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Reverse Osmosis Desalination Using the Thin Film Composite Polysulfone-Zinc Oxide Mixed Matrix Membrane

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ABSTRACT

The polysulfone-zinc oxide mixed matrix membrane (MMM) was fabricated via the phase inversion method. A polyamide layer was formed on the surface of the membranes using the interfacial polymerization process. The properties and structure of the membranes were investigated and the membranes were used for desalination in the reverse osmosis process. The cross-sectional images of the membranes substrate showed that the addition of zinc oxide nanoparticles to the polymer matrix resulted in a denser structure and increased the thickness of the sponge-like layer near the lower surface of the membrane. The addition of zinc oxide nanoparticles to the polymer matrix decreased the surface contact angle of the membrane with water, thereby having increased the hydrophilicity of the membrane surface. The pure water flux through both membranes decreased at the beginning of the process and after 60 min remained almost constant at the values of 19.50 ($\text{Lm}^{-2}\text{h}^{-1}$) and 30.20 ($\text{Lm}^{-2}\text{h}^{-1}$) for the membranes made with plain polymer and the MMM respectively. In the reverse osmosis process, the water flux of the membrane fabricated using plain polymer was 9.70 ($\text{Lm}^{-2}\text{h}^{-1}$) which increased by 39% and reached 13.50 ($\text{Lm}^{-2}\text{h}^{-1}$) by the addition of zinc oxide nanoparticles. The salt rejection of plain polysulfone membrane was 92.5% which increased to 97.21% with the addition of zinc oxide nanoparticles to the polymer matrix. The addition of zinc oxide nanoparticles to the polymer matrix significantly decreased the water permeability to salt permeability ratio (B/A) from 40.54 to 14.35 (kPa).

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1. Introduction

In the twenty first century, the lack of Freshwater has emerged as a major hazard due to many reasons, which include the population growth, reduced rainfall, and weather alteration [1]. The limitation of freshwater resources has forced human beings to think about finding new sources of water. Thus, saline seawater and industrial and hygienic wastewater were introduced as new sources to provide fresh and healthy water for various uses. The use of these resources required the desalination of seawater as well as the purification and sanitation of industrial and hygienic wastewater [2, 3]. Therefore, the improvement of techniques for the separation of salts from saline water and the wastewater remedy has attracted researchers' interest.

Desalination is carried out by various technologies in the world according to the amount of the water salinity and amount of the required fresh water. The main technologies used for desalination can be reverse osmosis, multistage distillation, thermal and ion exchange. Each of these methods has advantages and disadvantages based on the environmental conditions and the amount of the required fresh water. When choosing the type of desalination method, one of the factors to consider is the cost of the produced fresh water. Techniques such as distillation and thermal desalination require a lot of energy, which increases the cost of desalination. Studies have shown that the cost of desalination in the two processes of multi-stage evaporation and multi-stage distillation are almost similar, but the cost of reverse osmosis desalination is significantly lower [4]. Today, the membrane based reverse osmosis is widely used in domestic water treatment devices and industries for the salt and water pollution separation. In this method, a semipermeable membrane is used as a barrier

between the feed saline water and freshwater. By applying pressure to saline water, water molecules pass through the semipermeable membrane while the membrane prevents salt ions from passing. In this way, the salt molecules are separated from the water and fresh water is produced. The amount of water passing through the membrane and the rate of membrane salt rejection are largely dependent on the structure of the membrane. Reverse osmosis membranes are typically made of polymeric membranes, which form a hydrophilic polyamide film on their surface to increase their salt rejection[5]. Choosing the type of polymer used to make the membrane as well as the materials that are added as additives to the membrane structure has a great influence on the formation of the membrane structure, which in turn changes the membrane's separability. Polysulfone is a hydrophilic polymer widely used in the manufacture of reverse osmosis membranes. The appropriate mechanical and chemical resistance of this polymer as well as the ease of the fabrication of the membrane with this polymer has led to the use of reverse and forward osmosis in most studies related to the salt separation from water [6-12].

Because the membranes made for this process are porous membranes, the salt can penetrate into the pores of the membrane and cause problems such as the concentration polarization in the reverse osmosis process. In order to solve this problem in the reverse and forward osmosis process, porous polymer membranes with polyamide thin films are used. This is done by the surface polymerization using appropriate monomers to form a dense polymer film on the membrane surface to prevent the salt penetration into the pores.

