



Bentonite-loaded carboxy methylcellulose membrane for pervaporative desalination

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ABSTRACT

In this study, bentonite clay incorporated carboxy methylcellulose (CMC) membrane was prepared and used for pervaporative desalination of a NaCl–water solution at different operation conditions. The morphological properties of the mixed matrix membrane and inorganic–organic interfacial properties were determined using scanning electron microscopy. Thermal degradation behaviors and the effect of bentonite addition on the thermal durability of the membranes were observed. Effect of bentonite concentration in CMC range from 2.5 to 10 wt%, feed temperature (30°C–60°C) and NaCl concentration (1–4 wt%) in the feed water solution were experimented to determine the pervaporative desalination performance at the constant upstream (1 bar) and downstream pressure (5 mbar). All membranes exhibited greater than 99% of salt retention with reasonable water flux values at a given temperature. A higher water flux of 2.6 kg/m² h was achieved with a salt retention of 99.8% when the feed temperature was 60°C and the NaCl concentration was 3 wt% by using 7.5 wt% bentonite-loaded membrane. The highest salt retention of 99.9% was achieved with a flux of 1.9 kg/m² h using 10 wt% bentonite-loaded membrane at a feed temperature of 40°C.

Keywords: Pervaporative desalination; Carboxy methylcellulose; Bentonite

1. Introduction

In recent years, researchers have focused on pervaporation (PV) system, which is commercially used in industrial processes such as alcohol dehydration, separation of organic substances from water, aroma recovery [1–4]. The system offers an environmental friendly and energy-saving separation routes. In pervaporative desalination, water is selectively removed from other contaminants and ions. There are many commercial pervaporation systems to separate mixtures with a close-boiling point, azeotropic, and thermally sensitive without a need of any external heating energy or additional solvent. Large-scale pervaporation systems are commercially used especially in bio-ethanol industry where a small amount of alcohol must be selectively separated from the broth.

In the vacuum stripping pervaporation system, the driving force is the differences in chemical potential between the sides of the membrane [5,6]. For saline water desalination, dense polymeric, inorganic, composite, or mixed matrix membranes are generally used [3]. When the saline water contacts with the membrane, water selectively passes to the other side of the membrane. In the case of the polymeric membrane usage, the water permeation occurs through the molecular free volumes of the membrane according to the solution-diffusion phenomenon. If the material of the membrane is inorganic, then the separation occurs through the holes of inorganic based on the pore flow model.

Due to the vacuum pressure, which is created on the downstream sides of the membrane, the purified water evaporates and passes to the downstream which is called as “permeate”. The most important constituent of the system is the membrane. Therefore, most of the academic studies have been focused on proper and high-performance membrane production. It is possible to obtain very high purity water

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using pervaporation [PV]. The performance of the system is determined in terms of the flux and salt retention. In the literature, more than 99% of salt retention values have been obtained and the availability of the system for drinking and irrigation water has been demonstrated [3].

In the literature, the effects of pressure difference between the sides of the membrane, the temperature of the feed mixture, and salt concentration – if the sea water was synthetically prepared – have been investigated. Literature survey has shown that the big parts of the pervaporation membranes are suitable for seawater desalination. Duke et al. [7] carried out pervaporative NaCl–water desalination at 25°C feed temperature under the different upstream pressure by preparing alumina and silica inorganic membranes. The better performance was reported as 98% of salt retention with 1.8 kg/m² h flux using silica membrane at 25°C. In another study reported by Duke et al. [8], silicalite and ZSM-5 membranes were prepared with different ratios of Si/Al. They found 0.72 kg/m² h flux with a rejection of >99% at the optimal temperature of 80°C. Cho et al. [9] prepared an inorganic NaA membrane for pervaporative desalination and obtained salt retention capacity over 99.7% (between 40°C and 113°C).

