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Preparation, Characterization and Salt Rejection of Negatively Charged Polyamide Nanofiltration Membranes

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Abstract. Four thin-film composite (TFC) polyamide negatively charged nanofiltration (NF) membranes (NF-PS-1, NF-PS-2, NF-PS-3 and NF-PS-4) were prepared via interfacial polymerization technique which involved the formation of a polyamide thin film at the interfacial polysulfone (PS) microporous substrate between two immiscible liquid phases; an aqueous phase containing piperazine and an organic phase containing trimesoyl chloride (TMC = 0.25, 0.50, 1.00 and 2.00 wt%). Correlations of the intrinsic properties of these four NF filtration membranes, in regarding to the physical structures, surface negative charge density, pure water flux, pore size and the NF filtration performances, on the composition of the weight-% of TMC in the organic phase were investigated. Experimental results clearly demonstrated that NF membrane prepared from using 1.0 wt-% of TMC in hexane phase (i.e., NF-PS-3) gave a much higher salt rejections on salt containing negative divalent salts like Na_2SO_4 and $MgSO_4$; the maximum rejection of Na_2SO_4 and $MgSO_4$ were both to be 99.6 % for NF-PS-3 (TMC = 1.0 wt-%) while the rejections of Na_2SO_4 and $MgSO_4$ for the rest of the three NF membranes were in the order of NF-PS-2 (TMC = 0.50 wt-%) > NF-PS-1 (TMC = 0.25 wt-%) > NF-PS-4 (TMC = 2.00 wt-%). Effects of the pH of the feed and the applied filtration pressure on the $MgSO_4$ rejection were also investigated for this series of nanofiltration membranes.

Key words: Polyamide NF membrane, preparation, characterization, NF performances.

Resumen. Se preprararon cuatro membranas de nanofiltración (NF-PS-1, NF-PS-2, NF-PS-3, NF-PS-4) de película delgada (TFC) de poliamida cargadas negativamente, mediante la técnica de polimerización interfacial, la cual implica la formación de una película delgada en la interfase de un sustrato microporoso de polisulfona (PS) entre dos fases líquidas inmiscibles; una fase acuosa que contiene piperazina y una fase orgánica que contiene tricloruro de mesoilo (TMC) a diferentes concentraciones (0.25, 0.50. 1.00 y 2.00 % peso). Se investigaron las correlaciones entre las propiedades intrínsecas de las cuatro membranas de NF y la composición de la fase orgánica (% peso de TMC). Las propiedades estudiadas fueron; estructura física, densidad de carga superficial negativa, flujo a través de la membrana de agua pura, tamaño de poro y capacidad de filtración de las membranas. Los resultados experimentales demostraron claramente que la membrana de NF preparada con la solución que contiene 1.0 % de TMC (NF-PS-3) presenta mayor remoción de sales cuando tienen iones divalentes como el Na_2SO_4 y $MgSO_4$; la máxima remoción de Na_2SO_4 y $MgSO_4$ fue de 99.6 % para ambas sales, mientras que para las tres membranas restantes, el orden de remoción de las sales fue NF-PS-2 (TMC = 0.50 % peso) > NF-PS-1 (TMC = 0.25 % peso) > NF-PS-4 (TMC = 2.00 % peso). También se investigaron los efectos del pH de la solución alimentada al sistema y de la presión de filtración aplicada sobre la remoción de $MgSO_4$ para esta serie de membranas de nanofiltración.

Palabras clave: Membrana de NF de poliamida, preparación, caracterización, desempeño de NF.

Introduction

The development works on thin-film composite membranes for reverse osmosis and nanofiltration membranes had taken a great leap forward since John E. Cadotte [1] invented the process of making thin-film composite polyamide membrane on a microporous polysulfone substrate via interfacial polymerization of m-phenylenediamine in an aqueous phase with 1,3,5-Benzenetricarboxylic acid chloride in an organic phase. After the initial thin-film composite polyamide membrane is formed, the membrane is usually subjected to a series of post membrane treatment processes, this results an excellent salt rejection and high water permeability barrier on the surface of the microporous polysulfone substrate. Nowadays reverse osmosis (RO) and nanofiltration (NF) membranes are widely recognized as the best technology and energy efficient processes for production of potable water from marginal water sources [2-4].

A growing global demand on pure water for potable and for industrial uses and the increasingly stringent water quality regulations has accelerated the development of membrane technology for more than two decades. Due to the scarcity of fresh water in many aired regions of the world, it makes groundwater extraction to become a vital process for providing potable water in these areas. In many aired rural areas in Mexico, the main source of potable water comes from ground water. Reverse osmosis membrane system can produce high purity water, however the price of setting up reverse osmosis desalination plant is expensive, also water produced from the reverse osmosis process is not suitable for human consumption, this is due to the fact that the high purity RO water contains inadequate amount of minerals, thus RO water needs to be remineralized before for human consumption.

