

IMPACTS OF HYDROPHILIC NANOFILLERS ON SEPARATION PERFORMANCE OF THIN FILM NANOCOMPOSITE REVERSE OSMOSIS MEMBRANE

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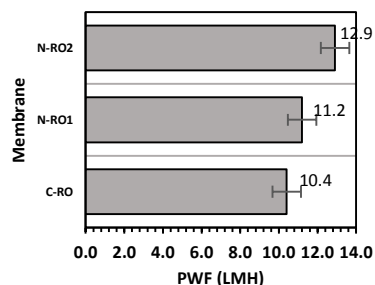
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Graphical Abstract



Abstract

The membrane technology is still considered a costly method to produce potable water. In view of this, RO membrane with enhanced water permeability without trade-off in salt rejection is desirable as it could further reduce the cost for water desalination. In this study, thin film nanocomposite (TFN) membranes containing 0.05 or 0.10 w/v% hydrophilic nanofillers in polyamide layer were synthesized via interfacial polymerization of piperazine and trimesoyl chloride monomers. The resultant TFN membranes were characterized and compared with a control thin film composite (TFC) membrane. Results from the filtration experiments showed that TFN membranes exhibited higher water permeability, salt rejection and fouling resistance compared to that of the TFC membrane. Excessive amount of nanofillers incorporated in the membrane PA layer however negatively affected the cross-linking in the polymer matrix, thus deteriorating the membrane salt rejection. TFN membrane containing 0.05 w/v% of nanofillers showed better performances than the TFC membrane, recording a pure water flux of 11.2 L/m²·h, and salt rejection of 95.4%, 97.3% and 97.5% against NaCl, Na₂SO₄ and MgSO₄, respectively.

Keywords: Nanofillers, TFN, RO, flux, rejection, fouling

Abstrak

Teknologi membran masih lagi dikategorikan sebagai satu proses yang mahal untuk penghasilan air bersih. Memandangkan ini, membran RO dengan kebolehtelapan air yang lebih tinggi tanpa menjejaskan keupayaannya untuk menapis garam amat diperlukan. Dalam kajian ini, membran berkomposit nano (TFN) yang mengandungi 0.05 atau 0.10 w/v% partikel dalam lapisan poliamida (PA) telah dihasilkan melalui proses pempolimeran. Membran TFN yang terhasil telah dicirikan dan dibandingkan dengan membran berkomposit (TFC). Keputusan daripada eksperimen penapisan menunjukkan bahawa membran TFN mempamerkan kebolehtelapan air, penolakan garam dan rintangan fouling yang lebih tinggi daripada membran TFC. Sementara itu, kandungan nanofiller yang berlebihan dalam PA membran pula menjejaskan penghubung silang dalam matriks polimer tersebut, lalu menyebabkan kemerosotan keupayaan membran untuk menapis garam. Membran TFN yang mengandungi 0.05 w/v% nanofillers menunjukkan prestasi yang lebih baik daripada membran TFC, ia merekodkan fluks air tulen sebanyak 11.2 L/m²·h, serta penolakan garam sebanyak 95.4%, 97.3% dan 97.5%, masing-masing terhadap NaCl,

Na₂SO₄ dan MgSO₄.

Kata kunci: Nanofillers, TFN, RO, fluks, penolakan, fouling

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1.0 INTRODUCTION

Water desalination was firstly made practicable through the introduction of cellulose acetate (CA) membrane by Loeb and Sourirajan in 1960s. It was reported that the permeability of the CA membrane synthesized was 10 times higher than any other membrane made available prior to its introduction [1]. However, CA membranes suffer from several drawbacks, which include high sensitivity to feed water pH (stable only in pH range 4.5-7.9), prone to biological fouling and easily compacted at high operating pressure [2]. These drove membrane scientists to fabricate new membranes which can outperform CA membranes.