In this study, in order to enhance the hydrophilicity of the reverse osmosis membrane substrate ZnO nanoparticles were used in the polysulfone membrane substrate fabrication and then a thin polymeric polyamide film was fabricated on the substrate surface of the polysulfone-zinc mixed matrix membrane by surface polymerization using phenylenediamine (MPD) and trimesoyl chloride (TMC) monomers and the fabricated membrane was used in the reverse osmosis process for desalination.

2. Experimental

2.1. Materials

The polysulfone polymer (PSf-Udel P-1700) was used for the fabrication of membrane substrates. Polysulfone is a polymer with good mechanical stability that has good resistance over a wide range of pH and also to chlorine. It is also convenient to fabricate the membrane using this polymer. Therefore, many researchers have used this polymer in forward and reverse osmosis desalination experiments [8,9, 13-15]. The polymer solvent used in this study was N, N-Dimethylacetamide (DMAC > 99%) produced by Sigma-Aldrich.

Zinc oxide nanoparticles (ZnO nanopowder <50 nm particle size (BET), > 97%, Sigma-Aldrich) were used to fabricate the polysulfone-ZnO mixed matrix membrane as the membrane substrate.

The membranes' polyamide layer was fabricated using phenylenediamine (MPD, > 99%, Merck), benzenetricarbonyl trichloride (trimesoyl chloride, TMC, > 98%, Merck) and n-hexane (n-Hexane > 99%, Merck).

The sodium chloride salt solution (NaCl, > 99.5%, Merck) in distilled water (made in laboratory) was used as the feed for the reverse osmosis process.

2.2. Dope solution preparation

The suitable membrane substrate for the formation of a polyamide film must be of a porous structure so that the polyamide film, on which it is made, will have good strength and stability. For this reason, polysulfone with a concentration of 17.5 wt.% was used to make this substrate. Two types of dope solutions were prepared for the substrate fabrication. To prepare 100 g of the first solution, 82 g of solvent was poured into a glass bottle and 0.50 g of ZnO nanoparticles were added. To make the nanoparticles disperse well in the solvent, the solvent bottle containing the nanoparticles was sonicated for 60 minutes at room temperature. As the solvent was stirred by mechanical stirring, 17.5 g of polysulfone polymer was added slowly. After the polymer pellets were completely dissolved in the solvent, the resulting solution was placed in the ultrasonic bath for 60 minutes at room temperature to remove the air bubbles trapped within the dope solution. Also for the preparation of the second type of the dope solution, everything was performed exactly according to the above method except that the second solution did not use ZnO nanoparticles. Table 1 shows the composition and viscosity of dope solutions. The viscosities of polymeric solutions were determined using the viscometer model EW-98965-40, Cole Parmer, USA.

Table 1

Composition and viscosity of dope solutions

Solution name	Polymer (wt.%)	ZnO (wt.%)	Solvent (wt.%)	Viscosity (cP)
S1	17.5	0.50	82	892
S2	17.5	0.0	82.5	1207

2.3. Membrane substrate fabrication

Two types of membranes including the polysulfone-ZnO mixed matrix membrane and plain polysulfone membrane were fabricated by the phase inversion method. To fabricate the membrane, an A4 size glass plate was first prepared and its surface thoroughly was cleaned. The polymer solution was then poured onto the glass plate and was cast with a casting knife. To perform the phase inversion process and the membrane fabrication, the glass plate was immediately immersed in distilled water tank as the coagulation bath at room temperature. To completely remove the solvent from the membrane pores, the prepared membrane was placed overnight in another distilled water tank and then stored in distilled water for subsequent experiments.

2.4. Formation of a thin polyamide layer on the substrates surface

The polyamide (PA) layer was formed on the membranes substrate surface by the interfacial polymerization method [7, 10]. 100 ml of the MPD solution (2% w/v) was dissolved in double-distilled water and poured onto the top surface of the substrate, which was held horizontally for 2 min to ensure the penetration of the MPD solution into the pores of the substrate. Then, the excess MPD solution was drained off from the substrate surface and the residual droplets on the membrane surface was removed by a plastic roller. Afterward 100 ml of the TMC solution was prepared in normal hexane (0.1% w/v) and poured onto the membrane surface. After 1 minute the surplus of the TMC solution was drained off from the membrane surface. The membrane surface was rinsed with pure n-hexane to remove unreacted monomers. The membrane was dried under ambient condition for 1 min and further in an oven at 60 °C for 8 min. The prepared thin film composite (TFC) membranes were stored in a

deionized water container for use in future experiments.