In the literature studies, it is mostly reported that the inorganic pervaporation membranes have resistance to heat, pressure, and chemicals. However, the production routes of the inorganic membranes are costly. Since they have a brittle structure, it is difficult to produce them in a desired structure and shape. Compared with inorganic membranes, polymeric ones have some advantages such as easy forming ability and good processability. However, the process stability and durability of the polymeric material is reported as low compared with inorganic membranes. Zwijnenberg et al. [10] used a polyether amide-based membrane for pervaporative desalination. They reported that the salt retention as 99.998% with a flux of 0.15 kg/m² h. Sule and colleagues [11] performed a study in 2013 and they obtained 99% of salt retention and 0.54 kg/m² h of flux using polyester-based polymeric membrane. Based on the observation obtained from previous studies, inorganic material incorporated polymeric membranes have been improved to achieve good retention with reasonable flux values. Xie et al. [12] prepared a poly(vinyl alcohol)/maleic anhydride/silica-based three-layer composite membranes and performed pervaporation studies. Effect of operation conditions on pervaporation was investigated and 99.9% salt retention was achieved. In a study performed by Liang et al. [13] graphene oxide was used as filler into polyacrylonitrile polymeric matrix and pervaporative desalination of synthetic saline water was performed. They found a very high flux (65.1 L/m²h) with retention of 99.8% at 90°C.

In this study, novel natural clay (bentonite) distributed carboxy methylcellulose (CMC) mixed matrix membrane was prepared and used for desalination the different concentration of the NaCl–water solution. Due to the good film forming ability and high hydrophilicity of CMC, it was selected as the membrane matrix [14]. Membrane morphology was studied using scanning electron microscope (SEM). Crystalline structure change in the polymeric matrix by bentonite addition was studied by differential scanning calorimetry (DSC). Cross-linked CMC bonds were also analyzed by Fourier-transform infrared (FTIR) spectroscopy. The performance of the system was evaluated as a function

of salt retention and water flux. Effects of NaCl concentration, bentonite addition into CMC, and the temperature on desalination performances were performed.

2. Materials and methods

2.1. Materials

CMC, acetone (99% purity), HCl (37% purity) were purchased from Aldrich Chemical, Turkey. Glutaraldehyde (GA) (50% in water) was purchased from Acros Organics, Turkey. Natural clay (bentonite) with an average particle size of 0.5–2 µm was kindly supplied from Karben (Ankara, Turkey).

2.2. Membrane preparation

Both the plain and bentonite-loaded membranes were synthesized using the solution-casting method based on phase inversion phenomenon. In the case of the unfilled (plain) membrane, 1.8 g of CMC polymer was solved in 100 g of water by continuous stirring with a stirring rate of 500 rpm at the room temperature until a homogeneous pre-membrane solution was obtained. Following the homogenization, the solution was cast onto a poly(methyl methacrylate) plate and dried at the room temperature.

In the case of the bentonite-filled membrane, the same amount of CMC–water mixture was firstly prepared by the same method. Due to the agglomeration tendency of the bentonite, it was not directly incorporated into the pre-membrane solution. In order to disperse them homogeneously and prevent the contact-free region between the clay and polymer, “priming method” was applied that was also reported in the previous study [15]. According to this procedure, bentonite was dispersed in water and stirred for 1 h. Then, decantation procedure was applied with one hourly interval during 24 h to obtain nano size clay. After decantation was finished, particles were dried at 160°C for 2 h. Following the drying, the desired amount of bentonite (2.5, 5, 7.5, 10 wt% with respect to the dry polymer’s weight) was dispersed in 10 mL water. A very small amount of pre-membrane solution (5 g) was added to bentonite–water solution and kept in a sonic mixer for 15 min to cover the clay particle with a thin polymer layer. Afterward, the bentonite–CMC–water solution was poured into the bulk polymer solution slowly and stirred again for 2 h. Once a homogeneous clay–polymer–solvent mixture was obtained, it was cast onto a poly(methyl methacrylate) plate and dried at the room temperature.

After the membranes formed as a flat sheet, they were immersed a cross-linking bath including 1 vol% of glutaraldehyde, 1 vol% of HCl, 73 vol% of acetone and water for 4 h. The chemical cross-linking reaction occurred between the aldehyde groups in GA and hydroxyl groups in CMC where the HCl was used as the catalyst. Following the cross-linking, the membranes were removed from the cross-linking bath, washed rapidly and kept at vacuum oven to remove the residual solvent.

2.3. Membrane characterization

The surface morphology of the bentonite-loaded membrane was determined by SEM (JEOL JSM-6335 F) by covering the membrane samples with platinum.

