Pervaporative desalination of seawater using a polyvinylidene fluoride based membrane

F. U. Nigiz and N. D. Hilmioglu

ABSTRACT

Producing a fresh water supply by converting non-potable water is an attractive solution when water is scarce. According to the energy strategies of different countries, various seawater purification techniques such as distillation and reverse osmosis (RO) are used to produce fresh water. Due to the selective separation capability and cost-effective properties, membrane based methods such as RO, electrodialysis, and ultra/micro/nano/filtration are prevalent, especially in Europe. Recently, innovative desalination technologies have been investigated by researchers. Among them, pervaporative separation, in which non-porous membranes are used, appears to be an emerging and promising method. The key part of the system is the membrane. Hence, scientific investigations are focused on the production of high-performance membranes. In this study, non-porous polyvinylidene fluoride (PVDF) and polyvinyl pyrrolidone (PVP) blend membranes were prepared in different PVDF/PVP ratios and Marmara seawater was desalinated using the pervaporation method at different temperatures. Desalination performance was evaluated as a function of flux and salt retention. The highest salt retention of 99.90% and flux of 1.60 kg/m^2.h were obtained at 60 °C when the PVDF/PVP ratio was 1.5.

Key words | pervaporative desalination, polyvinylidene fluoride (PVDF), polyvinyl pyrrolidone (PVP), salt retention, seawater desalination

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ABBREVIATIONS

DSC   Differential scanning calorimetry

FO   Forward osmosis

MD   Membrane distillation

PV   Pervaporation

PVDF   Polyvinylidene difluoride

PVP   Polyvinyl pyrrolidone

RO   Reverse osmosis

SEM   Scanning electron microscopy

$C_{f,p}$ Conductance of the feed and permeate

J Flux (kg/m^2.h)

R Salt retention (%)

t Operation time (h)

W_p Weight of permeate (kg)

SYMBOLS

A Effective membrane area (m^2).

INTRODUCTION

One of the factors causing an increase in water demand is the increase in human populations. Climate change and global warming are also responsible for depletion of natural fresh water sources. In the near future, it is predicted that

some countries, especially those with settlements in coastal areas, will face water scarcity problems. Today, more than 97% of the earth's water cannot be used directly for human consumption. Of fresh water, 0.5% has low salinity, so it can be used without further purification process (Schorr 2011; Nair & Kumar 2013; Kucera 2014). Saline water has different concentrations of salt with an average value of 2.5–3.5%. This concentration is very high for human consumption, drinking and agricultural purposes. Therefore, using natural water sources such as seawater or groundwater by converting it to fresh water becomes the key solution to the lack of water.

The purification of seawater, groundwater or other saline water from dissolved solids including dissolved salts, ions, or minerals is known as desalination (Kucera 2014). According to the energy consumption strategies of different countries, various purification techniques can be used for fresh water supply (Matsuura 2001; Elimelech & Phillip 2011). These techniques are basically classified into two main groups as thermal and membrane-based desalination. The separation principle in the thermal desalination techniques such as multi-stage distillation or multi-effect distillation depends on the evaporation of pure water from the saline water. The distillation technique is very effective, making it possible to separate almost all contaminants from the seawater. However, distillation requires higher heating energy costs compared to membrane-based processes.

Reverse osmosis is an energy-saving membrane process that is the most commonly used for desalination in Europe. The performance of the system is directly related to the membrane. Therefore, many attempts have been made to develop appropriate membranes to reduce the energy consumption (Greenlee et al. 2009; Lee et al. 2011; Hsu et al. 2012; Groot et al. 2015).