Nanofiltration membranes find its applications in wastewater and industrial water treatments (e.g. water softening, removal of colorants and organic matter) [5]. The NF membranes display separation characteristics in the intermediate range between reverse osmosis (RO) and ultrafiltration (UF). Compared to RO membranes, NF membranes have a loose structure and enable higher permeate fluxes and lower operating pressures. Compared to UF membranes, NF membranes have a tighter structure and are therefore able to reject small organic molecules having molecular weights as low as 200 to 300 Dalton [6,7]. Due to the special feature of the NF membrane surface (mostly having fixed negative surface charges), the capacity of separation is influenced by the steric effect (due to small pore diameter) and the charge on surface of the pore (Donnan exclusion phenomena) [8]. This explains why these membranes exhibit ion-selectivity. At low ionic environment (i.e., low concentration of ionic solute), the multivalent negative ions are separated by the NF membrane to a higher degree than monovalent ions, the latter can pass more freely through the pore of the membrane [9]. Generally speaking, nanofiltration membranes repulse divalent ions having the same charge as those at the surface of the pore. Due to the pore size of the NF membranes in nanometer dimension, NF membranes reject the bacteria and virus that may exist in the feed water. Because it requires lower operating pressure (~100 psi), NF membranes systems can be built with less capital investment; this is due to the fact that the pressure-vessel housing the NF membrane elements can be built with less expensive material like plastics, the pump and the rest of the hardware of the system should cost much less in comparison with high pressure RO membrane system. Because of lower operating pressure, NF membrane systems consume much less energy. Therefore NF membrane systems should be prime candidates for production of potable water using well water as feedstock in aired rural Mexico.

Thin film composite (TFC) membrane is a bilayer film consisting of a porous nonselective support layer with another ultra-thin selective barrier layer on top of it [10]. Thin-film composite membrane, produced via interfacial polymerization process, is well known for its high rejection and high permeate flux because of its thinner skin layer [11]. Some earlier works involved studying the effect of changing the pH; Szoke and coworkers [5] reported the composition of the feed and the surface charge density on the ion rejection by nanofiltration membranes.

In this work, studies were carried out to investigate the effect of changing the NF polyamide membrane preparation parameter, like the concentration of acid chloride in the hydrocarbon phase, on the intrinsic properties and the nanofiltration performance of the resultant NF polyamide membrane. The microporous substrate membrane was made from a membrane casting solution containing polysulfone (PS) dissolved in a mixed solvent of N-rnethyl-2-pyrrolidone (NMP) and propionic acid (PA) at 1:1 molar ratio. Four NF membranes (NF-PS-1, NF-PS-2, NF-PS-3 and NF-PS-4) were fabricated via interfacial polymerization between an aqueous phase containing piperazine and polyvinyl alcohol (solution A) and an organic phase containing trimesoyl chloride (TMC) at four different concentrations using hexane as solvent (solution B). The intrinsic properties of our NF membranes were determined; they included the membrane thickness, the molecular-weight-cut-off (MWCO), the surface charge density, the mean surface roughness of the NF membranes surface measurement by imaging technique using atomic force microscopy (AFM) and the scanning electronic microscopy (SEM) to reveal the surface and cross sectional structures of the membranes. In order to study the nanofiltration performance of these NF membranes, numerous experiments were performed; they include pure water permeate flux determination, salt rejection using salts such as NaCl, Na_2SO_4, $CaCl_2$ and $MgSO_4$ at different concentration and applied cross flow filtration pressure and the effect of changing pH of the feed on salt rejection.

Experimental

Materials, Equipments and Methods

Materials

Polysulfone (P-3500) was obtained from Solvay Advanced Polymers, U.S.A. All solvents and chemicals used in this work were ACS Reagent Grades, they were purchased from Aldrich Chemical Company, U.S.A. Gold of purity of 99.999 % was obtained from Aldrich Chemical company.

Equipment

Technic´s Hummer 5 sputter-coater and gold of 99.999 % purity were used to coat the membrane sample surfaces. JEOL JSM 5300 Scanning Electron Microscope was used to record the SEM photos. Digital Instrument Nanoscope III was used to measure the surface roughness of four nanofiltration polyamide membrane samples.