Thermal properties and crystalline structure of the bentonite-loaded membranes were measured by DSC (Mettler Toledo, Turkey). The thermal degradation temperatures of the plain and bentonite-loaded membranes were operated by thermogravimetric analysis (TGA instrument, Mettler Toledo) in the temperature from 25°C to 600°C at a heating rate of 10°C min⁻¹ under nitrogen atmosphere.

Cross-linking bonds were analyzed using FTIR spectra (Pyris 1, Perkin Elmer) that were operated in the region of 650–4,000 cm⁻¹.

Effect of bentonite addition on the surface's hydrophilicity of CMC membrane was investigated by means of contact angle measurements (Attension Instrument, Turkey).

2.4. Desalination experiments

Desalination experiments were carried out in a lab-scale pervaporation unit. Fig. 1 represents the pervaporation unit with circulation where the vacuum is used to create a concentration gradient. As it is shown in the figure, the pervaporation system consists of a membrane cell, a circulation pump, a vacuum pump and a condenser (in the experimental setup cold traps are used to condense the vapor permeate).

The effective separation area of the membrane is 19.6 cm², and the volume capacity of the vessel is about 250 cm³. In the present study, the feed side of the membrane was kept at atmospheric pressure and the downstream side of membrane was kept as 5 mbar by vacuum pump.

The pervaporative desalination experiments were carried out at different temperatures (30°C, 40°C, 50°C, 60°C) with varying concentration of NaCl–water solutions (1, 2, 3, 4 wt%). The effect of dispersed bentonite amount on the separation performance of the system was also investigated at a given temperature with a constant concentration of NaCl–water solution. The separation performance of the PV

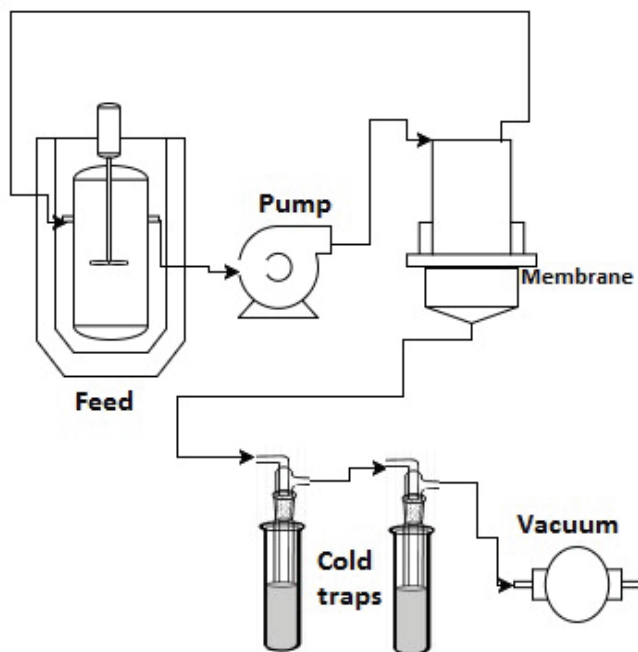


Fig. 1. A representative pervaporative desalination system.

was determined as a function of flux (J) (kg/m² h) and salt retention (R) (%).

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

$$R = (C_f - C_p) / C_f \times 100 \quad (2)$$

W_p (kg) represents the total weight of the permeate, A (m²) is the effective area of the membrane and t (h) is the operation time. C_f and C_p (kg/L) represent the salt concentration in the feed and permeate mixture, respectively. Salt concentrations were determined with conductance of the feed and permeate solution using Mettler Toledo Conductometry (Seven Compounds) with an accuracy of ± 2 μ S/cm.

3. Results and discussion

3.1. Characterization results

The surface and cross-sectional SEM micrographs of the plain, 5 wt% and 10 wt% bentonite-loaded CMC membranes are shown in Fig. 2. Fig. 2(a) represents the smooth and dense structure of CMC. The light particles represented in Fig. 2(b) are corresponding to bentonite. As seen in the micrograph, bentonite was homogeneously dispersed within the CMC matrix without any agglomeration. Compared with the 5 wt% bentonite-loaded membrane, some agglomerations were found on the surface of the 10 wt% bentonite-loaded membrane owing to the higher amount of filler (Fig. 2(c)).