Electrodialysis (ED) is another membrane-based desalination method that has been used on an industrial scale since the 1960s (Lee et al. 2011). The separation phenomenon in ED depends on the movement of dissolved anions towards the anode and cations towards the cathode. In this process, ion-selective membranes are used. The major drawback of the method is the high electricity requirement (Lee et al. 2011; Schorr 2011; Kucera 2014). The selection of the purification method is related to the salinity of the water to be desalinated and the final quality of the purified

water. Whereas ED is only appropriate to desalinate low-salinity water, distillation can be used over a wide range of salt concentration. Recently, novel membrane technologies such as pervaporation, forward osmosis and membrane distillation (MD) have been experimentally used by researchers (Hou et al. 2009; Naim et al. 2015; Jiang et al. 2016; Nigiz & Hilmioglu 2016; Wang et al. 2016). Pervaporation is a selective non-porous membrane separation process which has been used for a long time for alcohol dehydration, aroma recovery, and volatile organic compound removal from wastewater (Nunes & Peinemann 2006; Nigiz & Hilmioglu 2013; Olmo et al. 2014; Basile et al. 2015; Kujawa et al. 2015; Nigiz et al. 2015; Uragami et al. 2016). The performance of the system is directly related to the membrane performance of materials. Polymeric membranes have been frequently used due to their low-cost production and ease of modifying capability to increase both retention and permeability (Ulbricht 2006; Gao 2016). Inorganic membranes have also been preferred, especially where the polymeric materials cannot be used (in acidic or radioactive media).

Over the past few decades, significant investigations have been made into pervaporative seawater desalination. Khajavi et al. (2010) published research on pervaporative desalination of seawater at different temperatures by preparing hydroxy sodalite membrane, and they obtained 99.99% salt retention at 303 K. In addition, they reported that the purity of the permeated water was almost to drinking water quality. Xie et al. (2011a) prepared three-layered polyvinyl alcohol based membranes of different thicknesses to purify model saline water (different concentrations of NaCl in the range of 3.5–5%) by using the pervaporation technique. They reported very pure water with a salt retention above 99.5%. They also reported that the membranes preserved their separation performance without significant loss at the end of 50 hours. Cho et al. (2011) synthesized NaA based inorganic membranes and obtained very high salt retention (99.7%) when they performed pervaporative seawater desalination at a high temperature. The salt retention capacity of the polyvinyl alcohol/maleic acid/silica composite membrane was investigated in the study of Xie et al. (2011b) and the authors reported 99.9% salt retention. The literature survey has shown that academic attention has been paid to produce high-performance membranes.

It is very important to fabricate a high-performance commercial membrane with a high salt retention factor and high water flux.

In this study, pervaporative desalination experiments were performed at different temperatures using different ratios of polyvinylidene fluoride (PVDF) and polyvinyl pyrrolidone (PVP) blend membranes. PVDF is a well known hydrophobic polymer that is used in the MD process. It is used for making the membrane more resistant to salty water. This study has a new development in using a hydrophobic membrane for real seawater desalination. A PVP polymer was used to provide hydrophilic character to the membrane. According to the author's knowledge, this is the first study on pervaporative desalination that deals with the effect of the different ratios of PVDF/PVP blend membranes on desalination performance.

MATERIALS AND METHODS

PVDF (Kynar720) was kindly obtained from the distributor of Arkema, Turkey. Polyvinyl pyrrolidone (PVP360) and N,N-dimethylformamide (purity) were purchased from Sigma Aldrich, Turkey.

Membrane preparation

Non-porous membranes were prepared by the casting-evaporation method. Different ratios of PVDF/PVP polymers (the PVDF/PVP ratios were 5, 4, 1.5 and 0.2) were solved in N,N-dimethylformamide solvent at a temperature of 60 °C. After the homogeneous mixture was obtained, the mixture was kept in a cabin to remove the gas bubbles. Then, membrane solutions were poured on a Teflon plate and dried in the oven at 140 °C for 2 hours to form a flat-sheet membrane.

Membrane characterization

Characterization experiments were done to determine the separation capability of the blend membrane under different operating conditions. Compatibility of the PVDF/PVP membrane was investigated using scanning electron microscopy (JEOL JSM-6335 F). The effects of PVDF/PVP ratios on

total crystallinities of the pristine and PVP-loaded PVDF membranes were analyzed by means of differential scanning calorimetry (Mettler Toledo DSC instrument). The analysis was done with the temperature rising from −40 to 200 °C at a heating rate of 20 °C/min under a nitrogen atmosphere.

