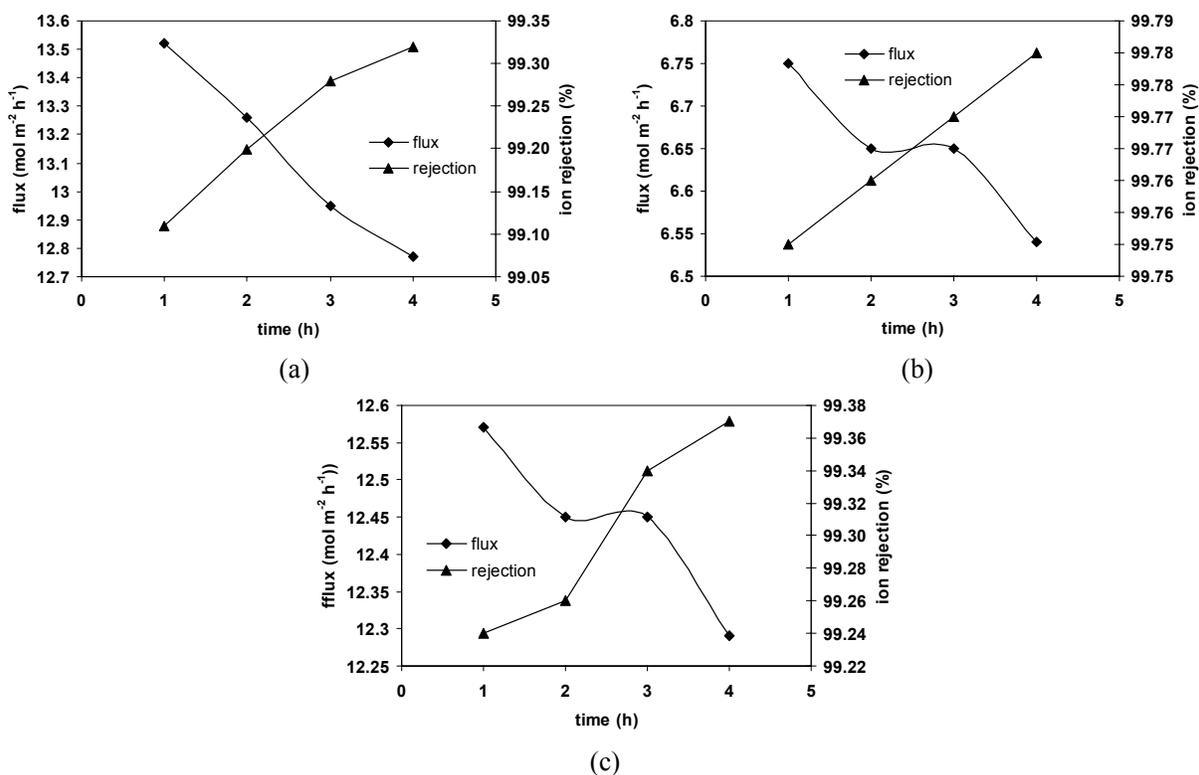


Figure 5: Flux and ion rejection vs. time for ionic solutions through a NaA membrane a) Cs<sup>+</sup>; b) Sr<sup>2+</sup>; c) I<sup>-</sup>