Fig. 2(d) indicates that the bentonite particle was covered by CMC polymer without a defect-free region between two different materials. Fig. 2(e) also shows the structure of the 5 wt% bentonite-filled membrane with a higher magnification to detect the filler–polymer compatibility. As seen in the figure, there was no contact-free region between the CMC and bentonite. This was due to the “priming” method that was applied to avoid the formation of non-selective voids between the bentonite–CMC interfaces [15]. Compared with the 5 wt% bentonite incorporated membrane, in the structure of the 10 wt% bentonite incorporated membrane, the particles occupied to others as seen in Fig. 3(f).

Fig. 3 indicates the FTIR spectra of the cross-linked and non-cross-linked plain CMC membrane. The broad bands around 3,420 cm⁻¹ are corresponding to OH bonding, and the intensity of the band that belongs to cross-linked CMC increases because of the OH groups in glutaraldehyde. The band at 2,924 cm⁻¹ is assigned to the C–H stretching of the –CH₂ and CH₃ groups [16]. The intensity of the peak at 1,631 cm⁻¹ that is assigned to H–C=O and CH₂–C=O bands increase to 1,780 cm⁻¹ due to the cross-linking reaction of glutaraldehyde with –OH groups of cellulose [17].

TGA results of membranes are shown in Fig. 4. The weight losses were seen in the range of 280°C–330°C corresponding to the decomposition period of CMC polymer. Although there was no significant change in the decomposition temperatures of the plain and bentonite-loaded membrane, weight loss of mixed matrix membrane was lower than that of the plain membrane due to the bentonite addition into CMC. While the weight lost in the plain membrane was about 75.1%,

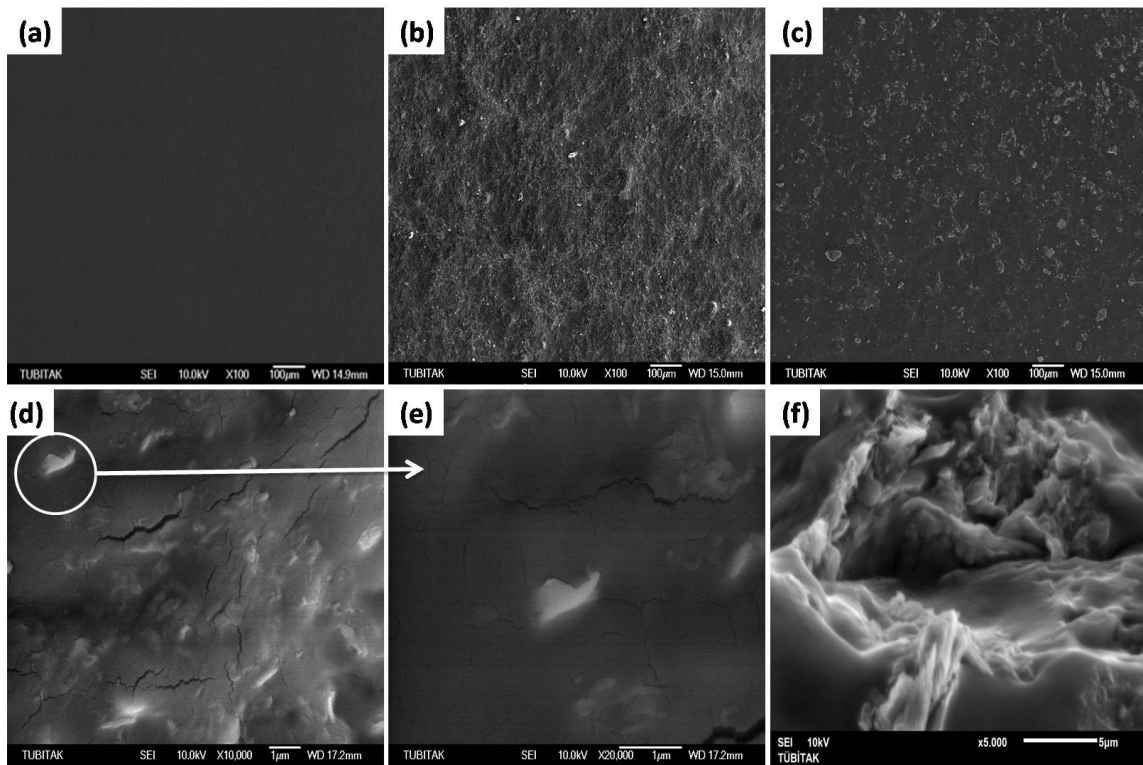


Fig. 2. Surface micrographs of the plain (a) 5 wt% bentonite loaded (b) 10 wt% bentonite-loaded (c) and cross-sectional micrographs of 5 wt% bentonite-loaded (d) 10 wt% bentonite-loaded (e) and CMC membranes (f).