Swelling experiment

The degree of swelling (DS) value is a quantitative definition of the membrane affinity to the target component. In this study, different ratios of PVDF/PVP membranes were immersed in seawater at room temperature. At hourly intervals, swollen membranes were removed from the seawater and weighed rapidly until they reached an equilibrium state of swelling. The DS was calculated from the weights of the dry (Wd) and swollen (Ws) membranes as shown in Equation (1).

$$DS(\%) = ((W_s - W_d)/W_d)*100 \tag{1}$$

Pervaporative desalination

Pervaporative desalination experiments were performed at different temperatures (40, 50, 60 °C). For this purpose, Marmara seawater (Turkey) was used. A constant volume membrane cell, placed in a temperature controlled oven, was used in the present study as seen in Figure 1. The effective separation area of the membrane was
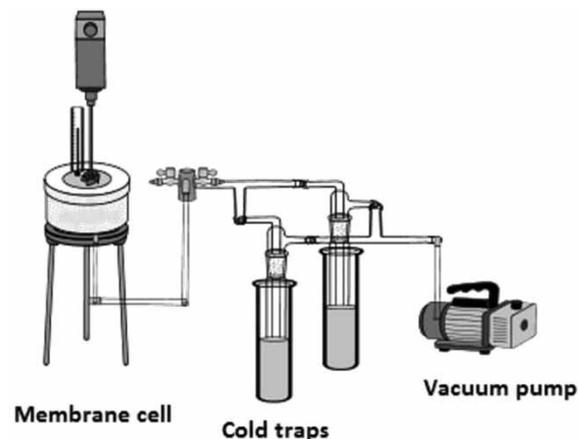

Figure 1 | Experimental pervaporative desalination set-up.

19.6 cm² and it had 250 ml volume capacity. While the feed side of the membrane cell was in atmospheric pressure, a constant vacuum was applied on the permeate side of the cell to ensure condensation of the permeated fresh water within the cold traps that were cooled with liquid nitrogen.

At hourly intervals, permeated fresh water was weighed and analyzed using the conductivity method. The performance of desalination was evaluated as a function of flux (J) and salt retention factor (R).

$$J = \frac{W_p}{A.t} \tag{2}$$

$$R = \left(\frac{(C_f - C_p)}{C_f}\right) * 100 \tag{3}$$

where W_p represents the total weight of the permeated sample, A is the effective area of the flat sheet membrane and t is the operation time. C_f and C_p are conductance of the feed and permeate respectively.