3. Membrane characterization

The structure of the cross-section and the polyamide layer of the membranes were investigated using the scanning electron microscopy (TM3000, HITACHI, Japan). A sample of membrane was inserted into the liquid nitrogen to break it down easily without damaging the structure. After breaking the sample, it was placed in an oven at 70 °C for 2 hours. Then, the membrane surface was coated with platinum.

In order to evaluate the hydrophilicity of the membrane surface, the contact angle of the membrane surface with water was measured. To measure the surface contact angle of the membrane with water, an optical contact angle measuring device (DATA Physics, OCA15plus, Germany) was used.

For the measurement of the overall porosity of the membrane substrate, a piece of membrane substrate that was kept in distilled water was selected and the water droplets on its surface were cleaned by air flow and the membrane sample was weighed. The sample was then placed in an oven at 90 °C for 60 minutes to dry and weighed after drying. The overall porosity of the membrane substrate (ε) was calculated using the following equation [15].

$$\varepsilon(\%) = \frac{W_w - W_d}{\rho_{water} \times A \times L} \times 100 \quad (1)$$

where A is the effective membrane surface area, L is the membrane thickness, ρ is the water density and W_w and W_d are the wet and dry membrane weights respectively.

The dispersive X-ray energy analysis instrument (Oxford instruments Swift ED3000, USA Analytical Ltd.) was used to investigate and confirm the presence of zinc

oxide nanoparticles in the membrane substrate structure. Using this analysis, the atomic percentage of the elements present in the substrates surface was determined.

4. Reverse osmosis desalination process

A schematic of the reverse osmosis experimental setup with cross-flow filtration mode is shown in Figure 1. In the reverse osmosis test, a stainless steel module with the total effective membrane area of 14 cm² was used. In order to minimize the concentration polarization, the cross-flow velocity was kept constant at 32.72 cm/s [15]. The reverse osmosis process was performed at a pressure of 2.5 bar at 25 °C. the sodium chloride (NaCl) salt solution in distilled water (2000 mg / L) was used as the feed solution. The pure water flux (J) and water permeability (A) of the membranes were calculated from the following equations [10, 15, 16].

$$J = \frac{\Delta V}{A_m \Delta t} \quad (2)$$

$$A = \frac{J}{\Delta P} \quad (3)$$

In these equations A_m is the effective surface area, ΔV is the permeate volume (L), Δt is the time (s) and ΔP is transmembrane pressure difference (Pa).

The percentage of the salt rejection, R (%) of the membrane was calculated from the following equation [10, 15, 16].

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (4)$$

where C_f and C_p are the salt concentration in the feed and in the permeate solution respectively. The salt permeability coefficient (B) was calculated from the following equation [10].

$$B = \left(\frac{1}{R} - 1\right) \times J \quad (5)$$

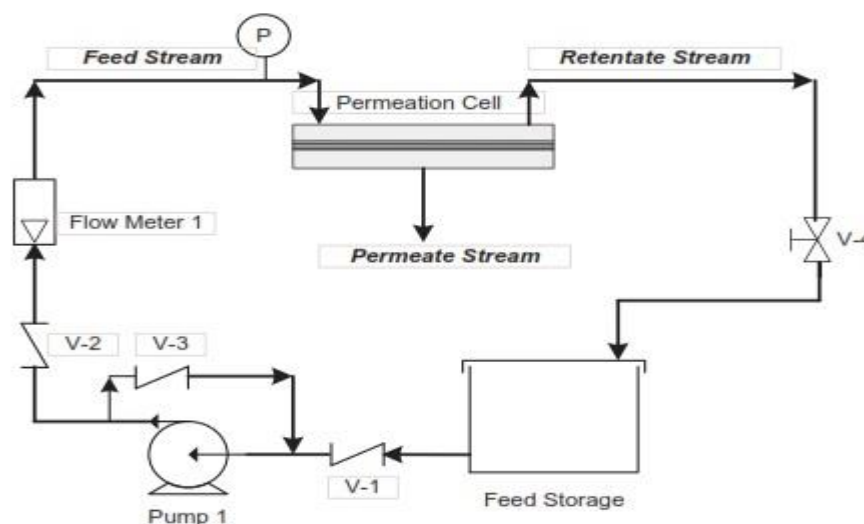


Figure 1. Schematic of the cross-flow reverse osmosis setup[15].

