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Preparation of a positively charged NF membrane by evaporation deposition and the reaction of PEI on the surface of the C-PES/PES blend UF membrane

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Abstract

A positive surface thin-film composite membrane was prepared via evaporation deposition and the reaction of polyethyleneimine (PEI) with the carboxyl groups on the surface of a carboxylated polysulfone (C-PES)/PES UF blend membrane. UF blend membranes with different C-PES/PES ratios were prepared and PEI solution was deposited on them, with subsequent crosslinking using glutaraldehyde. The optimal C-PES/PES ratio was used on the supporting UF blend membrane, with optimal crosslinking time using glutaraldehyde to obtain a significant rejection of salt and organic molecules rejection, while retaining the water flux at a reasonable level. The preparation of a UF blend membrane with a negative surface charge based on the C-PES/PES ratio and its interaction with PEI solutions of different concentrations was the key point in obtaining a membrane with the appropriate rejection of divalent cation and organic solutes. The effects of the membrane surface charge on the rejection of different salts and organic solutes were evaluated at different pressures to understand the rejection mechanism of the prepared NF membranes.

Keywords: Positively charged NF membrane; C-PES/PES blend UF membrane; Evaporation deposition of PEI molecules; Membrane surface charge; Membrane separation mechanism.

1. Introduction

Over the past few years, water pollution and industrial wastewater have become the most significant threats to the environment, human health, and economy. Due to the increasing world population, development of industry, and the increasing pollution of freshwater resources, access to a sufficient and clean water supply has become a crisis in many countries. The limited freshwater resources have been exposed to a variety of contaminants, which have entered the system through wastewater. The most common pollutants can be sourced from industrial wastewater, biological wastewater, heavy metals, chemical fertilizers, and pigments.

The treatment and reclamation of wastewater is an effective means by which to alleviate the global water stresses. Various methods have been developed for wastewater treatment while taking efficiency and energy consumption into consideration. Water treatment processes using membranes are promising techniques that have been rapidly developing over the last couple of decades on a commercial scale. The application of membranes in industrial separation processes has increased since the 1960s [1]. The term nanofiltration (NF) was first used in 1988 by Cadot et al. [2]. The NF process has properties that lie somewhere between ultrafiltration (UF) and reverse osmosis (RO), with pore sizes that range from 1 to 9 nm, and a molecular weight cut off (MWCO) of 300–500 Daltons [3]. Nanofiltration is used to separate inorganic salts and small organic molecules in a manner similar to that used in RO. One of the critical properties of NF is the low rejection of monovalent salts and the high rejection of multivalent salts. Polymeric membranes are more appropriate for use in this process because of their flexibility and ability to form asymmetric and composite structures [4]. NF is a complex process which depends on the hydrodynamic and interfacial phenomena that occur at the surface and the pores of the membrane. Membrane rejection during NF can be related to a combination of Donnan exclusion and sieving [1, 5]. When NF membranes are prepared with a considerable surface charge, ionic species can be rejected via the Donnan exclusion mechanism [6].

NF membranes have either negative or positive surface charge, and are therefore useful for separating ions. The surface of classical NF membranes is usually negatively charged, and is therefore useful for rejecting multivalent anions. The performance of NF membranes also depends on other important parameters, including the surface porosity of the dense layer and the number of effective pores in the active layer of the membrane [7]. Several studies have recently been carried out concerning the fabrication of charged nanofiltration membranes. Jamil et al. [8] prepared NF thin-film composite (TFC) membranes via interfacial polymerization using piperazine with isophthaloyl chloride on a porous PES/PAN blend membrane. A UF PES/PAN membrane was prepared via phase inversion and used as a substrate to produce TFC NF membranes using an interfacial polymerization process incrementally between PIP and IPC. The salt rejection was 99.9, 99, 82, and 72% for Na_2SO_4, $MgSO_4$, $CaCl_2$, and NaCl, respectively, when using this membrane. The molecular weight cut-off of the fabricated membrane reached approximately 600 Da with a pore size of 0.67 nm. In another study, Fang et al. [9] used interfacial polymerization on the inner surface of a PES UF hollow fiber membrane to develop a thin-film skin layer on the membrane. Instead of using PIP, branched PEI, a cationic polyelectrolyte with a high amount of primary and secondary amine functional groups, was used as the polymerization monomers, together with TMC to yield a positively charged selective layer. The thin selective layer prepared in this process shows a highly hydrophilic nature with a contact angle of around 41°. The membrane also exhibits a MWCO of 500 Da with an effective pore diameter of 1.29 nm and a positive charge. By using a combination of the Donan exclusion and steric hindrance, PWP around 17 L/m^2.h.bar and $MgCl_2$ (1000 ppm) rejection near to 97% was achieved under trans-membrane pressure of 2 bar.

One of the methods used for the preparation of NF composite membranes is cross-linking of the surface polymer with the support layer of the membrane. This cross-linking within the NF membrane results in a decrease in the size of the pores in the active layer and a limited pore size distribution [10, 11]. Recently Setiawan et al. [12] prepared a polyelectrolyte NF membrane with a positively surface charged using a dual-layer hollow fiber membrane with Torlon poly(amide-imide) (PAI) as the selective layer and PES as the porous support layer. A positively charged NF selective layer with MWCO < 6000 Da was then developed via simple polyelectrolyte cross-linking using polyallylamine (PAAm). NF hollow fiber membranes prepared using this method showed a saltwater permeability of 15.8 L/m^2.h·bar and high Mg^{2+} and Ca^{2+} rejections of 94.2% and 92.3%, respectively, using a 3000 ppm TDS feed solution. In another study carried out by the same group, Wei et al. [13] prepared NF membranes with hydroxyl groups ending in hyperbranched polyester (HPE), using a polysulfone (PSf) ultrafiltration membrane as the porous support. The PSf-UF membrane was wetted with ethanol and immersed in water that contained HPE, using sodium dodecyl sulfate (SDS) as a surfactant. The membrane subsequently underwent heat treatment in an oven. The NF membranes obtained using this method demonstrated an acceptable rejection with a high water permeability in the range of 40-45 L/m^2.h and a color (Rhodamine B and Xylenol) rejection that was close to 100% under 0.3 MPa. In another interesting study, Han et al. [14] developed NF hollow fiber membranes for the effective fractionation of dyes and inorganic salts for use in the treatment of wastewater from the textile industry. A Torlon/ sulfonated polyphenylene sulfone (sPPSU) blend UF hollow fiber membrane was prepared to control the membrane formation and optimize the membrane surface pore size and also water permeability, as well as introducing a negative charge onto the membrane surface. Hyperbranched PEI was then applied as the modification agent to further optimize the mechanical stability, pore size, surface chemistry, and charge properties of the membrane. The surface modification was done by hyperbranched PEI to decrease the pore diameter to around 0.85 nm and the MWCO to 680 Da. After this modification, membrane surface becomes more hydrophilic and positively charged. Because of the synergistic effects of size exclusion and charge repulsion, prepared hollow fibers showed high water fluxes in the range of 7.0 - 71.2 L/m^2.h and rejections of various dyes higher than 96% at operating pressure of 1 bar.

In our previously published paper [15], a PEI solution was used for electrostatic deposition and reaction on the prepared blend carboxylated polysulfone (C-PES)/PES membrane surface in order to obtain a membrane for the application of water softening at low pressure, which resulted in a membrane with a rejection of approximately 90%. Regardless of the enhancement in water permeability, this rejection never increased to higher than 95%. Most of the studied parameters showed an optimum water permeability and rejection. Although many of the parameters were changed over a wide range, a high rejection by the divalent membrane was not obtained.