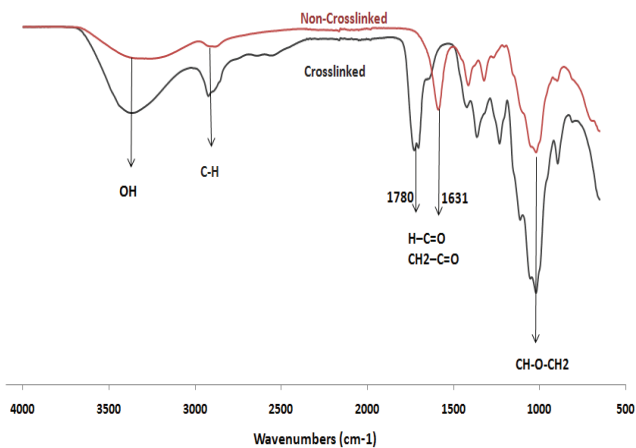


Fig. 3. FTIR spectra of cross-linked and non-cross-linked CMC membrane.

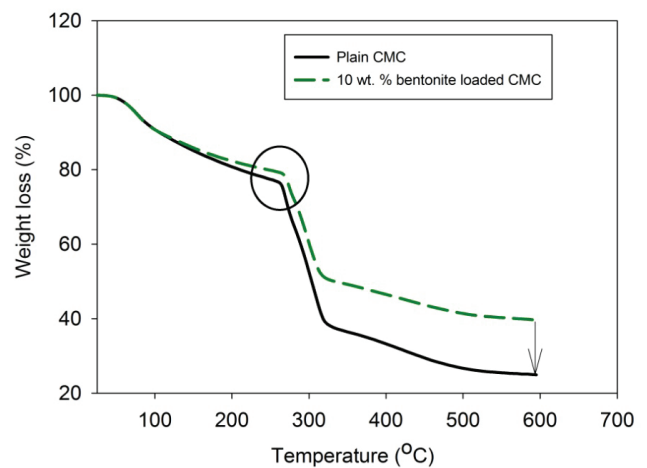


Fig. 4. TGA curves of the plain and bentonite-loaded CMC membrane.

the maximum weight loss was seen as 60.05% for the 10 wt% bentonite incorporated membrane. This result indicated that the clay provided reinforcing the thermal stability of the plain membrane.

DSC curves of the plain and 10 wt% bentonite-loaded membranes are indicated in Fig. 5. The plain CMC membrane showed a melting endotherm at 260°C. The melting temperature of the membrane shifted from 260°C to 269°C and a second melting temperature appeared at 277°C due to the bentonite addition.

3.2. Influence of clay content on desalination performance

Fig. 6 shows the pervaporation performance depending on increasing bentonite content in the membrane. With increasing content of bentonite from 0 to 10 wt% in the CMC matrix, the flux increased from 0.9 to 1.9 kg/m²h at 40°C due to the high water uptake capacity of the clay. Bentonite could act as hydrophilic adsorptive filler for water and higher flux was obtained. In order to determine the surface hydrophilicity of the cross-linked unfilled (plain) and bentonite-filled

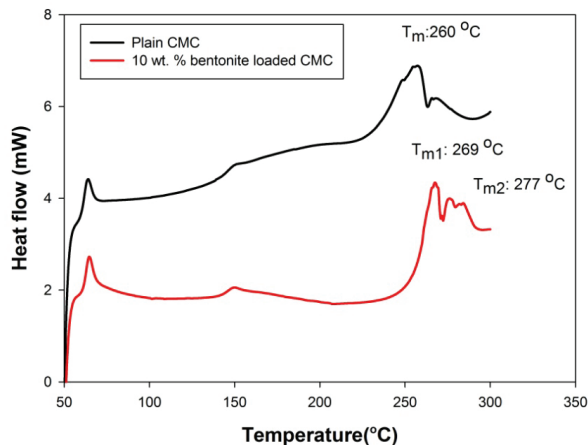


Fig. 5. DSC curves of the plain and bentonite-loaded CMC membrane.