Major breakthrough in membrane fabrication was reported in year 1970 when Cadotte and his co-workers invented a novel method to fabricate thin film composite (TFC) membrane. Comparing with CA membranes, TFC membranes exhibit higher water permeability and selectivity with lower energy consumption [3], higher resistance towards larger pH variations and high temperature of the feed water, and is less susceptible to biological fouling and pressure compaction [2]. Owing to these unique features, TFC membrane has been applied extensively for both seawater and brackish water desalination.

Today, desalination using reverse osmosis (RO) process dominates more than half of the market in seawater and brackish water desalination [4]. Nevertheless, RO is still considered a costly method to source potable water. To combat this problem, membrane scientists are constantly researching to fabricate membrane with higher water permeability. This is because by applying super-hydrophilic membranes, membrane area in membrane modules can be reduced; while maintaining the yield of potable water [5]. As such, this reduces the cost for membrane replacement, as well as the amount of chemicals needed for membrane cleaning; hence lowering the overall operating cost of seawater and brackish water desalination. Moreover, super-hydrophilic membranes are said to have high fouling resistance [6]. This helps prolong the membrane lifespan by lowering the propensity of membrane fouling, contributing to cost reduction for membrane replacement in long run.

One promising method to improve the hydrophilicity of TFC membrane is by embedding nanoparticles into polyamide (PA) layer of the membrane, forming a new type of composite

membrane named as thin film nanocomposite (TFN). This modification was firstly introduced by Hoek and his co-workers in year 2007, whereby they incorporated zeolite nanoparticles into the PA layer of TFC membrane formed by the interfacial polymerization (IP) of trimesoyl chloride (TMC) and *m*-phenylenediamine (MPD). The resulting TFN membrane was reported to have a remarkable increase in water permeability, along with the enhancement of fouling resistance. Ever since, many new TFN membranes for various applications such as ultrafiltration, nanofiltration and RO were reported in the literature. Some examples include polyethersulfone (PES)/ hydrous manganese dioxide (HMO) mixed matrix membrane (MMM) [7], graphene oxide-TFN membrane [8], amine-functionalized multiwalled carbon nanotube-TFN membrane [9], zeolite-TFN membrane [10], mesoporous silica-TFN membrane [11], titanate nanotube-TFN membrane [12], and MCM-48-TFN membrane [6].

Jamshidi Gohari *et al.* [7] fabricated PES/HMO mixed matrix ultrafiltration membranes for oily wastewater treatment. The authors reported that the incorporation of HMO into the PES membrane has successfully improved its water permeability (from 39.2 LMH of the pristine PES membrane to 336 LMH and 573.2 LMH of PES/HMO-1 and PES/HMO-2 membranes, respectively when increasing the HMO:PES ratio from 0 to 2) and fouling resistance (in terms of flux recovery from 42% of the PES membrane to 68% and ~75% of PES/HMO-1 and PES/HMO-2 membranes, respectively), while maintaining high oil rejections (almost complete oil rejection for PES/HMO-2 membrane, in comparison to 98.5-99.99% and 92.3-97.5% shown by PES/HMO-1 and PES membranes). The authors attributed the improved water permeability and fouling resistance of PES/HMO MMM to the increase in surface hydrophilicity owing to the abundance of -OH functional groups contributed by the HMO nanoparticles. Considering the promising results reported by Jamshidi Gohari *et al.* [7], this paper aims to study the effect of incorporating self-synthesized HMO nanoparticles into the PA layer of TFC membrane for salt removal under RO application. The performances of the resulting TFN membrane were characterized with respect to water permeability, salt rejection and flux recovery in addition to the instrumental characterization using FTIR.

