*Desalination and Water Treatment*
www.deswater.com
doi: 10.1080/19443994.2014.996770

57 (2016) 4749–4755
March

Taylor & Francis
Taylor & Francis Group

# Pervaporative desalination of seawater by using composite and blended poly (vinyl alcohol) membranes

Filiz Ugur Nigiz*, Nilufer Durmaz Hilmioglu

*Engineering Faculty, Departments of Chemical Engineering, Kocaeli University, Kocaeli 41380, Turkey, Tel. +90 262 303 35 38, +90 262 303 35 45; emails: filiz.ugur@kocaeli.edu.tr (F.U. Nigiz), niluferh@kocaeli.edu.tr (N.D. Hilmioglu)*

Received 17 February 2014; Accepted 30 November 2014

## ABSTRACT

In this study, pervaporative separation capability of poly(vinyl alcohol) (PVA) based different membranes were investigated. Pristine, zeolite-loaded and blended PVA membranes were prepared by solution-casting and cross-linking method. Zeolite 3A was used to make PVA more stable and durable during the different operation conditions. Sodium alginate has strong hydrophilic bond structure so it was used to enhance water flux. Flux and salt retention values were investigated over temperature range of 293–313 K. Pervaporation performances were evaluated as function of flux and salt retention. At low temperature, ion passage was prevented and 100% salt retention was achieved by all membrane types. As the temperature increased from 293 to 318 K, salt retention dramatically decreased. Increasing zeolite loading positively affected the water flux. Also, blended membrane gave better flux results than pristine PVA.

*Keywords:* Pervaporative desalination; Poly(vinyl alcohol); Sodium alginate; 3A

## 1. Introduction

Desalination is one of the important issues for the clean water and environment policies. Environmental impact, limited fresh water sources, uncontrolled discharging of industrial wastewater to the sea and oceans increase the importance of treatment technologies. Especially in countries with limited fresh water resource, water demands have been supplied from the sea or oceans. Treated water can be used as process, boiler or drinking water. For this reason, those countries have advanced desalination technology. If the global warming and climate change continue to rise rapidly, the other countries will soon come up against with lack of water. Therefore, it is necessary for all regions to create and develop their own water treatment technology.

Thermal treatment and membrane separation are mostly used as a commercial desalination system. Multi-stage distillation is one of the best-known thermal desalination techniques [1]. A large amount of sea, ocean or brackish water can be easily converted to fresh water by distillation method. However, energy consumption and complicated process steps have forced the researchers to develop more effective methods such as reverse osmosis (RO) [2].

RO is a well-known membrane separation system for producing drinking water from waste or ionic water resources. In this method, membrane is employed to retain the dissolved salt ions. It has nano-sized pore diameters and it allows to control the passage of minerals. So it is mostly used to treat drinking

---

*Corresponding author.

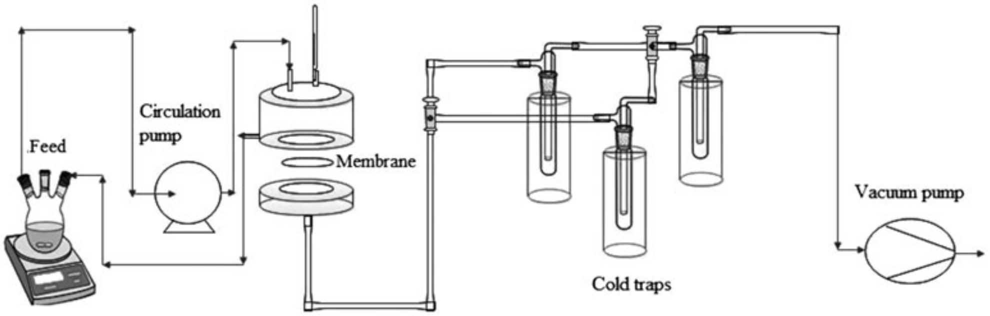

Fig. 1. Experimental pervaporation unit.

water. Because of the nanosized membranes used in RO, pressure demand is much higher than that of microfiltration and ultrafiltration [2]. Membrane life, cross-pressure difference, and water flux are the main factors for determining of the RO efficiency. Polymeric, inorganic or composite materials can be formed as RO membrane. Polymeric ones are selected due to easy membrane forming ability. However, polymeric ones are suffering from the membrane fouling. Because of the membranes direct contact with microorganism and inorganic impurities in water, inorganic or composite membranes are preferred in order to reinforce the membrane structure [3–6].