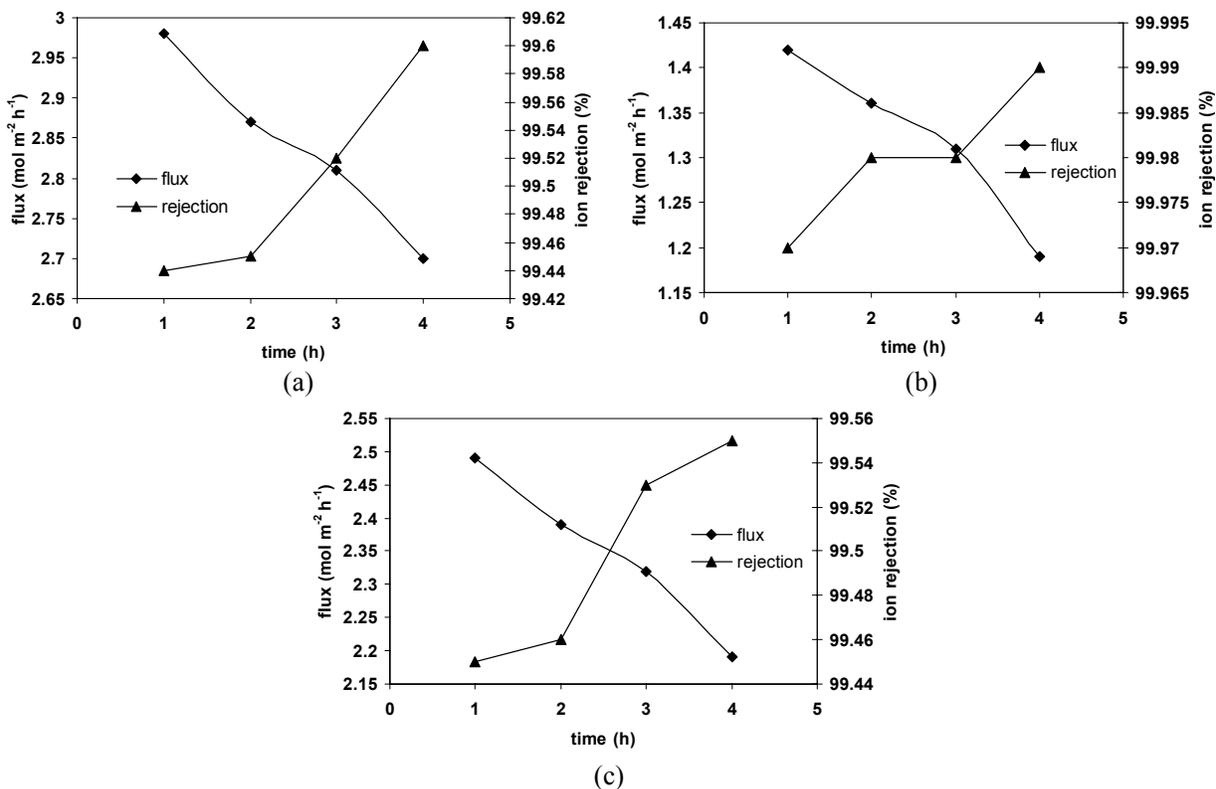


Figure 6: Flux and ion rejection vs. time for ionic solutions through a ZSM-5 membrane a) Cs<sup>+</sup>; b) Sr<sup>2+</sup>; c) I<sup>-</sup>

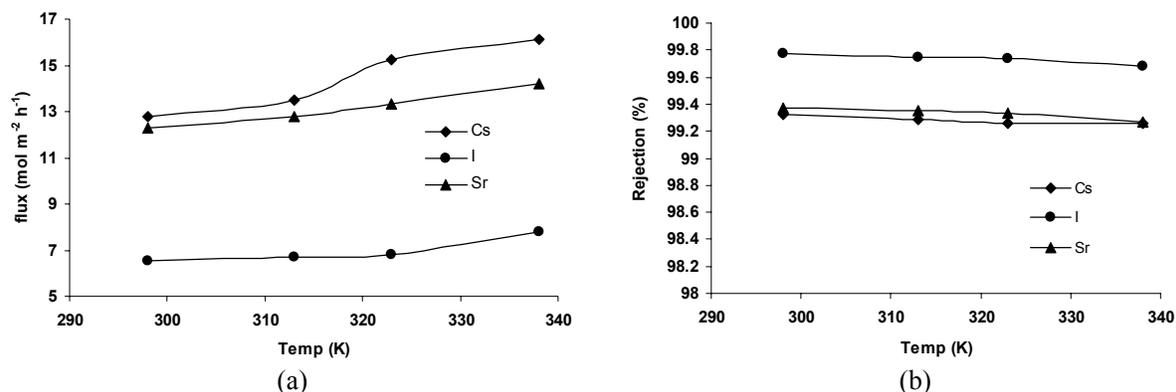
Temperature is an important parameter that can influence the membrane performance. Figs. 7 and 8 illustrate the effect of temperature on the pervaporation flux and ion rejection for different solutions. The results reveal that the fluxes are more temperature dependent than the ion permeance and rejection (the intrinsic membrane properties). The results indicated that the flux values increased with increasing temperature, whereas rejection values decreased smoothly. The effect of temperature on viscosity can be at least partially responsible for the flux increases. Therefore, with increasing temperature, the mobility of water molecules in zeolitic channels increases and thus fluxes increase.