High divalent and multivalent rejection is needed for water softening applications. In the current study, evaporation deposition assisted with the reaction of the PEI solution on the negative charge at the surface of a blend UF membrane was used to prepare membranes with high multi-valent rejection. The self-segregation of the C-PES carboxyl groups on the surface of the C-PES/PES blend UF membrane was used to prepare an appropriate substrate for the preparation of a NF membrane with high divalent and organic solute rejection. For the preparation of a UF support with an optimal C-PES/PES ratio, a negative charge at the surface of the blend UF membrane was the key point to obtain a NF membrane with an optimal filtration performance (Flux and Rejection), which ultimately resulted in a high positive surface charge on the NF membrane. Using the method employed in this study, membranes with lower surface porosity, lower water flux, and a much higher divalent cation rejection of approximately 99.5% were obtained, compared to our last study [15]. To understand the effect of the membrane surface charge and sieving on the membrane filtration performance (Flux and Rejection), different salts and organic molecules (methylene blue) were used. By using the method of PEI evaporation deposition and reaction on the blend UF membrane surface, the filtration performance of the membrane, with regards to the parameters investigated, was found to be different from that in our previously published paper [15].

2. Material and Method

2.1. Materials

The poly (ethyleneimine) (solution 50% in H_2O, Mw 600,000-1,000,000) was supplied by Sigma Aldrich. Polyethersulfone (PES, Ultrason E6020P, Mw=58,000 g/mol) was purchased from BASF, Germany. Analytical grade dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), glutaraldehyde (GA, 25%), magnesium sulfate ($MgSO_4$), calcium sulfate ($CaSO_4$), sodium chloride (NaCl), methylene blue (MB), acetyl chloride (C_2H_3ClO, M=78.49 g/mol), and potassium permanganate ($KMnO_4$, M= 158.03 g/mol) were purchased from Merck. All chemicals were used without further purification.

2.2. Synthesis of carboxylic polyethersulfone (C-PES)

For increasing the hydrophilicity of the membrane and inducing a negative charge on the prepared blend UF membrane to develop a support layer for the NF membrane, carboxylic groups were added to the polymeric PES chains and a C-PES/PES blend membrane was thus prepared. The carboxylic polyethersulfone (C-PES) was prepared by controlling the conditions of the acetylation and oxidation. PES with 20 wt. % was dissolved in a NMP solvent. Acetyl chloride and aluminum chloride (as a catalyst) were mixed with the NMP, added to the PES solution at 90 ° C in a three-neck distillation bottle, and stirred for 2 h. The product of this reaction (PES-COOH) was then washed twice with double distilled water and dried in the oven for 24 h. The product of the first step was dissolved in NMP with 20 wt. % concentration for oxidation. Potassium permanganate, sodium hydroxide, and double-distilled water were added to the NMP, and the solution was slowly added to the polymer solution at 80 °C. After 6 h, the resulting solution was centrifuged for 30 min at 4000 rpm, and was finally dried in the oven for 24 h to produce the red PES-COOH [16].

2.3. Fabrication of negative charged blend UF membrane by phase inversion method

PES, C-PES, and the solvent DMAC were mixed at a specific percentage in order to prepare the negatively charged UF blend membrane for use as a support layer in the preparation of the NF membrane. For this purpose, 14% of PES and a certain weight percentage of C-PES (C-PES/PES = 2%, C-PES/PES = 6% and C-PES/PES = 10%) was added to DMAC as a solvent and stirred at 250 rpm for 24 h. The polymeric solution was then placed in a heater at a temperature of 60 °C for 24 h to release the air bubbles. After that, the polymer solution was cast as a thin film on a flat glass surface with a thickness of 150 µm and immediately immersed in the coagulation bath at room temperature. The prepared UF blend membrane was also placed in the coagulation bath for 24 h. The C-PES on the membrane surface is responsible for its negative charge.

2.4. Fabrication of active layer film on prepared negative charged UF blend membrane

A poly(ethyleneimine) (PEI) layer was deposited on the negatively charged blend UF membrane using evaporation deposition and reaction. The PEI is bonded strongly to the surface of the membrane, based on the electrostatic interaction and cross-linking reaction at high temperatures [15]. The blend UF membrane was then immersed in a PEI solution at the specific concentration of (5/15/25 g/l) for 3 h at a high temperature, such that the PEI was deposited on the membrane surface after evaporation. This was then washed with distilled water. According to the initial results, the concentration of PEI solution in the active layer and the weight percentage of PES-COOH in the support layer of the membrane were selected as the most important factors, and each was evaluated at three levels. The conditions at which membrane fabrication took place are summarized in Table 1. The deposition of PEI on the surface of the membrane was found to increase the surface-active layer stability and decrease the pore size of the NF membrane. As a result, the membrane rejection was improved and the membrane flux was reduced. Due to the effects of the GA concentration and reaction time, crosslinking was selected. As seen in Fig. 1, the GA was dissolved in double-distilled water at pH = 7 at a concentration of 0.3 or 1 g/L. After preparation, the solution was poured onto the membrane surface for different crosslinking reaction times of 15 to 60 min. After the crosslinking of the PEI with the GA, the membranes were washed with double-distilled water and placed in the oven at 50 °C for drying, then retained between two layers of filter paper until evaluation.

Table 1. The NF membranes' preparation and optimization conditions.

Membrane number	Stage	C-PES/PES	PEI solution concentration (g/L)	GA solution concentration (g/L)	Cross-linking reaction time (min)
M1	Optimization of Cross-linking reaction with C-PES/PES of 6/100 and PEI concentration of 15 g/l	-	-	1	5
M2		-	-	0.3	5
M3		-	-	0.3	15
M4		-	-	0.3	35
M5		-	-	0.3	60
M6		-	-	0.3	180
M7		2/100	5	-	-

M8		2/100	15	-	-
M9		2/100	25	-	-
M10		6/100	5	-	-
M11	Optimization of the most important parameter with GA solution concentration of 0.3 g/l and cross-linking reaction time of 35 min	6/100	15	-	-
M12		6/100	15	-	-
M13		6/100	15	-	-
M14		6/100	25	-	-
M15		10/100	5	-	-
M16		10/100	15	-	-
M17		10/100	25	-	-

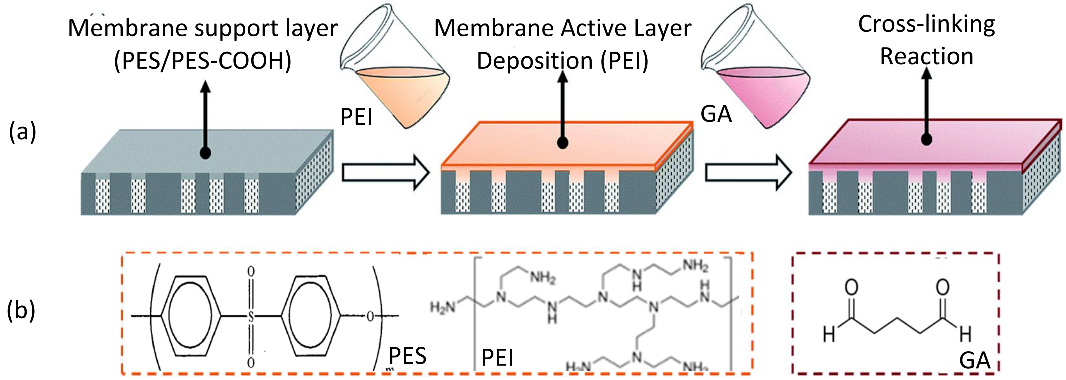


Fig. 1. Schematic procedure of (a) NF membrane preparation, and (b) the designed molecular structure of the membrane.