RESULTS AND DISCUSSION

Membrane characterization

Figure 2 shows cross-sectional and surface morphological structures of composite membranes with different ratios of PVDF/PVP. Scanning electron microscopy (SEM) micrographs give information about the harmony and compatibility of the two different polymers within the membrane. In Figure 2(a), leaf-like constructions are observed; in
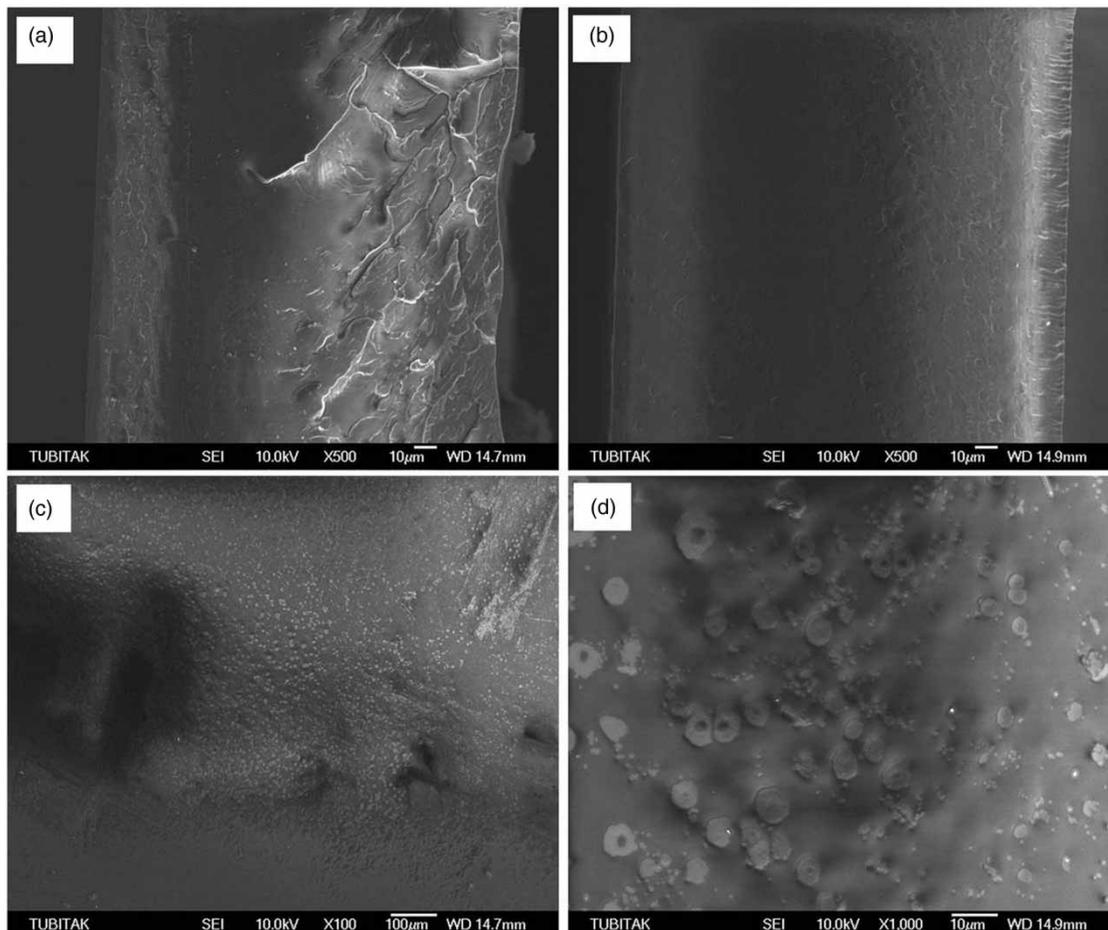

Figure 2 | Cross-sectional SEM images of PVDF/PVP = 4 (a), PVDF/PVP = 1.5 (b) and surface images of PVDF/PVP = 0.2 (c), (d) membranes.

Figure 2(b), a smooth structure is seen. This was due to the increasing amount of PVP polymer within the composite membrane. In addition to the hydrophilic property of PVP, it was used as a pore-forming agent in the literature studies. Increasing amounts of PVP increased the roughness of the membrane surface and caused a phase separation between structures of polymers as seen in Figure 2(c) and 2(d).

DSC spectra of the pure PVDF and PVDF/PVP composite membranes are shown in Figure 3. The pure PVDF polymer showed a melting temperature of 176 °C. In contrast to the plain membrane, the melting point was seen at a low temperature for blended membranes. PVP addition decreased melting temperatures. Regarding the DSC observation, it was predicted that the increasing amount of PVP would increase the chain mobility of the composite membrane. Consequently, water flux could increase. It also appears in the figure that the heat flow peak area of the pure PVDF was higher than those of the composite membranes. Therefore, it is clear that the percentage of the crystalline structure in the membrane decreased with the increasing ratio of PVP. This observation is very important to determine the performance of pervaporation depending on the membrane's structure. As the crystalline part of the polymer restricts the passage of components, amorphous regions in the polymer allow for permeation.

Swelling degrees

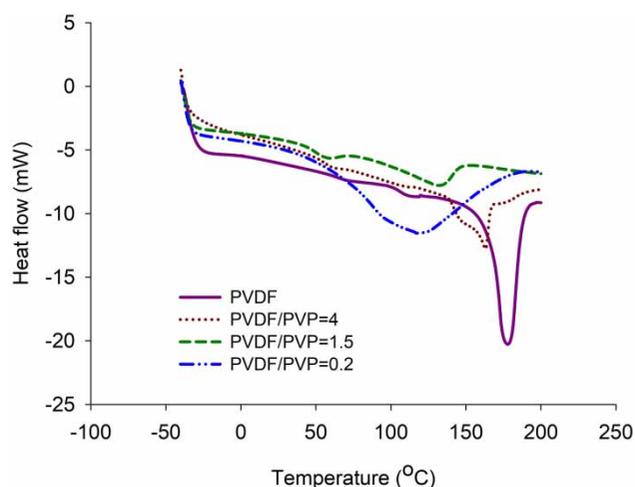PVDF is known as a hydrophobic material. In this study, hydrophilic PVP polymer was used to increase the water permeation rate through the membrane. Depending on the rule of mixture phenomenon, the aim was to combine the positive properties of PVDF and PVP by making a successful membrane fabrication. Depending on PVP addition into PVDF, the hydrophobic structure of PVDF was converted to hydrophilic without a change in its water resistance property. Figure 4 shows the swelling degrees of membranes containing different amounts of PVP within PVDF. Swelling measurement is the simplest experimental route to test the membrane's affinity to the target solvent. It is indicated in Figure 4 that the degree of swelling results were enhanced with the increasing amount of PVP in the membrane.