2.0 METHODOLOGY

2.1 Materials

Polysulfone (PSf, Udel P-3500) in pellet form, purchased from Solvay Specialty Polymers, USA, was used to fabricate a microporous substrate for TFC and TFN membranes. 1-methyl-2-pyrrolidinone (NMP, 99%) from Acros Organics and polyvinylpyrrolidone (PVP K30) from Sigma-Aldrich were used as solvent and pore forming agent, respectively in the substrate preparation. Both piperazine (PIP, 99%) and 1,3,5-benzenetricarbonyl trichloride (TMC, 98%) from Acros Organics were used as the active monomers for the fabrication of PA selective layer on the PSf substrate. Cyclohexane (Merck) was used as the solvent to dissolve TMC. Manganese (II) sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), potassium permanganate (KMnO_4) and sodium hydroxide (NaOH) from Merck were used in the preparation of hydrous manganese oxide (HMO) nanoparticles. Inorganic salts including sodium sulfate (Na_2SO_4 , Riedel-de Haen), sodium chloride (NaCl, Merck) and magnesium sulfate (MgSO_4 , Merck) were used in the filtration experiment to assess TFC and TFN membranes performances with respect to salt rejection. Bovine serum albumin (BSA, 66 kDa) from Sigma-Aldrich was used as the organic foulant in evaluating membranes fouling resistance. Milli-Q® RO water was used to dissolve the inorganic salts and BSA in the preparation of feed solutions for the filtration experiments. Other chemicals used in this experiment were of analytical grade, unless otherwise stated. All chemicals were used as received without further purification.

2.2 Preparation of Nanoparticles

Nanoparticles were prepared in accordance to the method described by Parida *et al.* [13]. First, 40g of KMnO_4 was dissolved in 500 mL of RO water, followed by pH adjustment to 12.5 using 1M NaOH solution. The prepared solution was thereafter added into an aqueous solution of MnSO_4 (prepared by dissolving 60g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ in 0.05M H_2SO_4 aqueous solution). The mixed solutions were then stirred vigorously until brownish precipitates were formed [7]. Subsequently, the resulting HMO powder was filtered and washed several times with RO water until pH 6-7 was achieved. Lastly, the HMO nanoparticles were dried in a vacuum oven at 60°C for 24 h, followed by grinding. The self-synthesized HMO nanoparticles were stored in a desiccator until use.

2.3 Preparation of Membrane Substrate

The preparation of PSf substrate membrane was performed according to the method reported by Emadzadeh *et al.* [14]. The PSf substrate was prepared from a dope solution comprising the

mixtures of 15 wt% PSf, 1.0 wt% PVP and 84 wt% NMP solvent. The mixed solution was stirred vigorously until a homogeneous solution was obtained. The dope solution prepared was left to stand for 2 h at room temperature so as to remove the trapped air bubbles in the solution. After that, a layer of dope solution was cast on a glass plate using a glass rod. The entire glass plate was then immersed into a water coagulation bath at room temperature to allow substrate formation via phase inversion process. Soon after the substrate was peeled off from the glass plate by itself, it was soaked in another water bath for 24 h to remove residual solvent. Lastly, the substrate membrane was stored in a RO water container before use.

2.4 Fabrication of Membranes

TFC membrane was fabricated in this study as the control membrane for comparison purposes with the TFN membranes. TFC membrane was synthesized via the IP of PIP and TMC. The IP process was initiated by pouring 2 w/v% PIP aqueous solution onto the prepared substrate (section 2.3). The substrate was then held horizontally for 2 min to ensure the penetration of aqueous solution into substrate pores [12]. The excess aqueous solution was drained off the substrate surface using a soft rubber roller. Next, the cyclohexane solvent which contained 0.15 w/v% TMC was poured onto the same substrate, followed by draining off after 1 min of contact time. Subsequently, the membrane was oven-dried at 60°C for 8 min. After the IP process, the unreacted monomers were rinsed off the membrane surface with RO water. The TFC membrane fabricated was stored in a DI water container until use.

TFN membranes were synthesized according to the steps abovementioned, except that the HMO nanoparticles (0.05 or 0.10 w/v%) were dispersed in the organic solution. To ensure that the HMO nanoparticles were well dispersed in the organic solution, the organic solution containing the nanoparticles were ultrasonicated for 30 min and used immediately after the ultrasonication process. TFN membranes prepared with the incorporation of 0.05 and 0.10 w/v% of HMO nanoparticles were labelled as N-RO1 and N-RO2, respectively. On the other hand, control TFC membrane was labelled as C-RO.