2.5. Evaluation of the synthesized C-PES polymer

The synthesized polymer was analyzed using nuclear magnetic resonance (NMR; JEOL ECZ400, Japan), with $DMSO_2$ as the solvent.

2.6. Evaluation of the prepared membranes

FTIR was employed to investigate the chemical structure of the prepared membrane surface for the presence of PES-COOH and PES-$COCH_3$ in the range of 400 - 4000 cm^{-1}, using the FTIR Spectrometer Perkin Elmer 56 Spectrum RX1.

The hydrophilicity of the prepared membrane surface was evaluated via measurement of the sessile drop contact angle. Clean membrane samples were mounted onto a glass slide and 5 µL of deionized water drops were placed upon the surface of the membrane. After 10 s, enlarged images were taken of the micro-droplets at random locations using a Nikon D300 digital camera.

The Zeta potential of the surface of the prepared membranes was then measured using the streaming potential (EKA Anton Paar electrokinetic analyzer). A 0.01 M solution of KCl was used as an electrolyte to specify the ionic strength for the zeta potential measurements.

Scanning electron microscopy (SEM, A VEGA, TESCAN, Czech Republic) images were used for investigation of the membrane surface and the cross-section morphologies. The membranes were broken in liquid nitrogen and then rendered electrically active via sputter-coating with a gold layer.

A nano-filtration setup with a similar design to that used in our previously published paper [15] was used for the membrane performance test. The NF setup was equipped with a high-pressure pump with the ability to supply feed solution at a pressure between 5 and 25 bar. The feed solution was pumped to the membrane module using the high-pressure pump, and contacted with the effective surface area of the membrane. The water flux and rejection performance of the NF membrane was investigated with methylene blue, calcium chloride salt, magnesium chloride, and sodium chloride solutions. The pressure was kept constant at 10 bar for the color removal tests and at 2, 6, and 10 bar for the salt removal tests. To accelerate reaching steady-state conditions of the membrane, the pressure was increased to 20% higher than the filtration pressure in the first hour of measurement. After approaching steady-state in terms of flux and ion rejection, the membrane separation performance was recorded. The flux of the NF membrane was determined based on the permeate mass flow from the effective area of the membrane (26.5 cm^2) at a specified time. The membrane flux (J) was calculated using the following equation [17]:

$$J = \frac{m_p}{A \times \rho \times \Delta t} \tag{1}$$

where J is the membrane flux in $L/m^2.h$, m_p represents the permeated in kg, A is the membrane area in m^2, ρ is water density in (kg/L), and Δt is the permeation time in h.

The membrane rejection was then calculated using the following [17]:

$$R\ (\%) = \frac{C_f - C_p}{C_f} \times 100 \tag{2}$$

where R (%), C_f and C_p are rejection, and the concentration of color/salt in the feed stream and the permeate stream, respectively. The concentration of the feed color was fixed at 100 ppm and that of the salt feed solution at 1000 ppm for the filtration experiments. Color molecules concentration were determined using a UV spectrophotometer (double-beam UV-VIS spectrophotometer Shimadzu (Kyoto, Japan) UV-1700) with a wavelength of 633 nm and the salt concentration was measured with an electro conductometer (HANNA HI 2300, USA). The permeated liquid absorption wavelength in the color removal and the permeated liquid electrical conductivity in the salt removal were then converted to color/ions using a calibrations curve.

3. Result and Discussion

3.1. Evaluation of the synthesized C-PES polymer

As antecedently mentioned, the synthesis of the C-PES polymer was carried out through PES polymer acetylation and oxidation reactions. The HNMR spectra of PES-$COCH_3$ and PES-COOH are shown in Fig. 2. As can clearly be seen, both spectra show intense peaks at $\delta=7.2$ and $\delta=7.9$, which are related to the chemical shifts of the phenyl rings in the main chain of the PES. The low intense peak at $\delta=2.6$, shown by the letter "b", was assigned to the chemical shift of acetyl group (–$COCH_3$), grafted to the phenyl ring of the PES chain after the acetylation reaction. A weak hump around $\delta=10.83$, shown by the letter "c", has appeared due to the formation of–COOH functional group during the oxidation reaction. The HNMR result indicates the successfulness of PES acetylation and carboxylation.