This system was also used to measure the pure water flux through the membrane at 200 min, ambient temperature and the pressure of 5 bar.

5. Results and discussion

5.1. Membranes structure

In general, the velocity of the phase inversion process affects the formation of the porous or dense structure in the membrane so that the finger-like and porous structure are the result

of the fast phase inversion process and the sponge-like and dense structure are the result of the slow phase inversion process. Figure 2 shows the cross-sectional and PA layer images of the membranes. The comparison of the cross-sectional images of the substrates shows that the addition of ZnO nanoparticles to the polymer matrix has led to the formation of a denser structure. The membrane made of pure polysulfone without the use of ZnO nanoparticles has large macrovoids close to the lower surface of the membrane that extend along the cross-section. By the addition of ZnO nanoparticles to the polymer matrix the number and size of these large macrovoids decreased and the thickness of the sponge-like

layer close to the lower surface of the membrane increased. This change in the membrane structure is due to the slow rate of the phase inversion process by increasing the viscosity (see table 1) of the solution in the presence of nanoparticles. The white spots on the cross-sectional area of the mixed matrix membrane also indicate the accumulation of ZnO nanoparticles at these points. Leaf-like structures on the surface of both membranes indicate the formation of a polyamide layer on the membrane surface. The polyamide layer fills the pores on the surface of both membranes and creates an integrated structure on the surface of the two membranes.