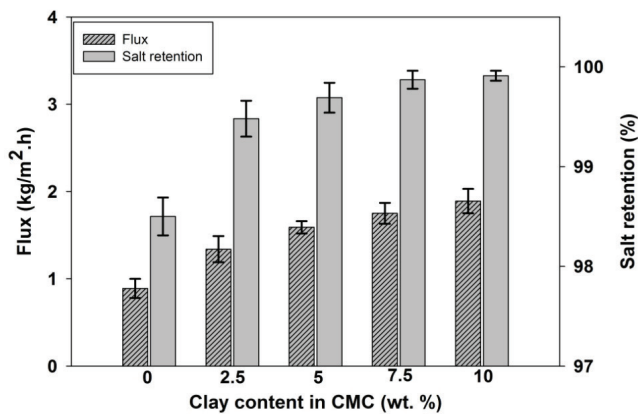


Fig. 6. Influence of the clay content on the desalination performance (3 wt% NaCl–water, 40°C).

membranes, contact angle experiments were performed using sessile drop methodology. Fig. 7 shows the contact angle measurements that were repeated for three times for the data accuracy.

The figure indicated that bentonite enhanced the surface hydrophilicity of the membrane. Contact angle decreased from 68° to 62° when 5 wt% bentonite was incorporated into plain CMC matrix. In addition, 7.5 wt% clay-loaded membrane also indicated very similar angle result. When the amount of bentonite increased to 10 wt%, a slight increase in angle was observed from 61° to 63°.

Hydrophilic behaviors of membranes depending on bentonite content were also examined by using the swelling experiments. Swelling experiments were applied to the plain membrane, 5 wt% and 10 wt% bentonite incorporated membranes during 10 h at the room temperature. The degree of swelling was calculated from the equation reported elsewhere [18]. As shown in Fig. 8, the swelling results of bentonite incorporated membrane were higher than that of the plain one. Nevertheless, the swelling results slightly decreased when the bentonite concentration increased from 5 to 10 wt% bentonite in CMC. This result could be attributed to the restricted active sorption sites of the clay by the excessive amount of filler.

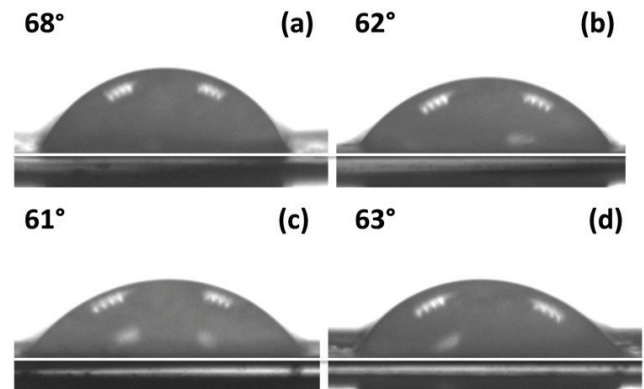


Fig. 7. Contact angle measurements of the plain (a), 5 wt% (b), 7.5 wt% (c) and 10 wt% (d) bentonite-loaded CMC membranes.

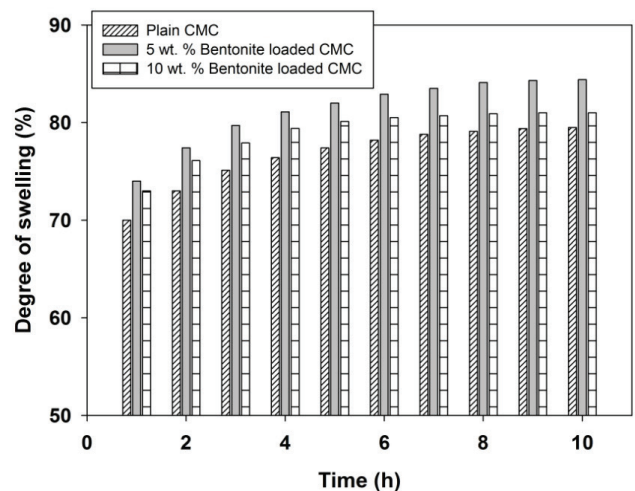


Fig. 8. Swelling results of the plain, 5 wt% and 10 wt% bentonite-filled membranes (3 wt% NaCl–water, room temperature).