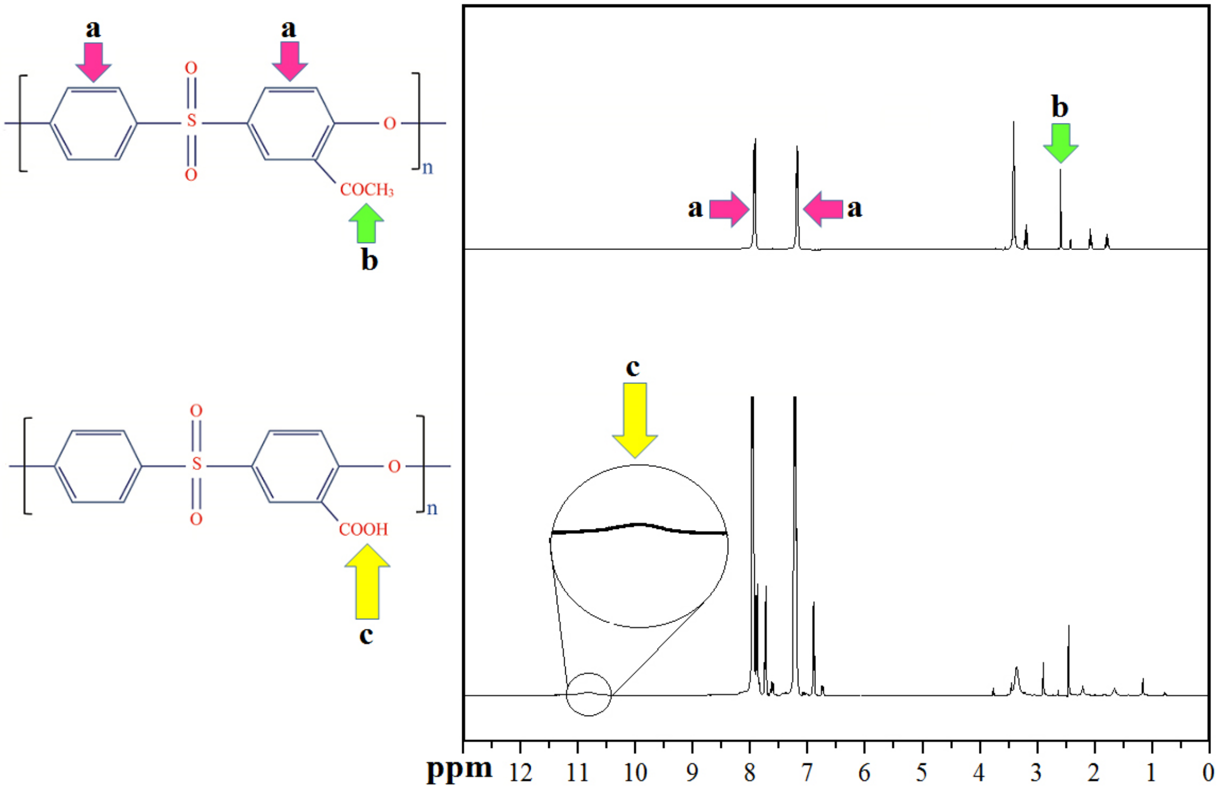


Fig. 2. ^{1}H NMR spectra of PES–COCH$_3$ and PES–COOH

3.2. Evaluation of the C-PES/PES blend UF membrane

To evaluate the chemical bonds of the fabricated membranes, ATR-FTIR analysis was performed in the range of 1000 to 4000 cm^{-1}. Fig. 3 illustrates the ATR-FTIR spectra of the neat PES UF membrane (spectrum a), C-PES/PES blend UF membrane (spectrum b), and the NF membrane formed on a PES porous substrate (spectrum c). The NF membrane was prepared by crosslinking PEI (1.0 wt. %) with C-PES molecules using GA (0.5 wt. %) as the cross-linker. As seen in Fig. 3, the appearance of absorption bands at 1670 and 3429 cm^{-1} can be attributed to a stretching vibration in the carboxyl functional groups (spectrum b). In spectrum c, the formation of the selective layer is confirmed by the emergence of two bands at 1148 and 1238 cm^{-1}, which are the results of the stretching vibration of tertiary amine functional groups (C-N) formed during crosslinking. Two other absorption bands at 1658 and 3403 cm^{-1} could be assigned to the stretching vibrations of the acetyl and carboxyl groups of the unreacted chemical reagents, respectively, on the surface of the C-PES membrane, or on some C-PES molecules that were deposited during the evaporation of the PEI solution.

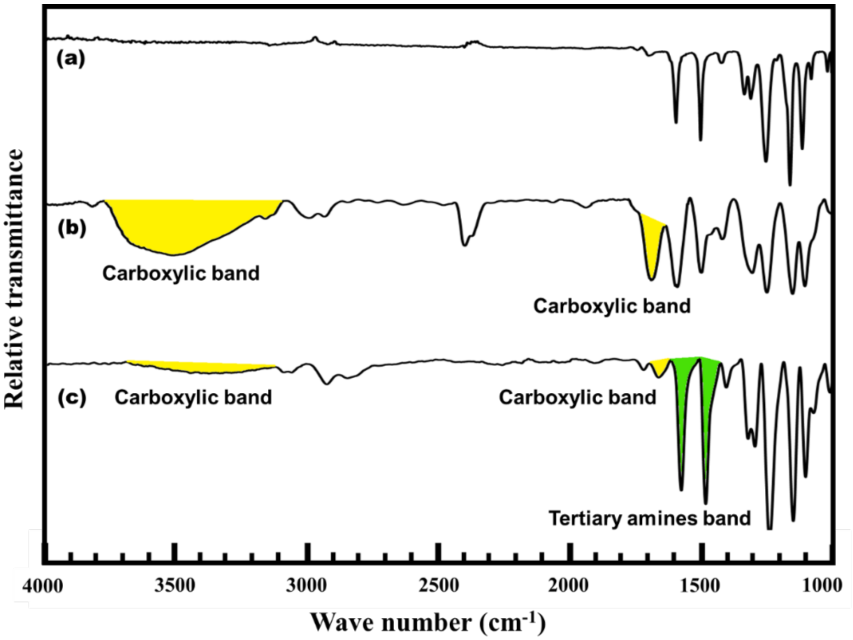


Fig. 3. ATR-FTIR spectra of (a) Neat PES UF membrane (b) (C-PES)/PES blend UF membrane (c) NF membrane formed on the (C-PES)/PES blend UF membrane.

3.3. Prepared membranes surface hydrophilicity

The hydrophilicity of the different prepared membranes was measured using the water contact angle. The results are summarized in Fig. 4. The effects of the addition of C-PES to the hydrophilicity of the blend UF membrane, and the C-PES/PES ratio and PEI concentration on the hydrophilicity of the prepared NF membranes is shown in Fig. 4. By blending C-PES at a ratio of 1/10 of the membrane, the contact angle decreased sharply from 75° for pure PES to 57°, which suggests that the hydrophilicity increased due to the presence of the carboxylic groups on the surface of the membrane [17-20]. As carboxylic groups are hydrophilic, they move to the water-polymer interface during phase separation, rendering the membrane surface hydrophilicity. This phenomenon was confirmed by measuring the surface charge of the prepared membranes. The deposition and reaction of the PEI molecules on the blend UF membrane surface caused a decrease in the hydrophilicity and an increase in the contact angle because the hydrophilicity of the PEI polymer is less than that of the carboxyl group [21]. It is clear from Fig. 4 that although the contact angle increased after PEI deposition, the prepared NF membrane surface is still slightly more hydrophilic than that of the neat PES membrane.

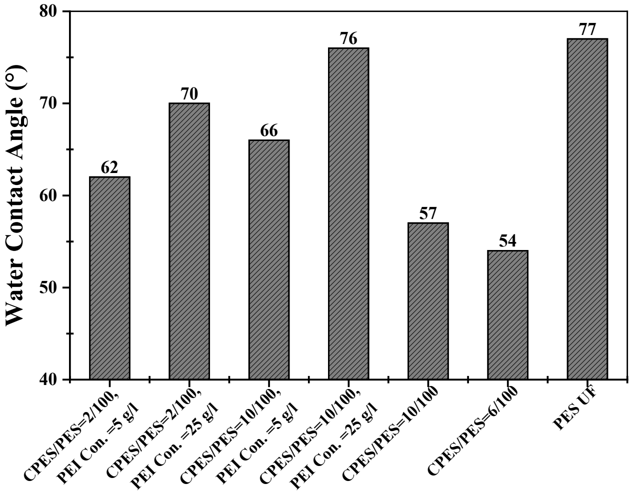


Fig. 4. Water contact angles of the prepared membranes with different C-PES and PEI contents, maximum tolerance of water contact angle analysis for each sample was around 2 °.

3.4. Zeta potential of prepared membranes surface

The effects that the addition of C-PES and PEI deposition and reaction had on the surface charge of the prepared membranes was also evaluated, and the results are shown in Fig. 5. It is clear that for the prepared PES and C-PES/PES UF membranes the negative charge at the surface increased along with the pH. The UF blend membrane prepared with a C-PES/PES ratio of 6/100 (dashed line) displayed a more negative charge than that of the neat PES (continuous line) membrane. As the carboxyl group in the C-PES structure includes the negative charge and is hydrophilic, it is expected that the carboxyl groups move to membrane surface during the phase separation, rendering it hydrophilic and increasing the negative charge on the surface of the membrane. However, when the C-PES/PES ratio was increased from 6/100 to 10/100, the surface negative charge sharply decreased (dashed line). This phenomenon can be explained as follows. Increasing the C-PES/PES ratio raises the hydrophilicity of the polymer solution, which results ina more rapid exchange of solvent and non-solvent (water) during phase inversion, and subsequently the movement of carboxyl groups to the surface of the membrane becomes difficult, resulting in a lower concentration of carboxylic groups and a negative charge on the surface of the membrane [17, 20]. Thus, it can be concluded that doping the solution with an optimal C-PES/PES ratio is needed to obtain a membrane with enough negative charge to cause a strong interaction between the PEI and the membrane surface for higher separation performance.