Influence of the PVDF/PVP ratio on desalination

In the literature, hydrophilic polymeric membranes were mostly used for pervaporative desalination. Due to the high swelling tendency of hydrophilic polymers, their separation performances are not stable under different operating conditions. In contrast, a hydrophobic polymer was fabricated in the present study. Promisingly, very high salt retention was achieved by using PVDF/PVP membranes. As seen in Figure 5, the change in ratio of PVP within the PVDF matrix had a great role in separation performances. The addition of PVP polymer into PVDF did not only affect the hydrophilic/hydrophobic balance of the membrane, but also improved the separation capability of the membrane. Consequently, both flux and retention were improved.
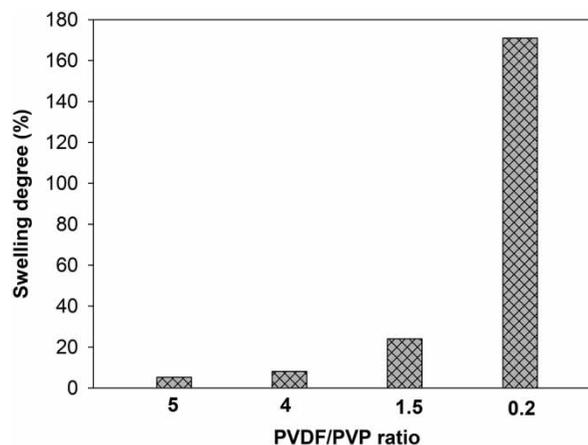

Figure 3 | DSC spectra of pristine and PVP loaded PVDF.
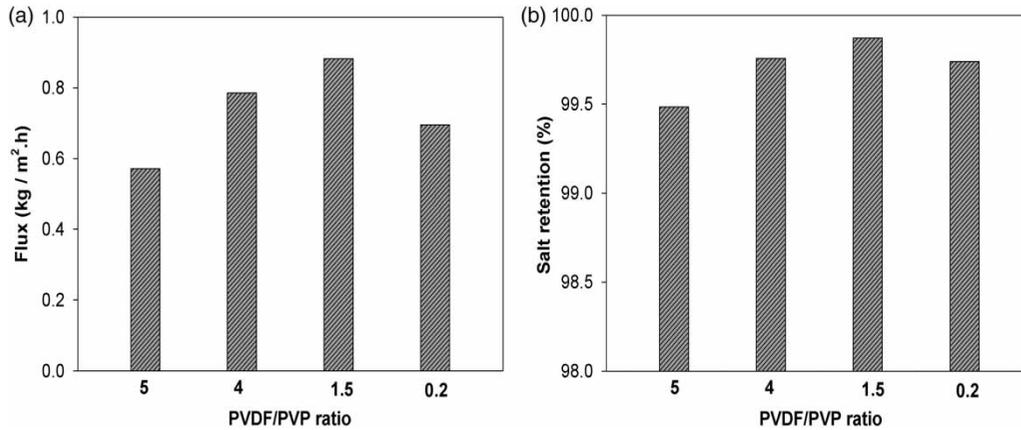

Figure 4 | DS results of hybrid membranes.

Figure 5 | Flux (a) and salt retention (b) variations with decreasing PVDF/PVP ratio (40 °C).

The highest retention of 99.86% and the best flux of 0.88 kg/m^2.h were obtained when the PVDF/PVP ratio was 1.5 at 40 °C.