Methods

1. Microporous polysulfone(PS) support membrane preparation

The microporous polymeric PS membrane was prepared via phase inversion process. The membrane casting polymer solution was prepared by dissolving 18-w/w% dried polysulfone in a mixed solvent of 1-Methyl-2-pyrrolidone (NMP) and propionic acid (PA) at 1:1 molar rate in a clear glass bottle by tumbling under a heat-lamp at ~50 ºC for about 48 hours until an uniform polymer solution was formed. A AWA#620 fabric of 26 × 12 inches (66 × 30.5 cm) was fixed flat on a glass plate and the polymeric solution was spread by a casting knife. The casting knife gap was set at 6/1000 inch (0.152 mm). The membrane casting speed was controlled by a DC motor. The glass plate was driven by a DC motor into a 25 ºC deionized water quench bath at 20 ft/min (0.102 m/s), the total thickness of the membrane so prepared was 5/1000 inch (0.127 mm).

1.1. Microporous polysulfone support membrane pure water determination (PWD)

Membrane samples of 1.5 × 3.5 inches were cut from the microporous polyslfone membrane, they were used to determine the pure water flux and the "A-value" constant, the rest of PS membrane was storage at 5 ºC in a sealed plastic bag for future uses. The permeated fluxes of the membrane were measured at 60 seconds after starting the cross-flow process, the test was run at 40 psig (275.6 kPa) using distilled water at 25 ºC as feed. The A-value of the microporous polysulfone support membrane was determined to be 431.9×10^{-5} kg/(kPa.m^2.s).

2. Nanofiltration membrane preparation

The nanofiltration membranes were prepared via interfacial polymerization process between an aqueous amine solution (Solution A) and an organic phase containing an acid chloride (Solution B) on the polysulfone micro porous support membrane. Aqueous amine solution contained piperazine (0.25 -w/w%), PVA (0.25 -w/w%) and NaOH (0.5 -w/w%) and solution B was prepared with TMC at four different concentrations (0.25, 0.5, 1.0 and 2.0 -w/w%) in hexane. Pieces of 12 × 10 inches (30.5 × 25.4 cm) microporous polysulfone membrane was fixed on a glass plate and rinsed with plenty of DI water. After this, solution A was brushed onto the membrane surface for 10 seconds, the excess aqueous amine solution on the PS membrane surface was removed with a hard rubber roller. Following a 10 seconds of air-drying time, a 50 mL of Solution B was poured onto the surface at once and let it react for 1 minute. The excess Solution B was decanted and nitrogen gas was used to flush the membrane surface for 2 minutes to remove the organic solvent-hexane. Finally, the thin-film composite membrane was cured in oven at 60 ºC for 10 minutes. Four nanofiltration membranes were prepared with different TMC concentration; NF-PS-1 (0.25 % TMC), NF-PS-2 (0.5 % TMC), NF-PS-3 (1.0 % TMC), NF-PS-4 (2.0 % TMC).

3. Nanofiltration polyamide membrane characterizations

In this work the NF membrane characterizations including A-value (or Pure Water Flux), surface charge density, molecular weight cut off (MWCO), SEM and AFM were performed. The NF membrane performance on salt rejection using NaCl, $CaCl_2$, Na_2SO_4 and $MgSO_4$ at 1000 ppm, 3000 ppm, 5000 ppm and 8000 ppm and at various pH and applied pressure were also investigated. The salt rejection experiments were made in a three cells system connected in series as shown in Figure 1. The experimental works on characterization of the NF membranes are summarized below.

3.1. A-Value determination

Four NF membranes were tested for A-value, small pieces of 1.5 × 3.5 inches (membrane area = 22.12 cm^2) were cut from each membrane sheet. The test was run at 60 psig (275.6 kPa) using distilled water at 25 ºC as the feed. The measurements of the permeate fluxes were made at 60 seconds after starting of the cross-flow filtration process. The experimental results of the pure water permeated fluxes were tabulated in Table 1.

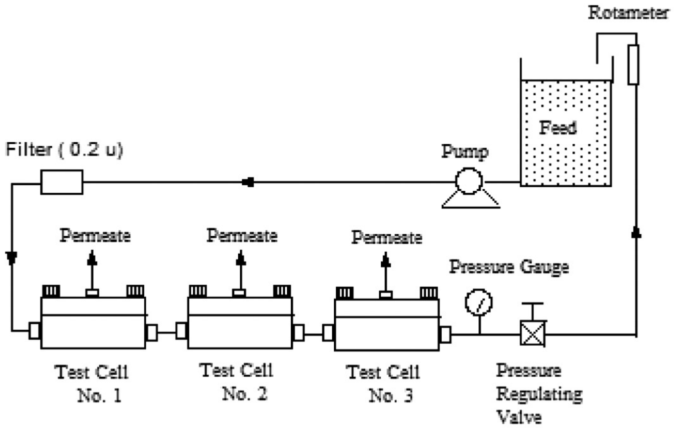


Fig. 1. Nanofiltration membrane performance test system.