To investigate the effect of PEI deposition and reaction on the NF membrane surface charge, the zeta potential of the samples in which PEI was deposited and reacted at a concentration of 25 g/L was measured. The deposition and reaction of PEI on the blend UF membrane with a negative charge caused the surface charge of the NF membrane became positive. This change in the surface charge is due to the presence of positively charged ammonium cations (NH_4^+) in the PEI polymer. From Fig. 5, it is evident that the prepared NF membrane showed a maximum surface charge in the studied pH range. At low pH, the PEI molecules remain non-protonated and therefore the membrane surface charge is slightly positive. With a further increase in pH from 7 to 10, the effect of the charge of the solution on the membrane surface surpasses the protonation and the positive charge at the surface decreases. It is apparent from Fig. 10 that after deposition of the PEI on the blend UF membrane, the membrane with the highest positive surface charge is the same one that had the most negative charge from the preparation of the UF membrane with a C-PES/PES ratio of 6/100. As explained above, we think that the amount of carboxyl functional groups on the membrane surface is higher at a C-PES/PES ratio of 6/100 than for the other ratios. The increase in the occurrence of the carboxylic groups leads to a stronger interaction of the carboxylic group with the PEI molecules. In another words, if more PEI molecules are deposited and/or reacted on the membrane surface, the result is a higher surface positive charge. It is expected that this membrane should show a higher rejection of divalent cations because of the high positive charge at the surface.

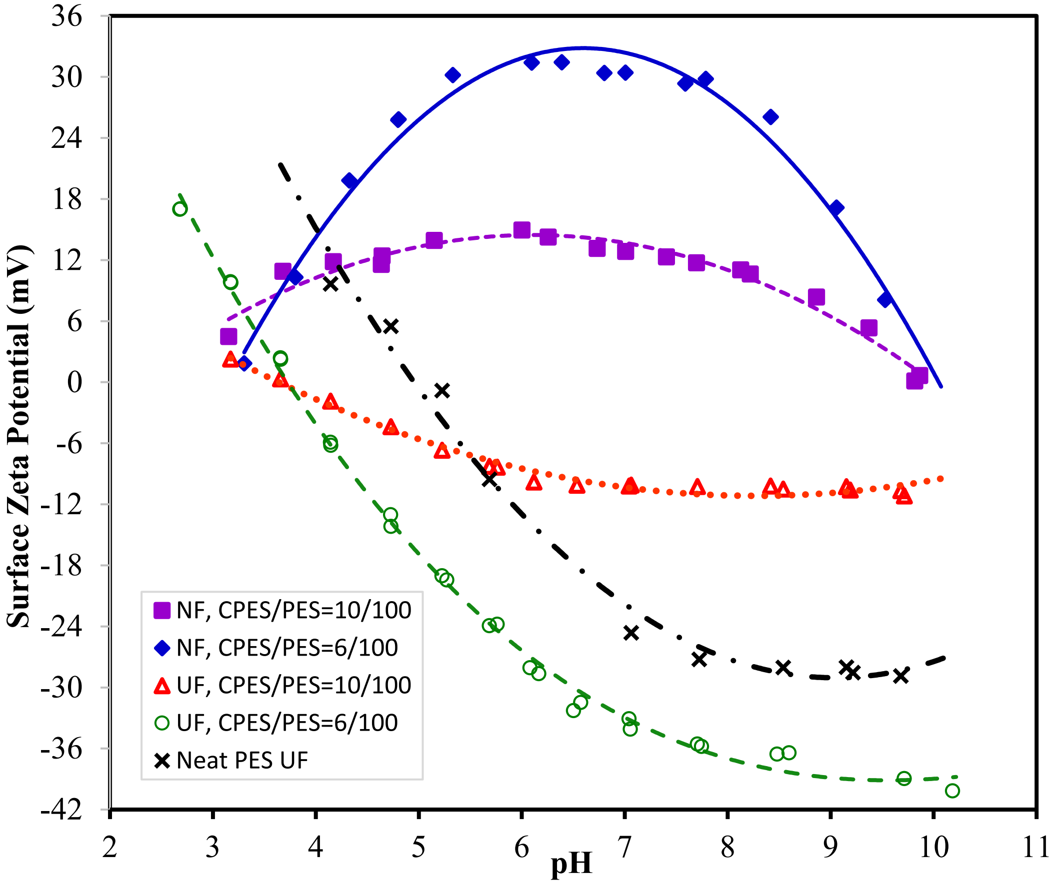
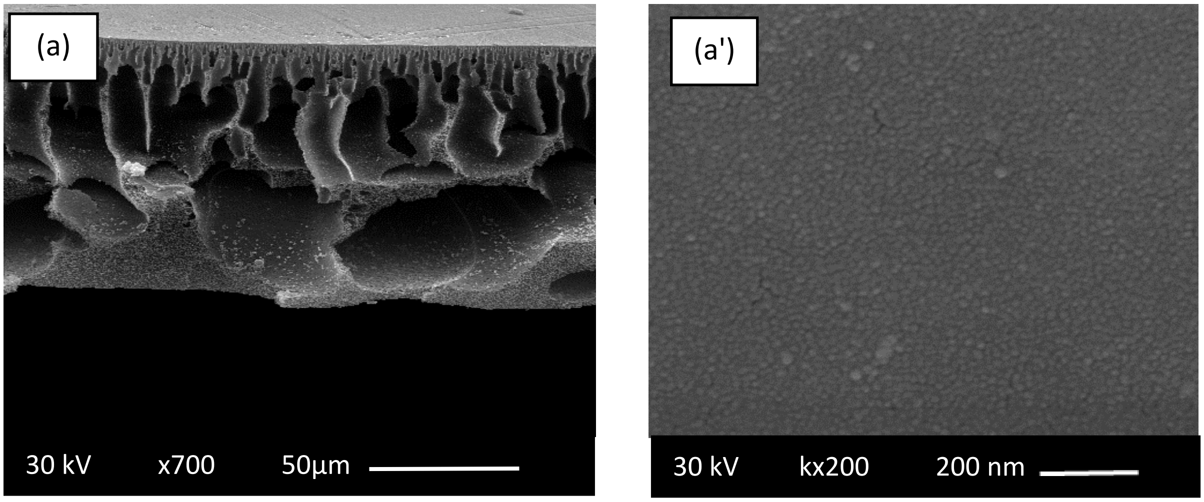


Fig. 5. Surface Zeta potential for the prepared blend UF membranes and NF membrane (after PEI deposition and reaction with a PEI concentration of 25 g/L)

3.5. FE-SEM images of the prepared membranes

The FE-SEM images of the cross-section and the outer surface of the prepared blend C-PES/PES UF membranes can be seen in Fig. 6, from which it is clear that by increasing the C-PES/PES ratio the macrovoid volume increased, and that this can be related to the faster exchange of the solvent and non-solvent in the polymeric solution due to the addition of hydrophilic C-PES [22]. While a notably large pore was observed at ~10 µm on the wall of the macrovoid in the membrane with C-PES/PES = 10/100 (Fig. 6 (C)), only smaller pores were observed on the macrovoid walls of the other prepared UF blend membranes. The larger porosity and pore size of a macrovoid wall is directly related to the exchange rate between the solvent and nonsolvent, which is increased by raising the C-PES content due to the higher hydrophilicity, better compatibility, and faster intrusion of the non-solvent to the polymer solution. For the same reason, the surface pore size and porosity of the prepared membranes can be increased by increasing the C-PES/PES ratio to some extent. Although not shown here, the pore size at the outer surface of the prepared NF membranes was very small, and cannot be detected with FE-SEM analysis.