Except for drinking water, in many of industrial processes—such as food and electricity manufacturing—it is necessary to use non-ionic water. So the deep desalination techniques are required [7,8]. Thermal treatment can supply non-ionic water. However, energy consumption prohibits the process efficiency. During the several years, researchers have investigated the availability of pervaporation as alternative to thermal treatment and RO for deep desalination [9–12].

Pervaporation (PV) is a promising technology for effective separation of ions, heavy metals, solvents, and impurities in water. PV is used for desulfurization, volatile organic compound removal, aroma recovery, alcohol dehydration, wastewater treatment, biofuel dehydration [13–19]. It is cost effective and environmental friendly method to separate azeotropic mixtures. It is also used to recover the thermal sensitive component without using any thermal separation technique. Therefore, it is safely used in the pharmaceutical industry. A simple laboratory scale PV unit for desalination has been shown in Fig. 1.

In PV, driving force is the concentration gradient and it is maintained by vacuum applying. Desalination by PV occurs in three main steps—dissolving of seawater on the top surface of the membrane, diffusion of water through the membrane, and desorption of water to the downstream side of the membrane. This transport system is known as solution–diffusion phenomena [20–22]. The important differences of PV from the other membrane processes are the non-porous membrane usage and phase change during the operation. Owing to the vacuum pressure, water transports to the downstream side as vapor phase. Just the same as RO membranes, polymeric, inorganic or composite membrane materials can be preferred to produce non-porous PV membrane. Differently from the RO, membrane affinity is much important than membrane porosity. Non-porous membrane usage provides selective separation ability to PV and it cannot allow the passage of ionic components or impurities. The major subjects that affect the pervaporative transition are—affinity of the membrane to the selected component, hydrogen bonding ability, and water-membrane interaction [20–23].

Salt is present as dissolved ion form in seawater so it is not possible to vaporize ions in PV. Hence, the passage of ions is prevented by non-porous PV membrane. Meanwhile, phase change provides an advantage in pervaporative seawater desalination method.

In this work, pristine, zeolite-loaded and blended poly(vinyl alcohol) (PVA) membranes have been prepared for pervaporative desalination of salt solution and seawater. Seawater has been supplied from the Marmara Sea in Turkey. Owing to the small cage size, zeolite 3A (0.27 nm cage size) has been preferred as inorganic filler to reinforce the polymer stability and durability. It is an appropriate zeolite type to retain the salt ions such as $Na^+$ (0.72 nm kinematic diameter) and $Cl^-$ (0.66 nm kinematic diameter) ions. Sodium alginate (NaAlg) has also been used as blending polymer to enhance the water flux. It is a well-known hydrophilic biopolymer.

## 2. Experimental

Pristine, zeolite-loaded and blended membranes were prepared by solution-casting method. All membranes were cross-linked with glutaraldehyde (GA) to make membranes insoluble in water.

### 2.1. Material

PVA, GA, sodium alginate, and zeolite 3A have been purchased from Aldrich Chemicals, 99.5% purity ethanol, acetone, HCl have been purchased from Merck Chemicals. Deionized water has been supplied from the laboratory. 3 wt.% NaCl test solution has been prepared in laboratory. Seawater has been supplied from the Gulf of Izmit, Kocaeli, Turkey.

### 2.2. Membrane preparation

Pristine PVA membrane preparation: 7 wt.% PVA-water solution was prepared and it was stirred for four hours at 90˚C. After a homogenous polymer solution was obtained, it was poured onto a glass petri dish and dried for 2 d at room temperature. After the pristine PVA membrane film had been formed, it was cross-linked in GA, acetone, water, and HCl bath.

Zeolite 3A-loaded PVA membrane preparation: Desired amount of zeolite (5, 10 wt.% zeolite with respect to pure polymer mass) was added to the 7 wt.% PVA-water solution. Polymer-zeolite solution was stirred for 24 h, poured onto a glass petri dish and dried at room temperature. Dried membranes were cross-linked in GA, HCl, acetone, and water bath.