Our results also confirmed that raising the temperature increased the water flux and ion diffusion and decreased slightly the ion rejection rate for both NaA and ZSM-5 zeolite membranes. We believe that, since the adsorption of water molecules on the membrane surface is exothermic, water molecules passing out from the zeolitic channels could be an important factor in the separation process. At high temperature, due to decreasing interaction between permeates and membrane, the permeation of diffusing molecules and ions through the membrane becomes easier and, consequently, it

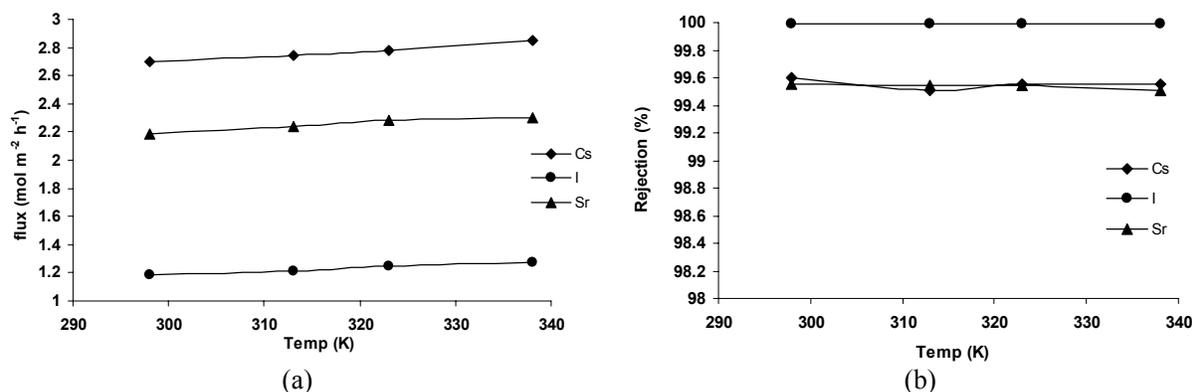
causes the flux to increase and decreases rejection. This fact is related to the fugacities of each component in the feed, which are the driving forces for adsorption from liquids during pervaporation. Fugacity is a form of the chemical potential and it is the driving force for mass transfer from one phase to another. At constant concentration, fugacity increases with temperature. As a result, the transfer of water molecules and ions increases throughout the NaA and ZSM-5 zeolite membranes. Therefore, the flux increases and rejection decreases with temperature.

The lowest flux was obtained for iodide solutions, although their rejection factor was high. Iodide anions diffuse slower than cesium and strontium cations because the iodide anion has a larger hydrated radius relative to cesium and strontium ions; therefore, the flux for iodide is the lowest relative to the other ions. Moreover, iodide anions can be less absorbed and more difficult to pass through the membrane because of the intrinsic negative charge in zeolite structures.

It must be emphasized that structural defects and non-zeolite pores in zeolite membranes could increase water transport. These not only cause lower separation factors during organic/water separations, but also should lower the rejection of ions from saline solutions.



**Figure 7:** Variation of flux (a) and rejection (b) versus temperature for  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$  and  $\text{I}^-$  ionic solutions for a NaA membrane



**Figure 8:** Variation of flux (a) and rejection (b) versus temperature for  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$  and  $\text{I}^-$  ionic solutions for a ZSM-5 membrane

## CONCLUSIONS

The NaA and ZSM-5 zeolite membranes not only can separate water from organic molecules, but are also capable of removing ions from aqueous solutions. The pervaporation studies with synthesized membranes demonstrated that the excellent properties of these membranes make them good candidates for concentration of hazardous wastewaters and also different ionic solutions. For all of the feed solutions, rejection values of more than 98 wt% were obtained. When the temperature is increased, there is an increase in permeation flux and a decrease in the rejection. Desalination experiments for several single-salt solutions confirmed that this method could be used for the processing and concentration of hazardous wastes such as radioactive waste with minimal consumption of energy and without air pollution problems. The results of this work can be used for developing a new method for removal of radionuclide species from heavy water in nuclear reactors.