The surface SEM images of the prepared membranes shown in Fig. 6 are in good agreement with the permeability of pure water, which increased by raising the C-PES/PES ratio from 35 LMH/bar for C-PES/PES = 2 to 63 LMH/bar for the ratio of C-PES/PES = 6/100 and 87 LMH/bar for the ratio of C-PES/PES = 10/100.



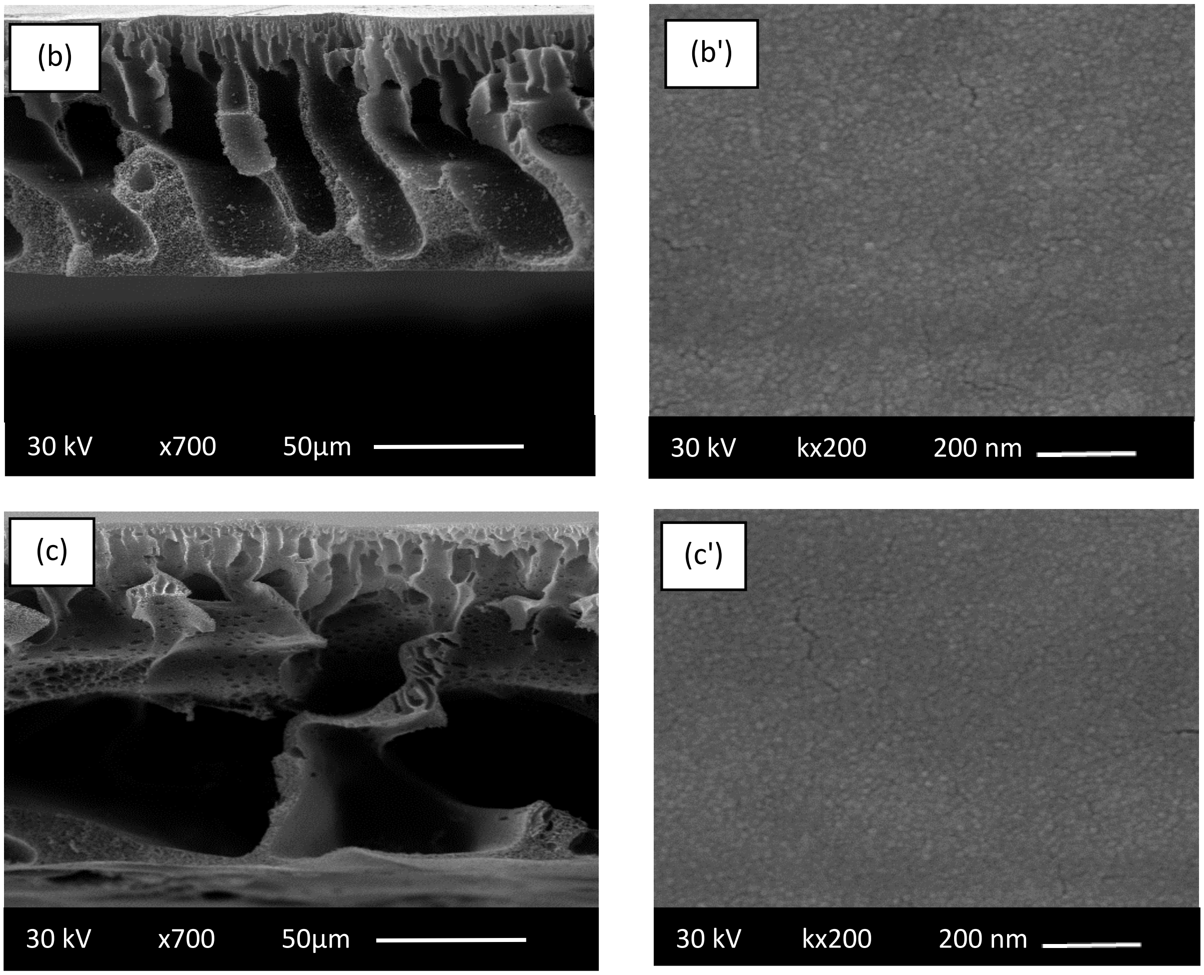


Fig. 6. Cross section and surface FESEM images of membranes prepared with different C-PES concentrations: a & a' (cross section and top surface, respectively) C-PES/PES = 2/100, b & b' (cross section and top surface, respectively) C-PES/PES = 6/100, and c & c' (cross section and top surface, respectively) C-PES/PES = 10/100.

3.6. Effect of crosslinking reaction condition on fabricated NF membranes

The effects from the concentration and reaction time of the crosslinking agent (GA) on the prepared NF membrane rejection and flux were evaluated using 1000 ppm of MB molecules as a feed solution. The results are shown in Fig. 7 and 8, respectively. It is apparent that by increasing the concentration and crosslinking reaction time of GA from 0.3 to 1 g/L and from 5 to 180 min, respectively, the water flux was reduced almost fourfold, and the rejection of the MB increased from 92% to 99%. Because MB is considered an organic molecule with a low charge, the increase in the membrane rejection performance can be related to the smaller pore size of the surface-active layer. From Fig. 7 and 8 it is clear that the flux and rejection of the membranes have a reciprocal relationship. By increasing the membrane flux the rejection decreases, and vice versa. To obtain an acceptable value for water flux and rejection, crosslinking the reaction with a GA solution concentration of 0.3 wt. % and a reaction time of 35 min was selected as the optimal conditions [23-25].

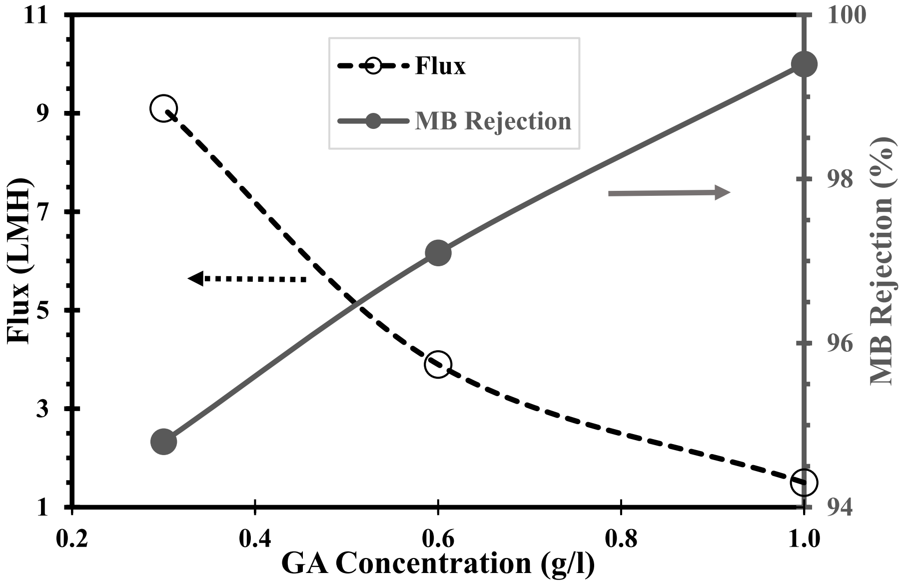


Fig. 7. Effect of GA concentration on the water flux and MB rejection of the prepared NF membranes at an operating pressure of 10 bar and an ambient temperature.