2.5 Filtration Experiments

The filtration experiments were conducted using a commercial stirred dead-end permeation cell (HP4750, Sterlitech Corp.) and it began with membrane compaction for 30 min under a pressure of 13 bar, until the flux became constant. Next, the performance of membranes was then evaluated for water permeability and rejection against Na_2SO_4

(1000 mg/L), NaCl (1000 mg/L), MgSO₄ (1000 mg/L) and BSA (200 mg/L) at a pressure of 12 bar. The volume of the permeate produced was measured at a fixed time interval, and it is used to calculate the pure water flux (J) using the following equation.

$$J = \frac{\Delta V}{A_m \times \Delta t} \quad (1)$$

where A_m is the effective membrane area (14.6 cm²), ΔV is the permeate volume and Δt is the filtration time.

Meanwhile, a bench conductivity meter (4520, Jenway) was used to measure the conductivity of the feed solution and the permeate produced. Thereafter, the salt rejection efficiency of the membranes was calculated using the following equation.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where C_f and C_p are the solute concentration in the feed and permeate, respectively.

In assessing the membranes fouling resistance, control TFC and TFN membranes were subject to a 4-h permeation test using BSA aqueous solution as the foulant. Both the initial and final water flux of the membranes were recorded to study the extend of membrane fouling. In addition, the concentration of BSA in the feed solution and the permeate was measured using a UV-vis spectrophotometer (DR5000, Hach) at a wavelength of 208 nm. The BSA rejection was determined using Eq. (2).

2.6 Membrane Characterization

An attenuated total reflectance Fourier transmission infrared (ATR-FTIR) spectroscope (Thermo Nicolet Avatar 360 FTIR spectrometer) was used to study the functional groups present in the control TFC and TFN membranes.

3.0 RESULTS & DISCUSSION

3.1 Characteristics of Control TFC and TFN membranes

FTIR spectra of C-RO, N-RO1 and N-RO2 are given in Figure 1. It is noticeable that the characteristic peak at 3335 cm⁻¹ for all the membranes synthesized is due to O-H stretching vibration band that is typically found in cross-linked PA layer. However, with the incorporation of hydrophilic HMO nanoparticles into PA layer, it is obvious that the intensity of the peak is increased. The strongest intensity is found in the N-RO2 membrane in which this membrane contains the highest nanoparticle amount. It is also worth mentioning that the peak at 1650 cm⁻¹ which depicts

the C=O stretching vibrations of amide is decreased for the membranes incorporated with nanoparticles (N-RO1 and N-RO2) when compared with the control membrane (C-RO). N-RO2 in particular, shows a more obvious plunge at this peak. This might be due to the reduced cross-linking in the membrane matrix upon the incorporation of nanoparticles. As such, it may be reasonable to presume that the degree of membrane cross-linking in the PA layer decreases in the order of C-RO > N-RO1 > N-RO2.

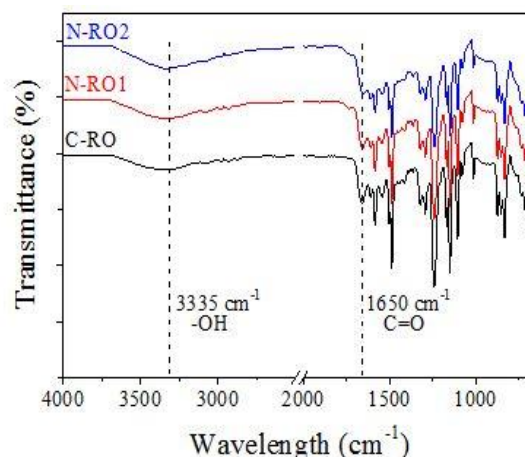


Figure 1 FTIR spectra of control TFC RO membrane (C-RO) and TFN RO membrane made of different nanoparticle loading (N-RO1 and N-RO2)