PVA-NaAlg blend membrane preparation: 4 wt.% NaAlg-water solution was prepared and stirred for 24 h at room temperature. After a homogenous solution was obtained, it was blended with the 7 wt.% PVA-water solution (3:1 PVA:Alg solution weight ratio). Blended solution was stirred for two hours and casted onto a glass petri dish. After membrane dried at room temperature, it was cross-linked.

### 2.3. Membrane characterization

Zeolite distribution in sodium alginate matrix and polymer characterization were analyzed using a JEOL JSM-6335 F field emission scanning electron microscope. Liquid nitrogen was used to break the membrane samples. The samples were coated with gold before the analysis.

### 2.4. Pervaporation experiments

PV experiments were carried out at three different temperatures (293, 303, 313 K) and with different zeolite loading (pristine, 5 and 10 wt.% 3A). The effective membrane area was 28.26 cm$^2$, the membrane cell capacity was 500 ml. Upstream side of the membrane was kept at atmospheric pressure and downstream side of the membrane was kept at 30 mbar. Pervaporative desalination of seawater was operated for five hours. Salt concentrations of permeate and retentate sample's were determined by using refractive index and conductivity. The performance of the system has been evaluated as a function of flux ($J$) and salt retention ($R$). In PV process, flux determines the membrane productivity and salt retention determines the selectivity of membrane.

$$J = W_p/A \cdot t \tag{1}$$

$$R = (C_f - C_p/C_f) * 100 \tag{2}$$

$W_p$ represents the total permeate mass of mixtures, $A$ is the effective area of the membrane, and $t$ is the time. $C_f$ and $C_p$ represent the salt concentration in the feed and permeate mixture, respectively [10,21].

## 3. Results and discussion

In this study, effects of the zeolite loading and temperature on PV flux and salt retention have been investigated. PV is mostly used for liquid–liquid separation. Alter from the other PV processes, one of the components is non-volatile in pervaporative desalination. Therefore, the transition performance is directly dependant on the membrane–water interaction.

### 3.1. SEM analysis of loaded and blended membranes

Cross-sectional and surface SEM micrographs of zeolite-loaded membrane have been shown in Fig. 2(a) and (b). Homogeneous zeolite distribution can be clearly seen in Fig. 2(a). Fig. 2(b) also indicates the zeolite-polymer compatibility.

Fig. 2(c) displays the alginate and PVA polymer structure. Alginate is a natural polymer whereas PVA is a synthetic polymer. Two structures can be clearly seen in SEM micrographs.

### 3.2. Effect of temperature and zeolite loading on membrane flux

As indicated from the Fig. 3 that the flux values enhanced as the temperature increased. Effect of temperature can be evaluated with regards to polymeric structure and solution thermodynamic. Due to the vapor pressure increment of the components, it is

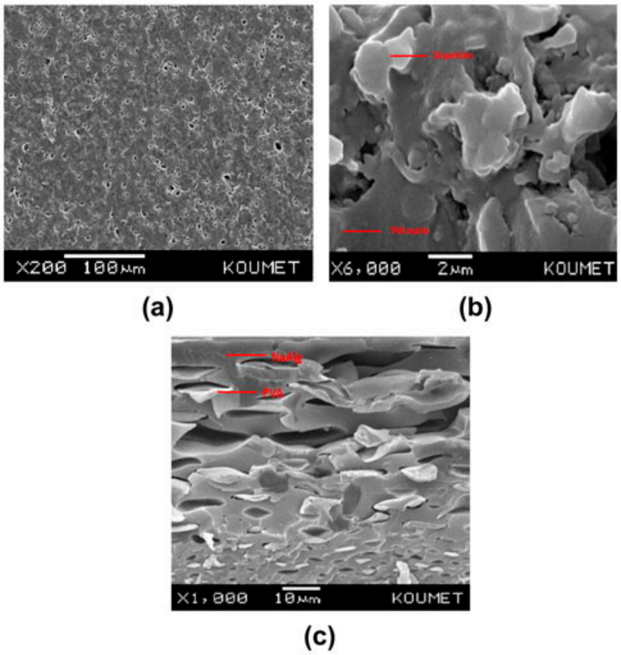

Fig. 2. (a) Surface and cross-sectional, (b) micrograph of 5 wt% zeolite-loaded membranes and cross-sectional, and (c) micrograph of NaALg-PVA-blended membrane.