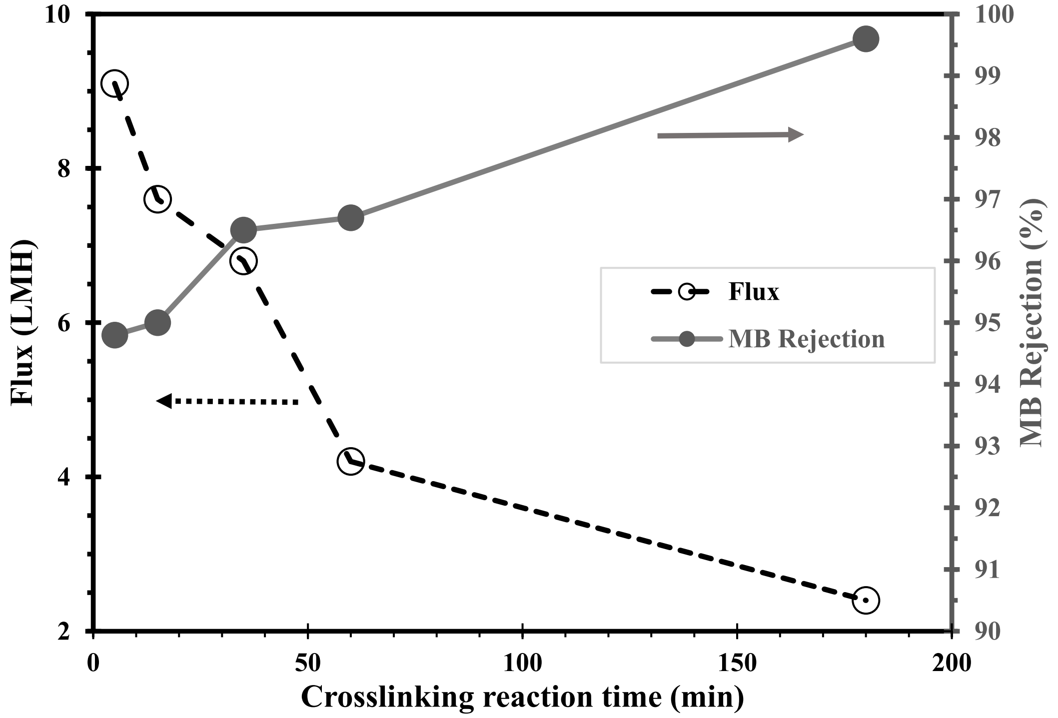


Fig. 8. Effect of crosslinking reaction time on the prepared NF membranes water flux and MB rejection at an operating pressure of 10 bar and an ambient temperature.

3.7. Effect of PES-COOH content on the NF membranes separation performance

The effect of the ratio of C-PES/PES used in the preparation of the blend UF membrane on the separation performance of the final prepared NF membrane is shown in Figure 9. As the C-PES/PES ratio is increased from 2 to 10, the NF membrane flux initially increased, and then decreased after reaching a maximum at C-PES/PES = 6. This phenomenon can easily be explained by considering the surface zeta potential of the UF membrane. As mentioned in section 3.4, the blend UF membrane with C-PES/PES = 6 had the most negative surface charge, and after the deposition of PEI = 25 g/L, the surface showed the highest positive charge. This is because high negative charge resulted in a stronger interaction between the PEI molecules and the surface of the membrane, meaning that more PEI molecules can interact and react with the COOH groups on the blend UF membrane surface, resulting in a denser layer that is coated with the reactive PEI molecules. The thicker PEI layer has a stronger resistance to the mass transfer of water molecules and thus the water flux decreases. However, the pores created after the PEI reaction were small enough to significantly reject the MB. Therefore, MB rejection did not change significantly under different C-PES/PES ratios.

From Fig. 9, it is clear that the effect of the concentration of the PEI solution on the membrane water flux and MB rejection was stronger than that of the C-PES/PES ratio. This trend can be explained by considering that the selective layer of the NF membrane plays a significant role in separation performance. In this study the evaporation deposition was assisted by the PEI reaction used to prepare the NF membrane, meaning that the thickness of the deposited layer directly affects the water flux and rejection. A higher concentration of PEI solution means a thicker layer of PEI, which strongly affects the membrane filtration performance.

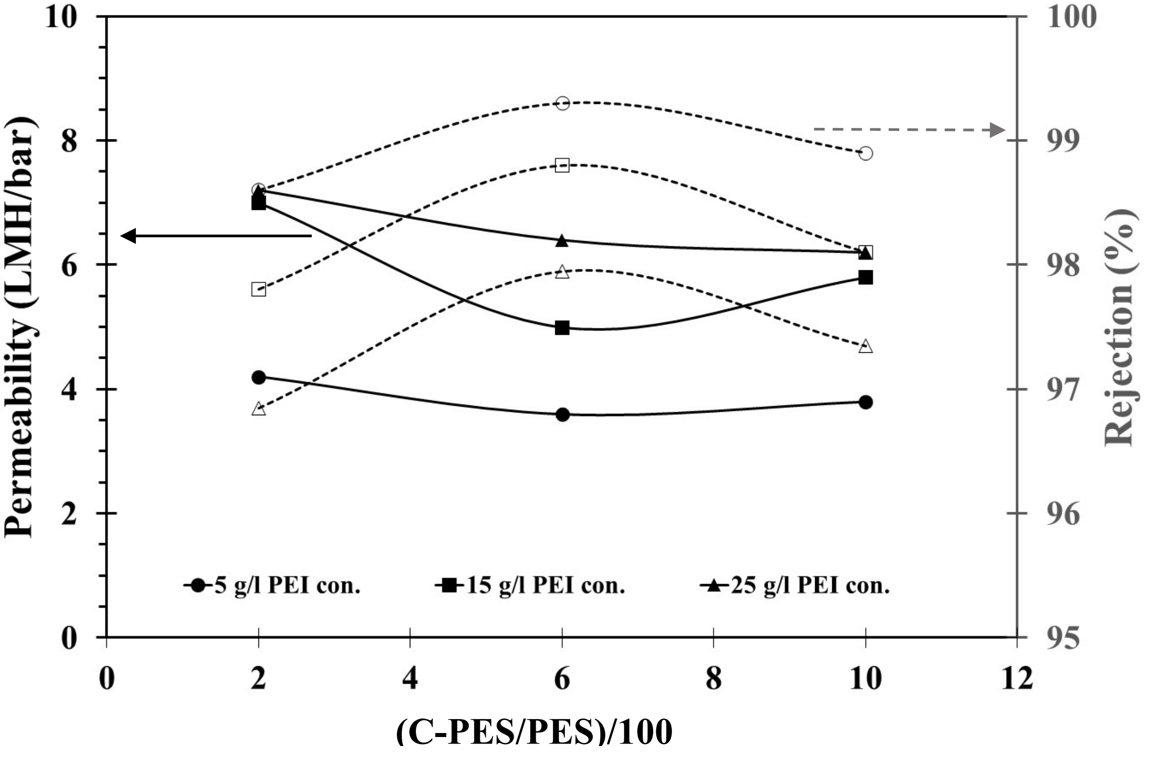


Fig. 9. NF membrane water flux and MB rejection as a function of the C-PES/PES ratio for different PEI solution concentrations; the operating pressure and temperature are 10 bar and 24 °C, respectively.