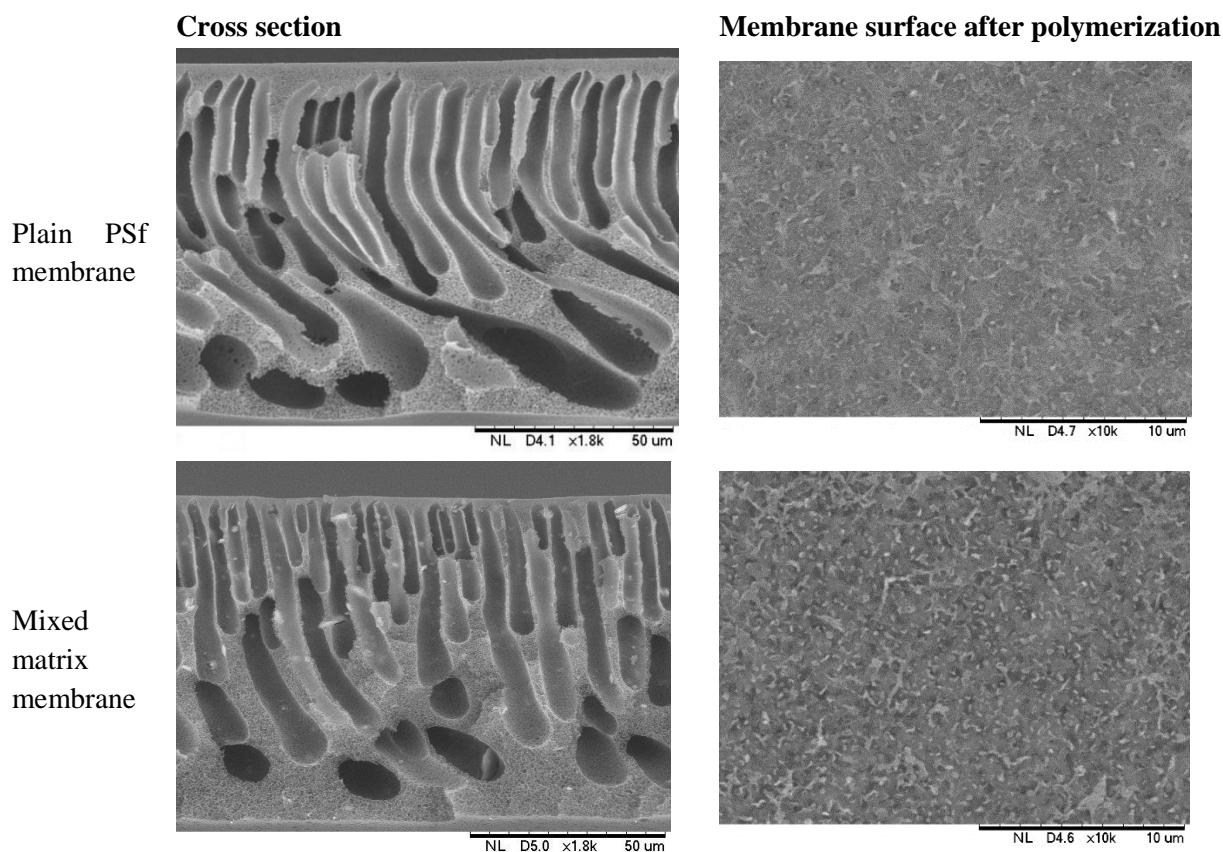


Figure 2. SEM images of the cross section and PA layer of membranes.

5.2. Contact angle of the membrane surface with water and the overall porosity of the membrane substrate

Table 2 shows the water contact angle with the membrane surface before and after the formation of the polyamide layer and the overall porosity of the membrane substrate.

The results show that the addition of ZnO nanoparticles to the polymer matrix decreased the contact angle of the membrane surface with water due to the hydrophilicity of the nanoparticles. In fact, the proper diffusion of ZnO nanoparticles into the polymer matrix resulted in the presence of these hydrophilic nanoparticles on the surface and in the structure of the membrane, which in turn reduced the contact angle with the membrane surface and increased the hydrophilicity of the membrane surface. The increment of the hydrophilicity of the membrane surface is desirable for the reverse osmosis process because it facilitates the water flux through the membrane. The polyamide layer on the surface of the membrane also reduces the water

contact angle with the membrane surface. The polyamide layer is hydrophilic in nature and therefore the formation of this layer contributes to the hydrophilicity of the membrane surface.

It is also seen from the results of table 2 that both membranes have high total porosity, which is due to the use of the low concentration polymer in the polymer solution. The addition of ZnO nanoparticles reduced the overall porosity of the membrane substrate. The addition of nanoparticles to the polymer matrix increased the viscosity of the polymer solution and, as a result, the phase inversion process was delayed and so a denser structure with less porosity has been formed.

Table 2

Water contact angle with the membrane surface and the overall porosity of substrates

Membrane type	Contact angle before polymerization (degree)	Contact angle after polymerization (degree)	Overall porosity of membrane substrate (%)
Plain PSf membrane	74.05	70.25	76.30
Mixed matrix membrane	51.36	46.55	72.93

5.3. Dispersive X-ray energy analysis results

The dispersive X-ray energy analysis (EDAX) was used to confirm the presence of ZnO

nanoparticles on the substrate surface and in the structure. The results are shown in table 3.

Table 3

EDAX analysis results

Plain PSf membrane		Mixed matrix membrane	
Element	Atom [at.%]	Element	Atom [at.%]
Carbon	81.05	Carbon	79.56
Oxygen	13.67	Oxygen	14.22
Sulfur	5.28	Sulfur	4.98
		Zinc	1.24
Total	100.00	Total	100.00

In the molecular structure of polysulfone there are elements of carbon, oxygen, hydrogen and sulfur, whereas in the structure of ZnO there

are elements of zinc and oxygen. Hydrogen atoms cannot be detected by the EDAX analysis therefore, the EDAX analysis only

shows the presence of carbon, oxygen and sulfur elements. The results of table 2 show that with the addition of ZnO nanoparticles to the membrane structure, the oxygen atomic percentage increased and also 1.24% of the

5.4. Results of the reverse osmosis process

In order to calculate the water permeability (A) from the equation 3, the pure water flux of membranes was measured. The pure water flux of both TFC membranes was measured for 200 min at ambient temperature and 5 bars. The results are presented in Fig. 3 and show that the pure water flux of both membranes decreased due to the system instability at the beginning of the process to about 60 min of the initial process and then remained almost constant to the end of the process for the plain PSf membrane and the mixed matrix membrane at the values of 19.50 ($\text{Lm}^{-2}\text{h}^{-1}$) and 30.20 ($\text{Lm}^{-2}\text{h}^{-1}$) respectively.