## REFERENCES

- Abdollahi, M., Ashrafizadeh, S. N., Malekpour, A., Preparation of zeolite ZSM-5 membrane by electrophoretic deposition method. *Microporous Mesoporous Mater.*, 106, No. 1-3, 192-200 (2007).
- Abusafa, A., Yucel, H., Removal of Cs-137 from aqueous solutions using different cationic forms of a natural zeolite: clinoptilolite. *Sep. Purif. Technol.*, 28, No. 2, 103-116 (2002).
- Ahn, H., Lee, H., Lee, S. B., Lee, Y., Pervaporation of an aqueous ethanol solution through hydrophilic zeolite membranes. *Desalination*, 193, No. 1-3, 244-251 (2006).
- Bowen, T. C., Li, S. G., Noble, R. D., Falconer, J. L., Driving force for pervaporation through zeolite membranes. *J. Membr. Sci.*, 225, No. 1-2, 165-176 (2003).
- Bowen, T. C., Wyss, J. C., Noble, R. D., Falconer, J. L., Measurements of diffusion through a zeolite membrane using isotopic-transient pervaporation. *Microporous Mesoporous Mater.*, 71, No. 1-3, 199-210 (2004).
- Chmielewski, A. G., Harasimowicz, M., Tyminski, B., Zakrzewska-Trznadel, G., Concentration of low- and medium-level radioactive wastes with three-stage reverse osmosis pilot plant. *Separation Science and Technology*, 36, No. 5-6, 1117-1127 (2001).
- Duke, M. C., Mee, S., da Costa, J. C. D., Performance of porous inorganic membranes in non-osmotic desalination. *Water Res.*, 41, No. 17, 3998-4004 (2007).
- Dyer, A., Aggarwal, S., Removal of fission products from mixed solvents using zeolites .1. Ruthenium removal. *J. Radioanal. Nucl. Chem.*, 198, No. 2, 467-474 (1995).
- IAEA, T. R. S. N., Application of Membrane Technologies for Liquid Radioactive Waste Processing. in, *International Atomic Energy Agency, Vienna*, pp. 431, (2004).
- Kazemian, H., Ph D. Thesis, University of Isfahan, Isfahan, Place Published (1999).
- Kumakiri, I., Yamaguchi, T., Nakao, S. I., Application of a zeolite A membrane to Reverse Osmosis Process. *J. Chem. Eng. Jpn.*, 33, No. 1, 333 (2000).
- Li, L. X., Dong, J. H., Nenoff, T. M., Transport of water and alkali metal ions through MFI zeolite membranes during reverse osmosis. *Sep. Purif. Technol.*, 53, No. 1, 42-48 (2007).
- Li, L. X., Dong, J. H., Nenoff, T. M., Lee, R., Reverse osmosis of ionic aqueous solutions on a MFI zeolite membrane. *Desalination*, 170, No. 3, 309-316 (2004).
- Malekpour, A., Millani, M. R., Kheirkhah, M., Synthesis and characterization of a NaA zeolite membrane and its applications for desalination of radioactive solutions. *Desalination*, 225, No. 1-3, 199-208 (2008).
- Okamoto, K., Kita, H., Horii, K., Tanaka, K., Kondo, M., Zeolite NaA membrane: Preparation, single-gas permeation, and pervaporation and vapor permeation of water/organic liquid mixtures. *Ind. Eng. Chem. Res.*, 40, No. 1, 163-175 (2001).
- Panayotova, M. I., Kinetics and thermodynamics of copper ions removal from wastewater by use of zeolite. *Waste Management*, 21, No. 7, 671-676 (2001).
- Pera-Titus, M., Mallada, R., Llorens, J., Cunill, F., Santamaria, J., Preparation of inner-side tubular zeolite NaA membranes in a semi-continuous synthesis system. *J. Membr. Sci.*, 278, No. 1-2, 401-409 (2006).
- Petruzzelli, D., Pagano, M., Tiravanti, G., Passino, R., Lead removal and recovery from battery wastewaters by natural zeolite clinoptilolite. *Solvent Extr. Ion Exch.*, 17, No. 3, 677-694 (1999).
- Pina, M. P., Arruebo, M., Felipe, A., Fleta, F., Bernal, M. P., Coronas, J., Menendez, M., Santamaria, J., A semi-continuous method for the synthesis of NaA zeolite membranes on tubular

- supports. *J. Membr. Sci.*, 244, No. 1-2, 141-150 (2004).
- Shah, D., Kissick, K., Ghorpade, A., Hannah, R., Bhattacharyya, D., Pervaporation of alcohol-water and dimethylformamide-water mixtures using hydrophilic zeolite NaA membranes: mechanisms and experimental results. *J. Membr. Sci.*, 179, No. 1-2, 185-205 (2000).
- Suzuki, H., Composite membrane having a surface layer of an ultrathin film of cage-shaped zeolite and processes for production thereof. U.S. Patent 4 699 892 (1987).
- Thompson, R. W., Huber, M. J., Verified Synthesis of Zeolitic Materials, *Journal of Crystallography*, 56, No. 711 (1982).
- Tuan, V. A., Li, S. G., Falconer, J. L., Noble, R. D., Separating organics from water by pervaporation with isomorphously-substituted MFI zeolite membranes. *J. Membr. Sci.*, 196, No. 1, 111-123 (2002).
- Wang, S. X., Wang, L. M., Ewing, R. C., Electron and ion irradiation of zeolites. *J. Nucl. Mater.*, 278, No. 2-3, 233-241 (2000).
- Zakrzewska-Trznadel, G., Harasimowicz, M., Chmielewski, A. G., Membrane processes in nuclear technology - application for liquid radioactive waste treatment. *Sep. Purif. Technol.*, 22-3, No. 1-3, 617-625 (2001).