3.2. Molecular weight cut-off (MWCO) determination

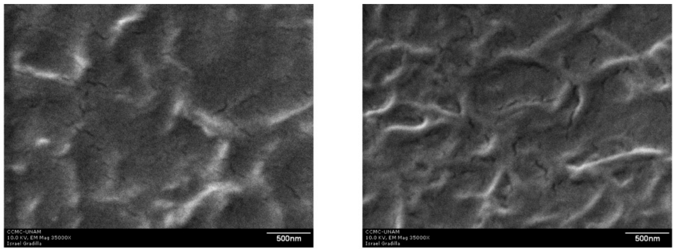
Three low molecular weight saccharides were used for this investigation; raffinose, sucrose and dextrose with molecular weight of 594.5, 342.3 and 180.2, respectively. The pH of the testing solutions were keep constant at 5.7, 4.3 and 4.5 for the corresponding saccharides. The MWCO of each membrane was determined by the separation efficiency which is defined as $R = (1 - C_p / C_f)$, where C_p is the concentration of the saccharide present in permeate and C_f is the concentration in the feed. Test runs were carried out under an applied cross flow filtration pressure of 413.4 kPa at 25 °C. 10 mL of permeate was collected at 30 minutes after the test run was started and the refractive index of permeate was determined. The content of the saccharide in the feed and in permeate was determined by an "Atago-refractometer" (0 to 10 %) at 25 °C by measuring the Refractive Index of the permeates and the feed against a blank and standard solution containing 0 % and 1.0 % saccharide, respectively. The size of the membrane coupons used was 1.5 × 3.5 inches (working membrane area 22.12 cm^2). The average MWCO of the test membrane is defined as the membrane sample having a 90 % or better rejection of the saccharide in the feed [11]. The experimental results of the MWCO are listed in Table 2.

3.3 NF membrane surface charge density determination

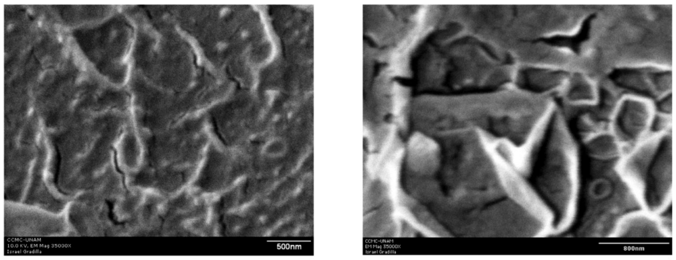
The membranes prepared have all a negative fixed charge on the surface and are dry. First step for this determination was to treat each membrane in distilled water at 80 ºC by one hour in a stainless steel container. After this the NF membrane was placed in distilled water at room temperature for 24 hours to leach out the remaining unreacted free amine in the porous substrate of the membrane. The membrane was mounted on a large special Teflon ring with an effective working membrane area of 221.67 cm^2 (0.022167 m^2). Treat the NF membrane surface side with a HCl (1.0 N) solution to replace the initial mobile Na^+ ions at the surface with H^+. The membrane was then rinsed with deionized water until the pH of water coming out from the ring was the same as the pH of the rinsing used (~7.0). After this 50 mL of NaOH (0.10 N) solution was added onto the membrane surface and let it to react for one minute. After this time, the sodium hydroxide solution was poured into a beaker and titrated with dilute HCl (0.100 N) solution. The negative surface charge density (meq/m^2) of the membrane was determined from the amount (meq) of NaOH used to neutralize the counter ion H$^+$ at the membrane surface area of 221.67 cm^2 (0.022167 m^2). The surface densities of the four NF membranes are shown in Table 3.

3.4. Scanning electronic microscopy (SEM) determination

Small pieces of NF membrane samples (0.5cm × 0.5cm) were used for SEM measurements. The surface and the cross-sectional of the membrane samples to be examined by SEM were fractured in liquid nitrogen. Then the dried and fractured membrane samples were sputtered with gold at a coating current of 15 mA for 3.5 minutes using a Technic's Hummer 5 sputter. The gold-coated membranes were viewed with a JSM 5300 Scanning Electron Microscope which was operated at an accelerating voltage of 10 kV. The scanning electron micrographs showing the morphologies of the surface and the feature of the cross-section of the membrane samples are revealed in Figures 2 and 3, respectively.