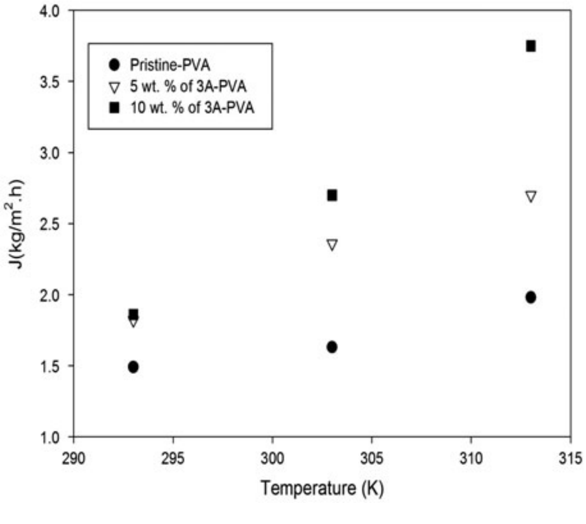

Fig. 3. Effect of temperature on flux.

expected that the flux enhances as the feed temperature increases. In addition to that diffusion rate of liquid component increases with temperature.

Temperature also affects the segmental motion of polymeric materials. Because of the non-porous membrane is used in PV, separation and molecular transition occur inside the intermolecular void spaces of the membrane material. In polymeric ones, segmental motions of flexible organic chains increase with temperature. Therefore, expanded voids increase the rate of permeation. As seen in Fig. 3, as the temperature increased from 293 to 313 K, flux increased from 1.86 to 3.75 kg/m$^2$h when 10 wt.% 3A-loaded membrane was used.

It was observed from the Fig. 4 that the zeolite loading enhanced the water flux. Zeolite 3A is the potassium form of A-type zeolites. It tends to absorb water. And the cage size of zeolite (2.7A) is appropriate to allow the passage of water molecules. As can be seen in Fig. 4, when zeolite loading increased from 0 to 10 wt.% flux values enhanced from 1.98 to 3.75 kg/m$^2$h at 313 K.

### 3.3. Effect of temperature and zeolite loading on salt retention

It is well known that the temperature directly affects the flexible chain mobility of polymers. As the temperature increases, chain motion of polymer increases and intermolecular free spaces enlarge. As mentioned in Section 3.2, void enlargement causes an increment in permeation through the membrane. However, this structural expansion can cause an unselective removal. Therefore, salt ions can be easily drifted with water and they can pass through the membrane. As expected, a decline trend in salt retention value was seen with increasing temperature as it was confirmed in Fig. 5.

This decrement trend was seen more significant when 10 wt.% 3A-loaded membrane was used. Salt retention decreased from 100 to 77% as the

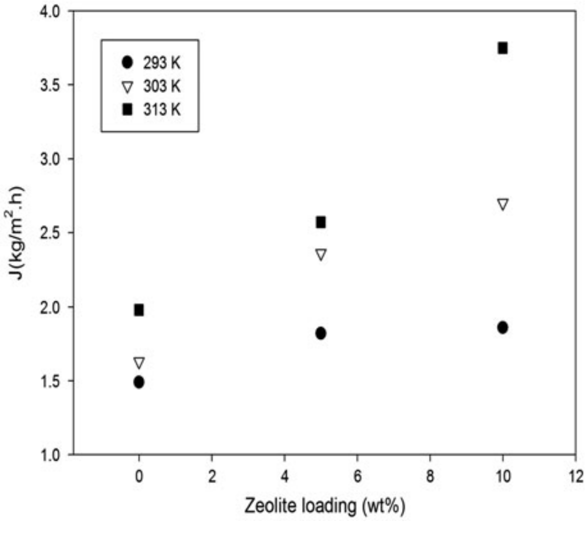

Fig. 4. Effect of zeolite loading on flux.