3.2 Filtration Performance

Figure 2 compares the pure water flux (PWF) of the control membrane and the membrane incorporated with different amount of nanoparticle. The results indicate that the incorporation of nanoparticles into the PA layer of TFC membrane has successfully improved the membrane hydrophilicity, as all the TFN membranes exhibited higher water permeability than that of TFC membrane. It is found that the PWF of the composite membrane increased from 10.4 LMH to 11.2 LMH (7.7% increment) and 12.9 LMH (24% increment) when the loadings of nanoparticles in the PA layer increased from 0 to 0.05 w/v% and from 0 to 0.10 w/v%, respectively. This finding is in line with the results reported by several authors, (Jamshidi Gohari *et al.* [7]; Dong *et al.* [10]; Yin *et al.* [15]). The increment in membrane PWF following the incorporation of nanoparticles can be attributed to the presence of greater amount of hydrophilic hydroxyl (-OH) functional groups in the fabricated TFN membrane, as confirmed by the FTIR spectra. In addition, the highest PWF shown by N-RO2 can be attributed by the formation of defect voids and/ or decreased PA cross-linking upon nanoparticle incorporation.

Meanwhile, results for the salt rejection of the membranes are shown in Figure 3. The salt rejection of C-RO, N-RO1 and N-RO2 against NaCl, Na₂SO₄ and MgSO₄ are reported to be 94.3%, 96.0% and 94.1%; 95.4%, 97.3% and 97.5%; and 83.5%, 85.3% and 91.2%, respectively. It is noticeable that the salt rejection of control membrane is improved when small loading (0.05 w/v%) of nanoparticles are embedded into the PA layer of the composite membrane. The improved salt rejection can be ascribed to the increased membrane surface charge, owing to the presence of more functional groups upon the addition of hydrophilic nanoparticles. This increases the repulsion between salt ions and the membrane surface via the Donnan effect [9], hence increasing the capability of the membranes in rejecting salts. Further increase the particle loadings from 0.05 to 0.10 w/v% however deteriorates the salt rejection rate. This could be mainly due to the lower PA cross-linking and/or enlarged microvoids between the particle and the polymer matrix as mentioned in previous work [14].

3.3 Antifouling Resistance Against BSA

The performance of membranes in filtrating BSA foulant is shown in Figure 4. As can be seen, the initial water flux for all the membranes is lower compared to their respective PWF, as shown in Figure 2 when all the membranes are tested at the same operating pressure. The reduction in water flux might be due to the membrane fouling caused by the deposition and adsorption of the BSA macromolecules on the membrane surface [16]. Of the three membranes tested, C-RO shows the highest flux reduction when it is subject to 200 mg/L BSA filtration process. Its initial permeate flux decreased from about 7.4 LMH to less than 5.0 LMH, recording >33% flux deterioration.

As a comparison, N-RO1 and N-RO2 membrane show a relatively constant permeate flux throughout the BSA filtration experiment, with overall flux decline of only 7.1% and 3.9%. This proves that both N-RO1 and N-RO2 exhibit better fouling resistance against organic foulant compared to the C-RO. For the membranes incorporated with hydrophilic nanoparticles, water molecules can easily adhere to the hydrophilic membrane surface via hydrogen bonding; thus forming a thin water boundary which restrain undesirable adhesion of hydrophobic foulants on the membrane surface. This as a consequence increase the membrane resistance against foulant deposition and adsorption.

With respect to BSA removal rate, all three membranes show complete rejection against BSA foulant. The excellent removal rate of membrane could be due to its extremely small surface pore size in comparison to the large size of the BSA. This, as a

result, prevents the passage of macromolecules to the membrane permeate side.