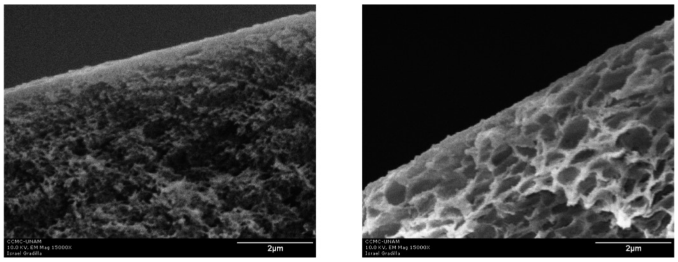


(a) NF-PS-1 (b) NF-PS-2

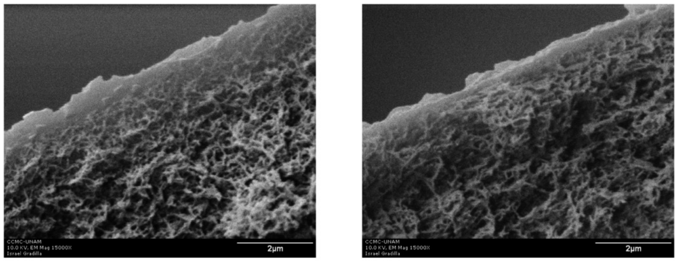


(c) NF-PS-3 (d) NF-PS-4

Fig. 2. Scanning Electron Micrographs (SEM) of nanofiltration membrane surfaces of (a) NF-PS-1, (b) NF-PS-2, (c) NF-PS-3 and (d) NF-PS-4 at 10 kV and 35,000 magnifications.



(a) NF-PS-1 (b) NF-PS-2



(c) NF-PS-3 (d) NF-PS-4

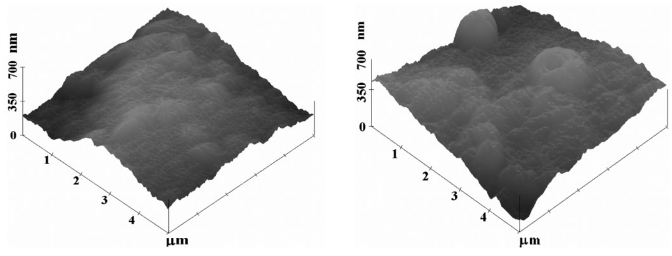
Fig. 3. Cross-section Scanning Electron Micrographs (SEM) of nanofiltration membranes (a) NF-PS-1, (b) NF-PS-2, (c) NF-PS-3 and (d) NF-PS-4 at 10 kV and 35,000 magnifications.

3.5. Membrane surface roughness determination via atomic force micrograph (AFM)

The surface morphologies of the wet membranes were characterized by tapping mode with a Nanoscope IIIa AFM, equipped with a non-contact/contact head and a 100 μ scanner, which was operated at a constant force mode (reference force 5 nN). The membrane samples were attached to a disc (0.5 inches: 1.27 cm diameter) sample holder that was mounted on the piezo scanner of the AFM. AFM images were acquired at a scan rate of 2.001 Hz and at an information density of 256 × 256 pixels, three scanning areas were selected, 5 × 5, 2.25 × 2.25 and 0.5 × 0.5 μm. Also the mean roughness and height is given by the average of the individual height determinations within the selected height profile. The atomic force micrographs of NF membrane prepared with four different concentrations of TMC(0.25, 0.5, 1.0 and 2.0 wt-% are shown in Figure 4.

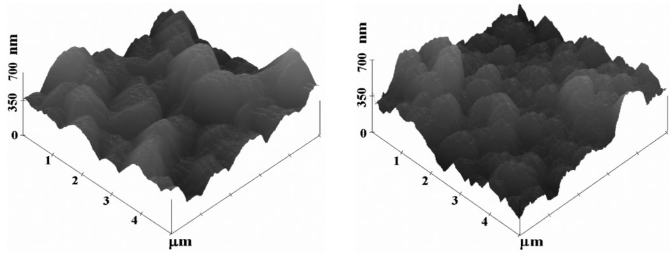
3.6. Salt rejection experiments

Three membrane samples of 3.81 cm × 8.89 cm were cut from each of the four different NF membrane sheets. These membrane samples were used to determine their salt rejection for each of the four different NF membranes. The membrane samples were placed in a three test cells system (Figure 1), then the system was rinsed with distilled water for one hour. Cross flow filtration experiments were carried out for each of four different NF membranes under a similar set of experimental conditions like salt concentration, composition of the salts and pH of the feed (15 liters). The applied cross filtration pressure was set at 100 psi (0.69 MPa) and at 25 ºC for all salt rejection experiments, except those for the investigation on the effect of the applied pressure. For each experiment about 30 mL of permeate collected initially was discarded, after this all collected permeate was returned to tank to keep the salt concentration constant. At the end of 60 minutes of filtration operation, permeate samples of 5 mL were collected from each of the three