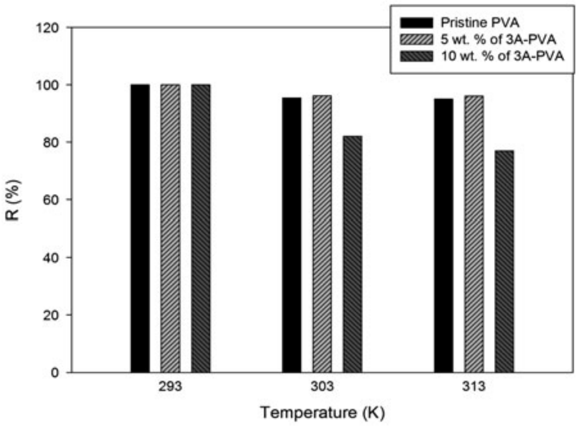

Fig. 5. Effect of temperature and zeolite loading on salt retention.

temperature increased from 293 to 313. Typically, zeolites prevent the sudden change, such as flux change, in polymer matrix caused by temperature. In this study, membrane preparation could change that viewpoint. PVA is a rigid polymer and it is difficult to produce a composite (polymer-zeolite) membrane without any contact-free regions in the matrix. If the adhesion between the zeolite and polymer is weak, non-selective contact free regions or holes occur. Overloading of zeolite and zeolite agglomeration can cause weaker adhesion due to the continuous zeolite phase forming. Zeolite should be homogeneously distributed in the polymer matrix. For this purpose, optimum zeolite loading should be selected. In this study, this status was clearly seen at 10 wt.% 3A-loaded membrane. With temperature increasing, the difference became more effective due to the increasing movement and relaxation trends of polymer chains. Higher flux value was achieved by this membrane, but it was not accompanied with higher salt retention. Flux and salt retention cannot be considered separately. Hence, it is possible to evaluate that the 5 wt.% 3A-loaded membrane showed better performance than that of pristine and 10 wt.% 3A-loaded ones. At low temperature, 100% salt retention values were achieved by all membranes. At high temperature, 96 and 95% salt retention values were achieved by 5 wt.% 3A-loaded and pristine membranes, respectively.

### 3.4. Effect of polymer blending on pervaporation performance

In our previous work, 3A filled sodium alginate membranes were used for pervaporative desalination. In the previous work, alginate membranes were prepared and performed to desalinate the salt solution and seawater [24]. Compared to PVA membranes, alginate membranes showed better flux. However, PVA exhibits selective behavior to retain the salt ions. Membrane productivity is important as membrane selectivity. Therefore, in this study, PVA was also blended with alginate. As seen in Fig. 6, flux values of blended membrane were higher than that of PVA but lower than that of alginate polymers.

According to the rule of mixing phenomena in polymers, blended membrane had the characteristics of both alginate and PVA polymers. Owing to the hydrophilic and water affinity properties of alginate, the flux increment was expected. However, the factors (such as temperature and NaAlg mixing) enhanced the flux, decreased the salt retention as seen in Table 1.

Hence it was concluded that the 5 wt.% 3A loading was appropriate membrane to obtain better performance in desalination process by PV.

### 3.5. Seawater desalination results of PVA membrane

In this study, 3.5 wt.% NaCl solution was used to determine the membrane behavior on pervaporative desalination. Best result was obtained by using 5 wt.% 3A-loaded membrane. Hence, 5 wt.% 3A-loaded membrane was used to desalinate Marmara seawater. Desalination results have been seen in Table 2.

Table 2 clearly shows that the flux and retention values of seawater desalination were higher than that of NaCl salt solution. Due to the presence of other salt ions—such as potassium, calcium—in seawater, the

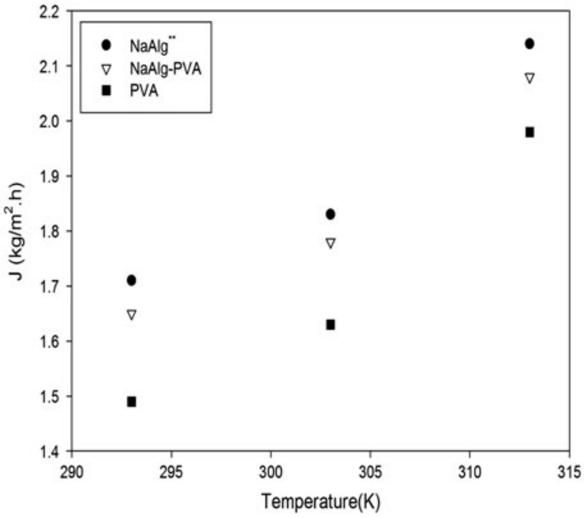

Fig. 6. Comparison of desalination flux (NaAlg** results referred from Nigiz and Hilmioglu [24].)