As also indicated in Fig. 6, flux increment was restricted in the case of the 10 wt% bentonite-loaded CMC membrane depending on the restricted swelling degree.

The increase in salt retention from 98.5% to 99.9% with increasing amount of bentonite was also represented in Fig. 6. The variation in desalination performance depending on the bentonite content could be attributed to size/charge exclusion mechanism during the pervaporative desalination process. Owing to the bentonite incorporation into the membrane, the free spaces between the polymer molecules would be restricted. According to the size exclusion phenomenon, the passages of the hydrated ions were retarded owing to the higher diameters of hydrated Na⁺ (0.712 nm) and Cl⁻ (0.664 nm) ions compared with the water (0.27 nm). Retention increment was also related to the charge exclusion mechanism. On a basis of the charge exclusion theory which was also reported by Cho et al. [9], the quantities of the surface charges of the membrane and the concentrations of the ions in feed solution play a key role for desalination performance. In this mechanism, if the membrane has the same charge with the feed solution, membrane exhibit repulsion, and the ions

retain in the feed side. Bentonite particles are characterized by a negative face charge and a positive edge charge [19]. Therefore, ion separation through the bentonite-loaded composite membrane depends on the conformation and surface/edge distribution of bentonite within the polymeric matrix. In the literature studies, surface charge of the bentonite, which was characterized by zeta potential, changed depending on the concentration of the bentonite in immersed solution, pH, content and type of salt in mixtures [19–21]. It was reported that salt concentration in water increased the negative zeta potential on the surface of the bentonite [20,21].

In the case of the NaCl–water separation, the negative surface of the bentonite is positively charged by Na^+ ions in saline water. Therefore, it is considered that the total salt retention of the membrane change depends on hydrated Cl^- ions in the permeated water according to the “charge exclusion” and “size exclusion” phenomena.

3.3. Influence of temperature on desalination performance

Temperature is an important and effective factor on the performance of the pervaporative desalination, especially in the process where a polymer-based membrane is used. It is known that the solubility of the water within the membrane, the diffusivity of the water through the membrane, and saturated vapor pressure of the water in the feed side are determinant factors for pervaporative separation [5,22,23]. These factors change depending on the temperature. Besides the thermodynamic properties of the feed, the segmental motions of the polymer chains in the membrane are affected as well. [24,25]. The effect of temperature on the flux and retention was observed as seen in Fig. 9. As the temperature of the feed solution was increased from 30°C to 60°C, flux enhanced from 1.3 to 2.6 $\text{kg/m}^2\text{h}$ due to the increasing driving force between the sides of the membrane that was occurred by increasing vapor pressure. Flux enhancement was also related to the positive effect of temperature on the diffusivity and solubility of water. Both the solution and the diffusion coefficients are temperature-dependent. When the binary interactions are neglected (within NaCl and water), both two coefficients of the water increase with temperature at the constant operating conditions (constant pressure differences), with the same membrane materials having the same intermolecular void spaces; consequently, flux enhances [26].

However, these mentioned reasons negatively affected the salt retention as seen in Fig. 9.

The increase in water flux and the decrease in salt retention – even it was very small – were also related to the increase in the segmental motion of the polymer resulted in larger free spaces between the chains of the polymer. Consequently, water permeation increased through the larger free spaces. On the other hand, a non-selective ion passage could also be occurred caused owing to the enlargement. Due to the bentonite incorporation, the decline in salt retention was not remarkable (from 99.9% to 99.8%) and could be negligible.