Mean Roughness: 61.04 nm
Maximum High: 370.3 nm

Mean Roughness: 58.94 nm
Maximum High: 459.5 nm



Mean Roughness: 80.8 nm
Maximum High: 607.5 nm

Mean Roughness: 78.55 nm
Maximum High: 569.2 nm

(c) NF-PS-3 (1% TMC)

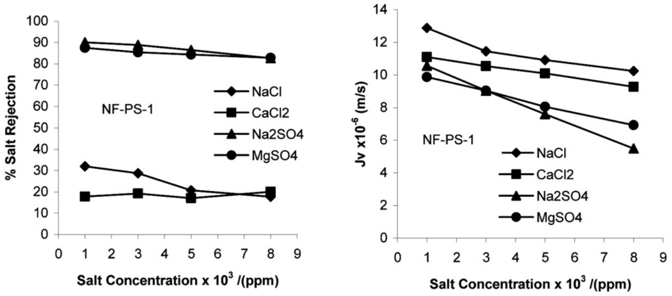
(d) NF-PS-4 (2.0% TMC)

Fig. 4. Atomic force micrographs (AFM) of nanofiltration membranes (a) NF-PS-1(0.25% TMC), (b) NF-PS-2(0.5% TMC), (c) NF-PS-3(1.0% TMC) and (d) NF-PS-4(2.0% TMC).

test cells and their conductivities were measured with a conductance cell, then permeates were returned to the feed container. In respected to the change of the salt content of the feed, the salt concentration of the feed was increased by adding salt. The cross flow filtration system was allowed to run for 30 minutes to stabilize the filtration operation condition. The permeated in this time was returned to the container, this was made for each salt concentration change. In case of changing the type of salt in the feed, the system was washed with distilled water for two hours; one hour by rinsing the system and the other hour was under cross flow filtration operation. The results of the experimental are shown in Table 5 and Figures 5 to 8.

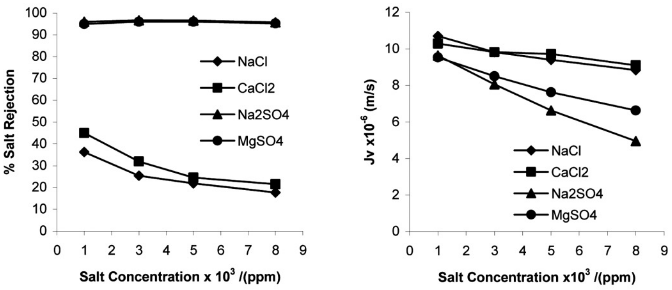
3.7. Experiments of changing pH of the feed

The experiments of changing pH were carried out at a pH range of 10.0 to 3.0 for a feed of 15 liters containing 8000 ppm in $MgSO_4$. The pH of the feed was controlled by addition of NaOH (1.0 N) or HCl (1.0 N) solution. Initially, the pH of the feed was adjusted to 10.0 by adding NaOH(1.0 N), the subsequent pH values were obtained by addition of HCl until pH = 3.0. The initial ~30 mL of permeate collected from each cell was discarded, after this all collected permeate was returned to tank to keep the salt concentration constant. At 60 min first permeate sample was collected for conductance measurement, then the pH was adjusted, system was let run for 30 min to stabilizing, the permeated volume was returned to the container. That was done for each pH change. The experimental results are shown in Table 5 and Figure 9.



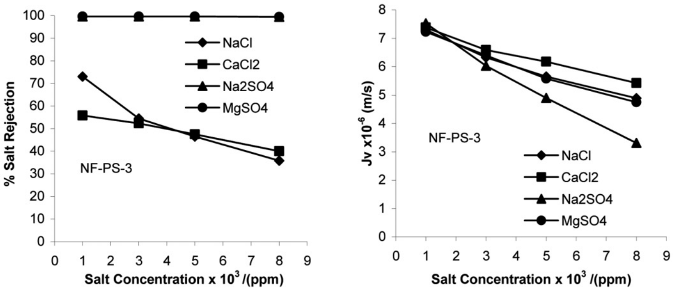
(a) (b)

Fig. 5. Effect of concentration and kind of salt on: (a) percentage of removal for NF-PS-1 (at 100 psig, 25 ºC at pH = 6.0) and (b) permeate flux *Jv* through membrane.



(a) (b)

Fig. 6. Effect of concentration and kind of salt on: (a) percentage of salt removal for NF-PS-2 (at 100 psig, 25 ºC and pH = 6.0) and (b) permeate flux *Jv* through membrane.