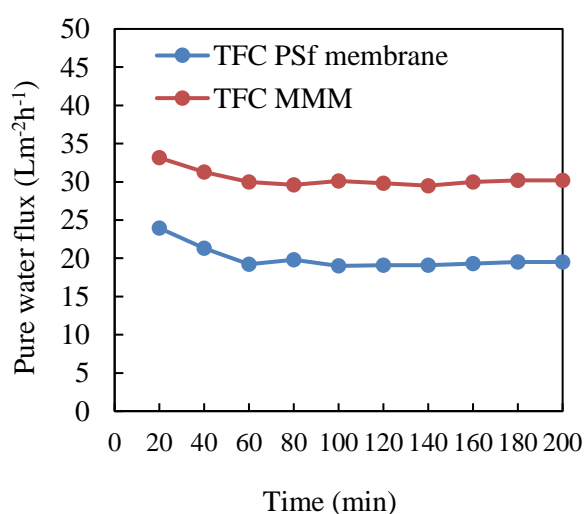


Figure 3. Pure water flux through the membranes over time.

The desalination performance of the fabricated membranes in the reverse osmosis process at the pressure of 2.5 bar and temperature of 25 °C was studied for 10 hours, in which the water flux and salt rejection rate from the aqueous NaCl solution were measured. The feed solution used in the reverse osmosis process

atomic zinc content of the mixed matrix membrane was observed, indicating the presence of zinc oxide in the mixed matrix membrane structure.

was the aqueous NaCl solution with the concentration of 2000 (mg / L). The results of this experiment are presented in Figure 4. As it can be seen, the addition of hydrophilic ZnO nanoparticles to the polymer matrix increases the water flux and salt rejection percentage. The increase in water flux is due to the increased hydrophilicity of the membrane with the presence of hydrophilic ZnO nanoparticles. Given that the polyamide film formed on the surface of the both types of membrane is similar, it can be concluded that the modification of the membrane substrate structure has a significant effect on the desalination performance of the reverse osmosis membrane.

According to the results shown in Figure 4, the water flux through the membrane made of plain polymer was 9.70 ($\text{Lm}^{-2}\text{h}^{-1}$) which increased about 39% by the addition of ZnO nanoparticles and reached 13.50 ($\text{Lm}^{-2}\text{h}^{-1}$). Emadzadeh et al. [15] used different amounts of titanium dioxide (TiO_2) nanoparticles to fabricate polysulfone membranes with a polyamide layer and used the fabricated membranes in the reverse osmosis process. According to the results of their work, the maximum water flux was 7.50 ($\text{Lm}^{-2}\text{h}^{-1}$), which is about 80% lower than the results obtained in this study.

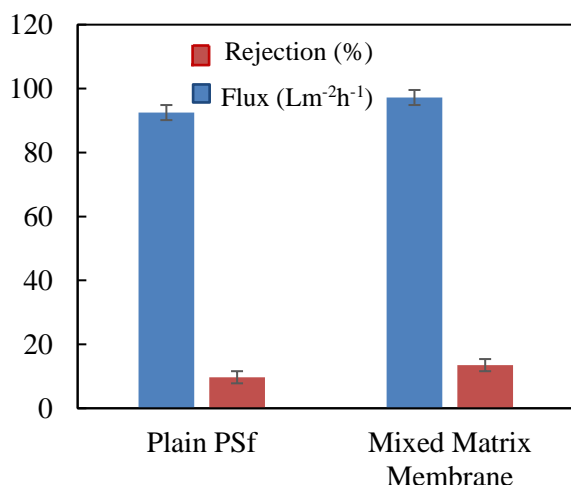


Figure 4. Water flux and salt rejection of TFC membranes.

It is also seen from the results of Fig. 4 that the percentage of the salt rejection of the plain polysulfone membrane was 92.5% which increased to 97.21% by the addition of ZnO nanoparticles to the polymer matrix. The added nanoparticles to the polymer matrix block some membrane pores and prevent the salt molecules passing through the membrane resulting in the increment of the salt rejection efficiency. In a study by Emadzadeh et al. [15], using a TFC PSf-TiO₂ mixed matrix

membrane, the maximum salt rejection was 94.05%, which is lower than the salt rejection obtained in the current research.