3.8. Separation performance of NF membrane for different salt solutions

Based on the results obtained above, an NF membrane prepared with a PEI concentration and C-PES/PES ratio of 15 g/l and 6/100, respectively, has the best performance for application in the separation of several different salt solutions, when considering flux and rejection performance. The measured fluxes and rejections of the NF membrane at different pressures can be seen in Fig. 10. In general, the mechanism by which separation takes place at charged membranes is based on screening and Donnan exclusion [17, 26]. Accordingly, the positively charged NF membranes have good separation performances for high-density multi-charge cations.

As shown in Fig. 10, a higher rejection was observed for magnesium cations than for calcium cations. Magnesium cations have a higher surface charge density (120 C mm^{-3}) than calcium cations (52 C mm^{-3}). The hydrated diameter of the magnesium cation (0.347 nm) is also greater than that of the calcium cation (0.309 nm) [27-29]. The positive charge of the membrane surface, together with the higher charge density and larger hydrated diameter of magnesium cations resulted in the higher magnesium cation rejection. Among the salts studied, sodium cations with a charge density of 24 Cm^{-3} and a hydrated diameter of 0.184 nm showed the lowest rejection of approximately 40-50%, because of the low electrostatic repulsion force and sieving effect.

It is suggested that the induction of positive charges onto the surface of a NF membrane led to an incremental contribution from the Donnan exclusion effect on the NF membrane function. Therefore, in order to separate the impact of the Donnan exclusion mechanism from that of the sieving effect, the NF membrane performance was investigated at different operating pressures of 2, 6, and 10 bar with magnesium chloride, calcium chloride, and sodium chloride salt solutions. The results are shown in Fig. 10. Increasing the operating pressure has two opposing effects on the performance of the prepared membrane separation. As a basic rule, by increasing the operating pressure, the net driving force (transmembrane pressure minus osmotic pressure) increases, resulting in an increase in the flux and rejection of a membrane. On the other hand, as the operating pressure increases, the membrane flux also increases, resulting in a higher polarization effect on the membrane surface, which results in pore-clogging and a corresponding decrease in the permeation flux and rejections [15, 30, 31]. As the concentration of the salt solutions was low (1000 ppm) and filtration time was short in this study, pore-clogging is not likely to occur. Fig. 10 shows that the rejection of different salts remained largely the same (for $CaCl_2$ and NaCl) and changed only marginally in $MgCl_2$. On the other hand, the flux increased sharply and almost linearly with pressure because the osmotic pressure of the 1000 ppm salt solutions (~ 0.04 bar) is not so high and can be ignored compared to the applied pressure. Although more detailed study is required in this regard, based on the available results and analysis in this study we suggest that salt rejection is mainly due to Donnan exclusion because if sieving was the main mechanism for separation we would expect to see a decrease in the rejection when the flux is increased. However, such a trend was not observed in this study.

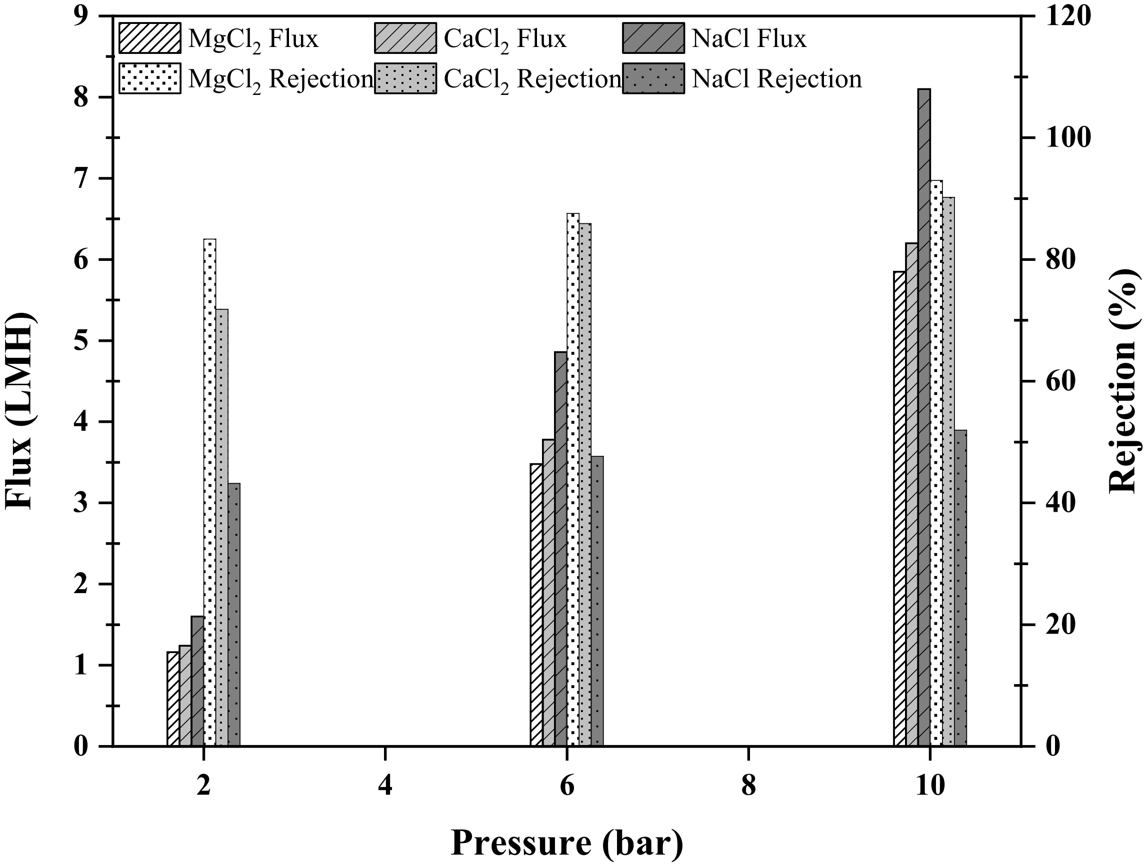


Figure 10: Separation performance of NF membranes for the separation of salt solutions operating at a pressure and temperature of 10 bar and 24 °C, respectively; NF membrane prepared with PEI = 15 g/l and C-PES/PES = 6/100; Feed salt concentration 1000 ppm

Conclusion:

A C-PES/PES blend UF membrane was prepared using a synthesized C-PES as a negatively charged substrate for the preparation of a NF membrane after deposition of PEI. The addition of a small amount of C-PES to dope the solution resulted in a sharp increase in membrane hydrophilicity, decreasing the contact angle from 75° to 55°. By increasing the C-PES/PES ratio, the pore size of the membrane surface increased slightly, resulting in an rise in the permeability of pure water from 30 to 85 L/m^2.h.atm. A ratio of C-PES/PES = 6/100 resulted in the membrane with the most surface negative charge, which is crucial for preparing an NF membrane with an appropriate filtration performance. Although increasing the crosslinking time and crosslinking agent (GA) concentration caused a decrease in the water flux and an increase in rejection, an optimal cross-linking reaction time and concentration was selected to obtain an appropriate filtration performance. Different salts and organic solutes under different operating conditions were then used to evaluate the interaction of the solutes with the surface of the membrane finally selected for its appropriate flux and rejection.

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