3.4. Influence of NaCl concentration on desalination performance

Fig. 10 indicates the influence of NaCl amount in the feed mixture on flux and salt retention at a given temperature (40°C) when the 7.5 wt% bentonite incorporated membrane

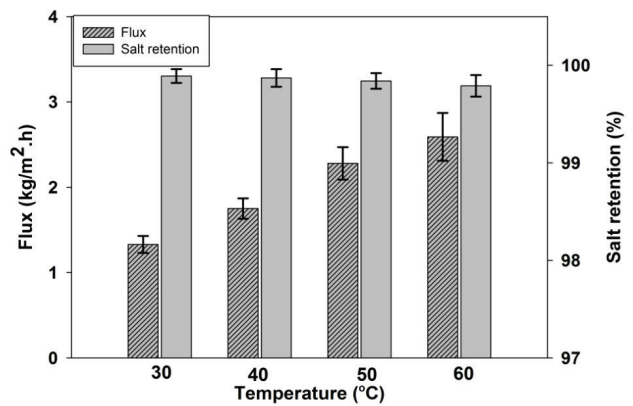


Fig. 9. Influence of the temperature on the desalination performance (7.5 wt% bentonite-loaded membrane, 3 wt% NaCl concentration).

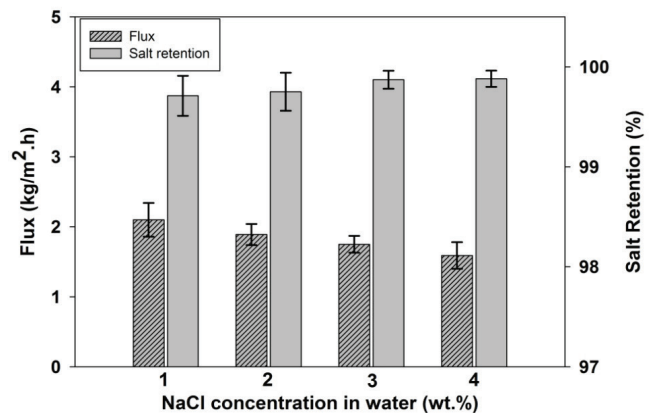


Fig. 10. Influence of NaCl concentration on the desalination performance (7.5 wt% bentonite-loaded membrane, 40°C temperature).

was used. When the salt concentration increased from 1 to 4 wt%, flux decreased from 2.1 to 1.6 $\text{kg/m}^2\text{h}$ and salt retention increased from 99.7% to 99.9%. Due to the very little variation (+0.18%) in salt retention, influence of salt concentration on retention could be negligible. However, the decrease in flux (–32%) should be considered.

Flux decrement is directly related to sorption capacity of the membrane to water and the diffusivity of the water through the membrane. It is believed that both diffusivity and solubility of the water are constant at a given low temperature and not much affected by the varying concentration of the feed solution [12,13]. However, the thermodynamic property of the component in water and the chemical feature of the membrane are important as the operating conditions of the experiment. In the pervaporative separation process, feed mixture contains different amount of dissolved ions in different charges. With increasing concentration of salt in the feed mixture, the vapor pressure of the water decreases and the driving force across the membrane declines, consequently, water flux decreases. In the present study, this event showed a positive effect on salt retention increment. This result was attributed to the charge/size exclusion and surface evaporation mechanism during the pervaporative desalination.

The flux decrement-retention increment could also be attributed to the segmental motion of the polymer chain. The free volume of the polymer would be filled with non-volatile salt residuals. Therefore, the flux decreased and the retention increased caused by the restricted void spaces of the polymer.

4. Conclusions

In the present study, the pervaporative desalination of the aqueous salt solution was performed using bentonite-loaded CMC membrane. Influence of bentonite content, feed temperature, and salt concentration on desalination performance can be summarized as follows:

- As bentonite content increased in CMC, both flux and salt retention enhanced.
- The temperature positively affected the water flux. However, salt retention decreased.
- Salt retention of >99% obtained with reasonable water flux by using all membrane types.
- A higher water flux of 2.6 kg/m² h was achieved with a salt retention of 99.8% at the feed temperature of 60°C and NaCl concentration of 3 wt% using 7.5 wt% bentonite-loaded membrane.
- The highest salt retention of 99.9% was achieved with a flux of 1.9 kg/m² h using 10 wt% bentonite-loaded membrane at the feed temperature of 40°C.

In conclusion, the novel mixed matrix membrane showed an excellent pervaporation performance for saline water desalination and it is a promising membrane to be used for commercial scale.

Symbols

- A — Effective membrane area, m²
 C — Conductance of the feed and permeate
 $J_{f,p}$ — Flux, kg/m² h
 R — Salt retention, %
 t — Operation time, h
 W_p — Weight of permeate, kg

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