The water permeability (A), salt permeability (B) and their ratio (B/A) were calculated using equations 3 and 5, which are presented in Figure 5. The ratio of the salt permeability to the water permeability (B/A) is considered as a suitable criterion to study the membrane desalination performance, of which the lower value indicates better membrane performance in the reverse osmosis desalination process. The results show that the mixed matrix membrane has the higher water permeability and lower salt permeability than the plain polymer membrane. As a result, B/A ratio has dropped significantly from 40.54 to 14.35 (kPa). The reduction of the B/A ratio indicates the better desalination ability of the mixed matrix membrane than the plain polymer membrane. Therefore, it can be concluded that the addition of ZnO nanoparticles to the membrane substrate has significantly improved the membrane salt separation properties.

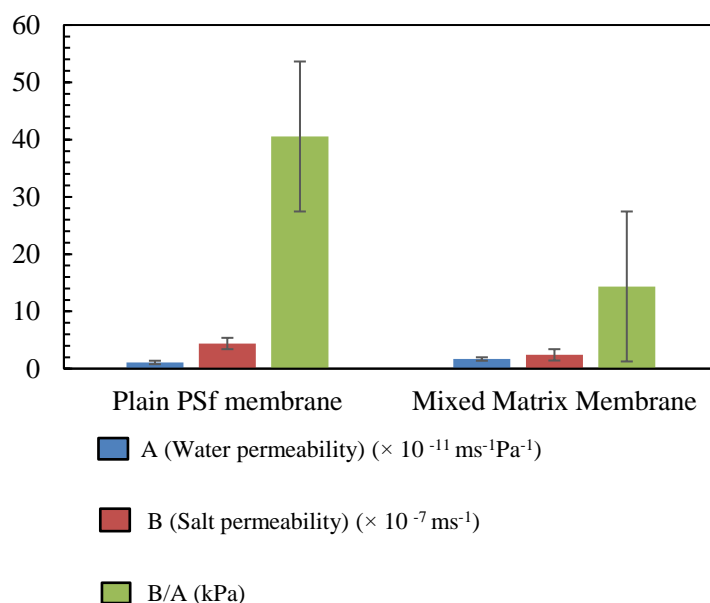


Figure 5. Separation characteristics of TFC membranes.

6. Conclusion

In this study, plain PSf and PSf-ZnO mixed matrix membranes were fabricated via the phase inversion method. Then a polyamide thin film was fabricated by the interfacial polymerization on the membranes surface. The morphology and properties of the membranes were investigated then, the fabricated membranes were used in reverse osmosis desalination. The comparison of the cross-sectional images of the substrates of membranes shows that the addition of ZnO nanoparticles to the polymer matrix creates a denser structure and increases the thickness of the sponge-like layer close to the lower surface of the membranes. Also the images of the membranes surface after polymerization confirmed the formation of a dense and integrated polyamide film on the membrane surface. The addition of ZnO nanoparticles to the polymer matrix decreased the contact angle of the membrane surface with water, thereby having increased the hydrophilicity of the membrane surface. The membranes substrates made of Plain polymer and the mixed matrix membrane have a total porosity of 76.30% and 72.93% respectively, which are suitable for the formation of a polyamide film. The values of the pure water flux through both membranes decreased at the beginning of the process and after 60 min remained almost constant at $19.50 \text{ (Lm}^{-2}\text{h}^{-1}\text{)}$ and $30.20 \text{ (Lm}^{-2}\text{h}^{-1}\text{)}$ for the plain PSf membrane and mixed matrix membrane respectively. The results of the reverse osmosis process showed that the water flux of the plain PSf membrane was $9.70 \text{ (Lm}^{-2}\text{h}^{-1}\text{)}$ which increased about 39% by the addition of ZnO nanoparticles and reached $13.50 \text{ (Lm}^{-2}\text{h}^{-1}\text{)}$. Also, the salt rejection of the plain PSf membrane was 92.5% which increased to 97.21% by the addition of ZnO nanoparticles to the polymer matrix. With the addition of ZnO nanoparticles to the polymer matrix, the ratio of the salt permeability to the

water permeability (B/A) decreased significantly from 40.54 to 14.35 (kPa) which indicates the better desalination ability of the mixed matrix membrane than that of plain polymer membrane. Therefore, it can be concluded that the addition of ZnO nanoparticles to the membrane substrate has significantly improved the membrane desalination performance.

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