Table 1
Comparison of pervaporative desalination results with different membranes

| Membrane type | Temperature (K) | Flux (kg/m$^2$ h) | Retention (%) |
|---|---|---|---|
| PVA | 293 | 1.49 | 100 |
| | 303 | 1.63 | 95.8 |
| | 313 | 1.98 | 95 |
| NaAlg** | 293 | 1.71 | 99.9 |
| | 303 | 1.83 | 94.4 |
| | 313 | 2.14 | 89.5 |
| PVA-Alg | 293 | 1.65 | 100 |
| | 303 | 1.78 | 95.4 |
| | 313 | 2.08 | 92.1 |

Note: NaAlg**, results referred from Nigiz and Hilmioglu [24].

Table 2
Comparison of pervaporation performance of seawater with salt solution

| Membrane type | Mixture | Temperature (K) | Flux (kg/m$^2$.h) | Retention (%) |
|---|---|---|---|---|
| wt. 5% zeolite-loaded PVA | Seawater | 293 | 2.71 | 100 |
| | | 303 | 3.21 | 99.9 |
| | | 313 | 3.45 | 97.6 |
| wt. 5% zeolite-loaded PVA | wt. 3.5% NaCl | 293 | 1.82 | 100 |
| | | 303 | 2.36 | 96.1 |
| | | 313 | 2.57 | 96 |

concentration was higher than NaCl solution. Higher concentration gradient between the sides of membrane accompanied with the higher flux. Also the salt retention values proved that the desalination was efficiently achieved with optimum-loaded PVA membrane. At low temperature, it was not seen any salt ions in the permeate phase within an hour.

## 4. Conclusions

This study focused on the pervaporative desalination performance of non-porous pristine, composite and blended PVA membranes. Owing to the mechanical stability and durability of the PVA polymer, it was selected as polymer matrix. Effects of zeolite loading, temperature, and membrane types were evaluated as a function of flux and salt retention. The significant results of this study were summarized below:

(1) Zeolite incorporation increased the flux values for all membranes at all temperatures. As zeolite loading was increased from 0 to 10 wt. %, flux enhanced from 1.98 to 3.75 kg/m$^2$.h at 313 K.
(2) NaAlg-PVA-blended membrane gave better flux value than pristine PVA due to the high hydrophilic character of alginate polymer.
(3) At low temperature, 100% salt retention was achieved by all membrane types (pristine, composite, and blended). However, as the temperature increased from 293 to 313 K, retention values decreased. Significant decrement trend was seen (from 100 to 77%) with 10 wt.% 3A-loaded membrane.
(4) Better flux was accompanied with better salt retention with 5 wt.% 3A-loaded membrane.

These results supported the consideration of PV that being an effective method to purify water at low temperature. Better performance was achieved by using 5 wt.% zeolite-loaded membrane. Therefore, the seawater experiment was performed by 5 wt.% 3A-loaded membrane. In seawater experiment, better flux and retention results were obtained.

## Acknowledgments

This study was financially supported by Scientific Research Projects Unit of Kocaeli University.

## Nomenclature

*Abbreviations*

| | | |
|---|---|---|
| NaAlg | — | sodium alginate |
| PVA | — | polyvinylalcohol |
| HCl | — | hydrochloric acid |
| GA | — | gluteraldehyde |
| RO | — | reverse osmosis |
| NaCl | — | sodium chloride |
| PV | — | pervaporation |

*Symbols*

| | | |
|---|---|---|
| $A$ | — | effective membrane area |
| $J$ | — | flux |
| $t$ | — | operation time |
| $W_p$ | — | weight of permeate |
| $R$ | — | salt retention |
| $C_f$ | — | salt concentration in feed |
| $C_p$ | — | salt concentration in permeate |

## References

[1] H. Ettouney, Conventional Thermal Processes, Seawater Desalination, Green Energy and Technology, Springer-Verlag, Berlin Heidelberg, 2009, pp. 17–40.

[2] T. Younos, K.E. Tulou, Overview of desalination techniques, J. Contemp. Water. Res. Educ. Issue 132 (2005) 3–10.

[3] K.P. Lee, T.C. Arnot, D. Mattia, A review of reverse osmosis membrane materials for desalination—Development to date and future potential, J. Membr. Sci. 370 (2011) 1–22.