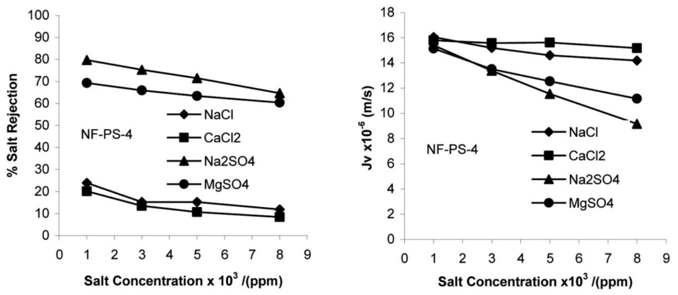


(a) (b)

Fig. 7. Effect of concentration and kind of salt on: (a) percentage of salt removal for NF-PS-3 (at 100 psig, 25 ºC and pH = 6.0) and (b) permeate flux *Jv* through membrane.

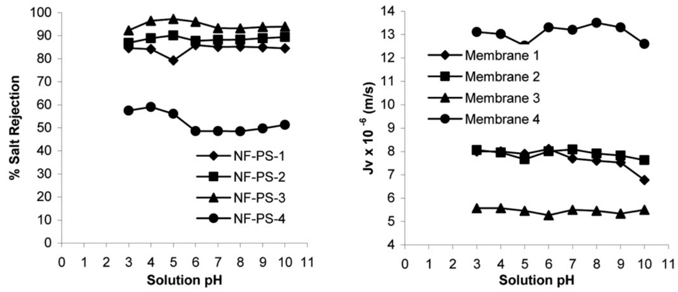
3.8. Experiments of changing applied cross flow filtration pressure

The cross flow filtration pressure was controlled by a valve after the cells (Figure 1). Also the flow was kept at 1.0 gal-



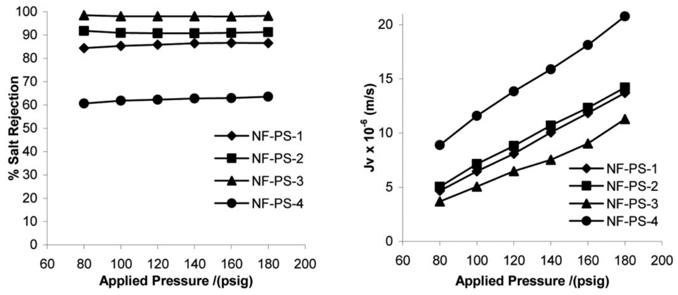
(a) (b)

Fig. 8. Effect of concentration and kina of salt on: (a) percentage of salt removal for NF-PS-4 (at 100 psig, 25 ºC and pH = 6.0) and (b) permeate flux *Jv* through membrane.



(a) (b)

Fig. 9. Effect of pH on: (a) percentage of $MgSO_4$ (8,000 ppm) removal and (b) permeate flux *Jv* through membrane at 100 psig and 25 ºC for NF-PS-1, NF-PS-2, NF-PS-3 and NF-PS-4.



(a) (b)

Fig. 10. Effect of applied pressure on: (a) percentage of $MgSO_4$ (8,000 ppm) removal and (b) permeate flux *Jv* through membrane at 100 psig and 25 ºC for NF-PS-1, NF-PS-2, NF-PS-3 and NF-PS-4.

lon/minute (3.785 liter/minute). The applied pressures were increasing from 80 psig (0.552 Mpa) to 180 psig (1.242 MPa) at a 20 psig interval. In all tests $MgSO_4$ (8000 ppm) at 25 ºC was used. The pH was mostly kept constant at 6.4. Another parameter calculated from applied pressure experiments was the flux (m/s), which refers to volumetric flow across membrane and the applied pressure onto membrane surface. The results of the experimental are shown in Figure 10.

Results and discussion

Wide acceptance of membrane technologies in potable water production, wastewater treatment and pharmaceutical industries helps to stimulate further research and development works in recent years on improving the performance of the membrane systems in general. Nanofiltration membranes (NF) find its applications mostly in wastewater and industrial water treatment processes (e.g. water softening, removal of colorants and organic matter) [5]. The NF membranes display separation characteristics in the intermediate range between reverse osmosis (RO) and ultrafiltration (UF) membranes. Compared to RO membranes, NF membranes have a loose structure and enable higher permeate fluxes at lower operating pressures. This lower filtration operation pressure directly transfers to lower in capital investment needed for the NF membrane systems; this is due to the fact that the pressure vessel housing the NF membrane spiral-wound elements, the pump and other accessories cost much less for lower pressure system than the RO high pressure membrane system. This lowering in the cost of setting up a NF membrane system is especially to benefit the developing countries in need of improving their potable water quality in areas where virus and bacteria may be present in the source of the water supply.