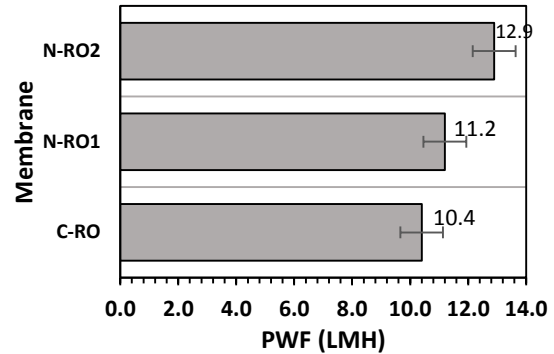


Figure 2 Comparison of pure water flux (LMH, L/m²·h) of control TFC membrane (C-RO) and TFN membranes loading (N-RO1 and N-RO2) at operating pressure of 12 bar

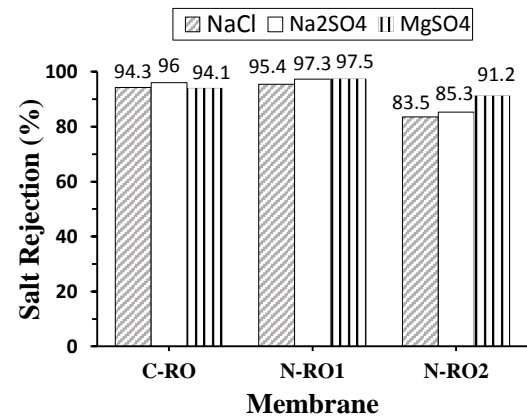
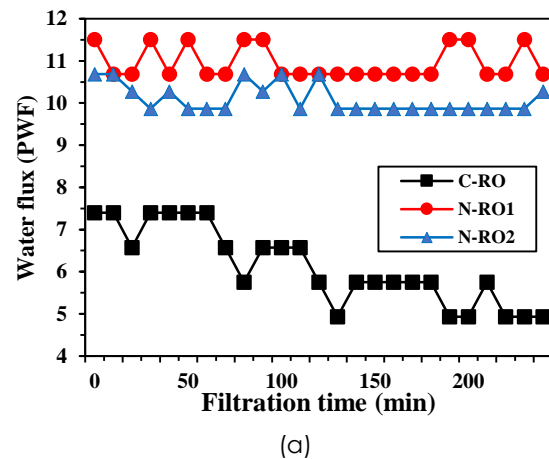


Figure 3 Separation characteristics of RO membranes with respect to NaCl, Na₂SO₄ and MgSO₄



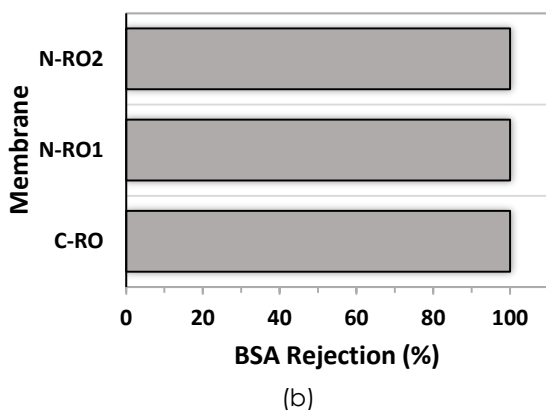


Figure 4 Performance comparison of RO membranes in filtrating BSA aqueous solution, (a) water flux profile as a function of time and (b) BSA rejection

4.0 CONCLUSION

Thin film nanocomposite RO membranes were successfully prepared by incorporating self-synthesized HMO nanoparticles into the PA layer of TFC membrane formed from PIP and TMC monomers. Results showed that the incorporation of small loading (0.05 w/v%) of HMO nanoparticles improved both the membrane hydrophilicity and surface charge through the introduction of more hydrophilic -OH functional groups. Subsequently, this improved the membrane water permeability, salt rejection and fouling resistance. Further increase the nanoparticle loadings to 0.1 w/v% however lowers the cross-linking in the polymer matrix, resulting in a plunge in membrane salt rejection. Evidently, TFN membrane with the incorporation of 0.05 w/v% nanoparticles exhibited higher PWF (11.2 LMH vs. 10.4 LMH) and better salt rejection against NaCl (95.4% vs. 94.3%), Na₂SO₄ (97.3% vs. 96%) and MgSO₄ (97.5% vs. 94.1%) than that of the TFC membrane. Considering the higher water permeability with no trade-off for salt rejection and better fouling resistance, TFN membrane is believed to be able to further reduce the cost of water desalination.

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