Influence of the temperature on desalination

The effect of temperature on separation performance is indicated in Figure 6. In many aspects, the temperature of the system had a significant effect on flux and retention. Firstly, the driving force between the sides of the membrane increased depending on the increase in vapor pressure of the feed mixture. As expected, flux values of all membranes were enhanced. Secondly, solubility and diffusivity of the water into the membrane were enhanced with increasing temperature. In addition to the physicochemical properties

of water, the temperature had a great effect on the number and size of the free volumes within the polymer. It was previously mentioned that the ratio of the crystalline structure in blended membranes decreased when PVP content increased in PVDF. In accordance with the increasing temperature, segmental motions of molecules in blended polymer membranes would accelerate. Therefore, the total number and size of free volumes within the polymer would increase. However, these explanations were not valid for the flux results of the membrane with a PVDF/PVP ratio of 0.2. The excess ratio of PVP restricted the segmental motions of molecules in the membrane. This case was also indicated in the DSC results. The membrane in which the PVDF/PVP ratio was 0.2 had higher enthalpy depending on its higher crystallinity.
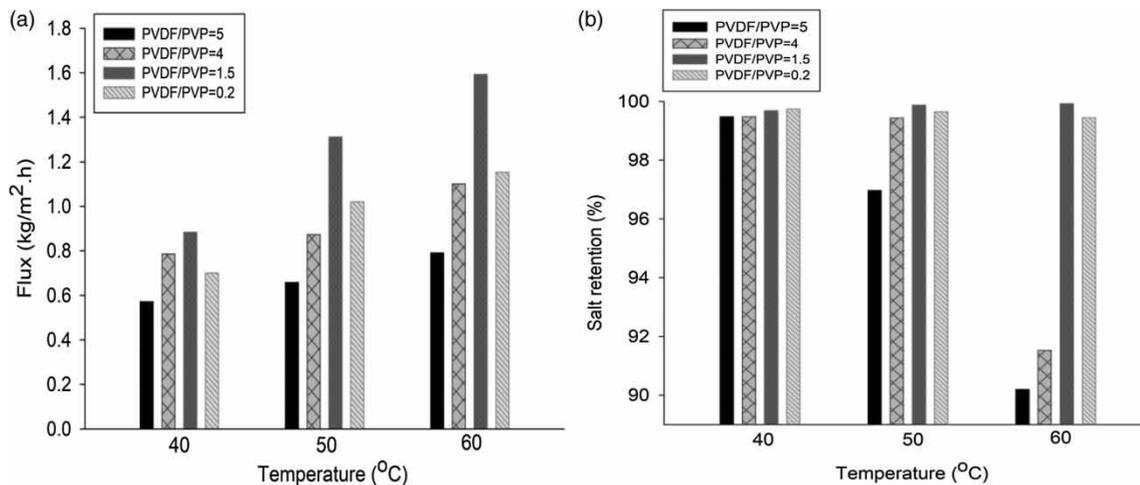

Figure 6 | Effect of temperature on flux (a) and salt retention (b).

Contrary to the flux results, the salt retention factor was not significantly influenced by the temperature change. The salt retention of 99.86% and the flux of 0.88 kg/m^2.h were obtained when the PVDF/PVP ratio was 1.5 at 40 °C. When the temperature increased from 40 °C to 60 °C, the salt retention of 99.9% and the flux of 1.60 kg/m^2.h were achieved.

CONCLUSIONS

In this study, Marmara seawater desalination was performed using an innovative desalination technology. For this purpose, PVDF and PVP blend membranes were fabricated using different ratios of PVDF/PVP polymers. Membranes were used for seawater desalination in temperatures ranging from 40 °C to 60 °C. With increasing ratios of PVP polymer in the PVDF matrix, both the flux and salt retention were enhanced. More than 99.5% of salt retention values were achieved by using all PVDF/PVP membranes. The highest salt retention of 99.9% and highest flux of 1.60 kg/m^2.h were achieved at 60 °C when the PVDF/PVP ratio was 1.5. Consequently, this study proved the efficiency of the pervaporative desalination technique by using PVDF/PVP composite membranes that are both permselective for water and resistant to seawater.

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