The objective of this work is to investigate the effect of changing the NF membrane preparation parameter, like the concentration of acid chloride (TMC) in the hydrocarbon phase, on the intrinsic properties and the nanofiltration performance of the resultant NF polyamide membrane. As revealed in the scanning electron micrographs (SEM) shown in Figures 2 and 3, and the atomic force micrographs (AFM) Figures 4 and 5, the composition of the acid chloride (TMC) in the hydrocarbon phase directly affected the nature of the surface and the uniformity of the polyamide layer formed at the top of the resultant NF membranes. As shown in Figure 2, the polyamide thin-film formed on the surface of the microporous substrate becomes more winkled as the concentration of the TMC was increased from 0.05 to 1.0 wt-%, further increase the TMC to 2.0 wt-%, the winkled pattern was broken down to form larger ridge-like surface. The cross-sectional SEM imaging shown in Figure 3 have revealed the existence of the upper dense polyamide layer; at TMC = 1.0 wt-% (Figure 3 (c)) the polyamide layer formed at the top of the microporous substrate was quite thick and uniform. The surface roughness by AFM, shown in Figure 4, further revealing the physical nature of this series NF membranes; it reveals a pattern which indicates a different topography on membranes surfaces (Figure 4). NF-PS-1 and NF-PS-2 micrographs show a very relative homogeneous surface with no pronounced peaks, they look more smooth. In case of membranes NF-PS-3 and NF-PS-4, their structures on surface have more heterogeneous topography distribution. This confirms that the physical properties of the polyamide membranes are affected by the composition of the TMC/hydrocarbon phase. Among these four NF membranes, NF-PS-3 membrane gave a much tight NF membrane as demonstrated by the water permeability test (Table 1, A-

Value) and the molecular-weight-cut-off (MWCO) test (Table 2). The NF membrane formed by using TMC = 1.0 wt-% yielded a narrower pore size distribution; the MWCO of NF-PS-3 is much closer to FW 342.3 than the rest of the NF membranes prepared in this series. Also at concentration of TMC = 1.0 wt-%, it gave a highest negative surface charge density of 36.0 meq/m^2 (Table 3). This higher negative surface density may contribute to the fact that the surface of NF-PS-3 membrane is being the roughest one (Table 4) among this series of membranes, the actual surface area under investigation would be larger than the physical measurement of the membrane surface area. This higher negative surface charge density at the surface of the NF membranes affects the salt rejection of the NF membranes. As indicated in Table 5, the maximum % removal of salts contain negative divalent increases as the TMC is increased from 0.25 to 1.0 wt-%; NF-PS-3 has the highest "maximum salt rejection" of 99.6 % removal of both Na_2SO_4 and $MgSO_4$. Further increase the TMC to 2.0 wt-%, it leads to a less desirable NF membrane which rejects 79.8 % of Na_2SO_4 and 69.3 % of $MgSO_4$. The effects of concentration and kind of salt on the % salt removal and the permeate fluxes are illustrated in Figures 5 to 9. Among these four nanofiltration membranes, NF-PS-3 (TMC = 1.0 wt-%) showed having the highest rejection of salts containing divalent anion like Na_2SO_4 and $MgSO_4$. As the concentration of salt is increased, the permeate flux decreased for all membranes tested. Since NF-PS-3 is being the tightest membrane, it reflects by its lowest permeated flux as it is expected. The wide range change of the pH from 3.0 to 10.0 of the feed did not alter the salt rejection very much for this series of membranes (Figure 9). This may imply that the change of the pH of the feed did not change the physical structure of the polyamide lay at the porous polysulfone substrate; like swelling or contracting. The change of the salt rejections for this series of membrane toward to the change of applied cross-flow filtration pressure from 80 to 180 psig was found to be minimal (Figure 10) for this series of nanofiltration membranes.

Conclusions

Through this work, it has been demonstrated that the intrinsic properties and the nanofiltration performances of the thin-film composite polyamide nanofiltration membranes prepared via interfacial polymerization technique strongly depend on the concentration of Trimesoyl Chloride (TMC) in the organic phase. The optimal concentration of the TMC in the organic phase was determined to be 1.0 wt-% as shown in the preparation of NF-PS-3. The divalent salt rejections for $MgSO_4$ and Na_2SO_4 by NF-PS-3 membrane were both 99.6 % which is far better than the membranes prepared by using TMC = 0.25, 0.5 and 2.0 wt-%.

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