[4] S.G. Kim, D.H. Hyeon, J.H. Chun, B.H. Chun, S.H. Kim, Nanocomposite poly(arylene ether sulfone) reverse osmosis membrane containing functional zeolite nanoparticles for seawater desalination, J. Membr. Sci. 443 (2013) 10–18.

[5] N. Misdan, W.J. Lau, A.F. Ismail, Seawater Reverse Osmosis (SWRO) desalination by thin-film composite membrane—Current development, challenges and future prospects, Desalination 287 (2012) 228–237.

[6] A. Matin, Z. Khan, S.M.J. Zaidi, M.C. Boyce, Biofouling in reverse osmosis membranes for seawater desalination: Phenomena and prevention, Desalination 281 (2011) 1–16.

[7] P. Swenson, B. Tanchuk, A. Gupta, W. An, S.M. Kuznicki, Pervaporative desalination of water using natural zeolite membranes, Desalination 285 (2012) 68–72.

[8] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: Water sources, technology, and today's challenges, Water Res. 43 (2009) 2317–2348.

[9] M. Drobek, C. Yacou, J. Motuzas, A. Julbe, L. Ding, J.C.D. Costa, Long term pervaporation desalination of tubular MFI zeolite membranes, J. Membr. Sci. 415–416 (2012) 816–823.

[10] Z. Xie, M. Hoang, T. Duong, D. Ng, B. Dao, S. Gray, Sol–gel derived poly(vinyl alcohol)/maleic acid/silica hybrid membrane for desalination by pervaporation, J. Membr. Sci. 383 (2011) 96–103.

[11] H.J. Zwijnenberg, G.H. Koops, M. Wessling, Solar driven membrane pervaporation for desalination processes, J. Membr. Sci. 250 (2005) 235–246.

[12] E. Korin, I. Ladizhensky, E. Korngold, Hydrophilic hollow fiber membranes for water desalination by the pervaporation method, Chem. Eng. Process. 35 (1996) 451–457.

[13] L.M. Vane, A review of pervaporation for product recovery from biomass fermentation processes, J. Chem. Technol. Biotechnol. 80 (2008) 603–629.

[14] L.S. White, Development of large-scale applications in organic solvent nanofiltration and pervaporation for chemical and refining processes, J. Membr. Sci. 286 (2006) 26–35.

[15] L. Lin, Y. Zhang, H. Li, Pervaporation and sorption behavior of zeolite-filled polyethylene glycol hybrid membranes for the removal of thiophene species, J. Colloid Interface Sci. 350 (2010) 355–360.

[16] L. Lin, Y. Zhang, Y. Kong, Recent advances in sulfur removal from gasoline by pervaporation, Fuel 88 (2009) 1799–1809.

[17] M. Peng, L.M. Vane, S.X. Liu, Recent advances in VOCs removal from water by pervaporation, J. Hazard. Mater. B98 (2003) 69–90.

[18] M.B. Patil, R.S. Veerapur, S.D. Bhat, C.D. Madhusoodana, T.M. Aminabhavi, Hybrid composite membranes of sodium alginate for pervaporation dehydration of 1,4-dioxane and tetrahydrofuran, Desalin. Water Treat. 3 (2009) 11–20.

[19] Y. Wu, G. Tian, H. Tan, X. Fu, Pervaporation of phenol wastewater with PVDF–PU blend membrane, Desalin. Water Treat. 51 (2013) 5311–5318.

[20] S. Semenova, H. Ohya, K. Soontarapa, Hydrophilic membranes for pervaporation: An analytical review, Desalination 110 (1997) 251–286.

[21] S.P. Nunes, K.V. Peinemann, Membrane Technology in the Chemical Industry, second ed., Wiley-VCH, Weinheim, 2006.

[22] J.G. Wijmans, R.W. Baker, The solution-diffusion model: A review, J. Membr. Sci. 107 (1995) 1–21.

[23] R.W. Baker, Membrane Technology and Applications, second ed., Wiley, Chichester, 2004.

[24] F.U. Nigiz, N.D. Hilmioglu, Desalination via innovative membrane process, Journal of Selcuk University Natural and Applied Science, ICOEST conference special volume (2) (2013) 459–466.