Surface modification of commercial seawater reverse osmosis membranes by grafting of hydrophilic monomer blended with carboxylated multiwalled carbon nanotubes

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Abstract

In this study, modification of commercial seawater reverse osmosis membranes was carried out with simultaneous use of surface grafting and nanoparticle incorporation. Membrane grafting with a hydrophilic acrylic acid monomer and thermal initiator was used to increase membrane surface hydrophilicity. The used nanomaterial was carboxylated multiwalled carbon nanotubes (MWCNTs), which were dispersed in the grafting solution and deposited on membrane surface to reduce fouling by creating polymer brushes and hydrodynamic resistance. Effectiveness of the grafting process (formation of graft layer on membrane surface) was proved by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analyses. Increase of membrane surface hydrophilicity was approved with contact angle test. First, the grafting was performed on the membrane surfaces with different monomer concentrations, various contact times and several membrane curing times (three variables for optimization). The modified membranes were tested by a cross-flow setup using saline solution for permeability and rejection tests, and bovine serum albumin (BSA) solution for fouling test. The results showed that the modified membranes with 0.75 M of monomer, 3 minutes contact time and 80 minutes curing time in an oven at 50 °C presented the highest flux and lowest rejection decline related to the commercial reverse osmosis membrane. In the next step, the optimum grafting condition was selected and the nanotubes with different weight percentages were dispersed in the acrylic acid monomer solution. The membrane containing 0.25 wt% COOH-MWCNTs showed the highest fouling resistance.

Keywords: Polyamide reverse osmosis membrane; Desalination; grafting; multiwalled carbon nanotubes; antifouling

1. Introduction

Nowadays, the need to fresh water is ever more serious. In recent years, the use of membranes for water purification and desalination has increased rapidly [1]. Most of these methods have used a reverse osmosis membrane [2, 3] and most of these membranes are made by interfacial polymerization process [4, 5]. The greatest important problem in these membranes is the fouling [6]. The reverse osmosis membrane surfaces are usually rough; a rougher surface has more wettability and higher surface area (and therefore more water flux), but it has less fouling resistance [7]. A surface with more hydrophilicity could provide more wettability (and therefore more water throughput) and induce more fouling resistance. However, thin film composite (TFC) reverse osmosis membranes have high cross-linked polymer network membrane surface and poor hydrophilic characteristics.

There are various ways for modification of membranes and making them more resistance against the fouling. Among them, surface modification (grafting) and nanoparticle incorporation have been identified to be the most effective ones [8]. The polyamide membrane surfaces have free amino and carboxyl groups on their surface inherently due to incomplete polymer crosslinking. It has been confirmed that large negatively charged functional groups are on the surface of TFC polyamide membranes [8, 9].

There are two problems in reverse osmosis membranes surface modification: first is membrane flux decline because of creating an additional layer for mass transfer, which this problem can be reduced using more hydrophilic surface modification materials. Second, in some cases, is salt rejection decrease because some grafting layers could reduce surface charge and thus, could decrease effect of the Donnan repulsion [8, 10].

It is confirmed that the surface charge of membrane depends on protonation and deprotonation of different functional groups such as carboxyl and amino groups on the surface of membrane. Therefore, hydrophilic grafting materials containing carboxyl and

amine functional groups are ideal to improve antifouling characteristic of membranes. One of these materials is acrylic acid, which is hydrophilic and has carboxyl groups.

Freger et al. [11] have examined modifying commercial RO and NF polyamide membranes with grafting of acrylic acid hydrophilic monomer. They prepared solutions containing 0.1 to 1 molar concentration of acrylic acid, 0.01 M ethylene glycol dimethacrylate (as a cross-linker) and redox system of 0.01 M $K_2S_2O_5$ /0.01 M $K_2S_2O_8$ as initiators. They illustrated that attaching of the grafted layer on the membrane surface did not cause any important change in the surface morphology, while a certain decline of roughness was observed. However, if more decrease of the surface roughness is necessary for more enhance antifouling properties, the explained grafting technique will need further modification.

Yu et al. [12] modified a commercial TFC aromatic polyamide RO membrane by depositing N-isopropylacrylamide-co-acrylic acid copolymers (P(NIPAm-co-AAc)) on the membrane surface. The modified membrane showed enhanced membrane property.

Because of the similarity of fluid transport properties of carbon nanotubes (CNTs) with water channels in biological membranes, the CNTs have attracted much attention in preparation of filtration membranes [13]. Special transport properties of the carbon nanotubes are result of uniform surface potential energy inside the nanotubes. The observed enhancements in nanofluidic flows and gas diffusivities have been primarily attributed to nanoscale inner diameter, molecular smoothness of graphitic walls, along with hydrophobic character of the nanosized CNT pores, which force polar water molecules to take linear arrangement. Thus, in usages such as water purification, large volumes of water could pass through the CNT membranes, while blocking the passing of bulky hydrated ions [14]. It is reported that addition of charges using functional groups in the entrance of the tubes can help to prevent the passage of ions, however functionalizing partly could increase water flux. In addition, the antimicrobial and protein anti-adhesion properties have been listed for the carbon nanotubes

modified reverse osmosis membranes in literatures [15]. Therefore, carboxylated-MWCNTs can be used as an effective nanomaterial for modification of membranes.

The purpose of this research is modification of a commercial polyamide seawater reverse osmosis membrane with simultaneously grafting of a hydrophilic acrylic acid monomer and carboxylated multiwalled carbon nanotubes to reach the membranes with improved hydrophilicity and fouling resistance. This layer should be enhanced flux, rejection and performance of the original membrane and make the membranes useable for longer periods. The COOH-MWCNTs in combination with grafting method could add new properties to the grafting layer. The MWCNTs could increase the grafting layer porosity causes to increase in water flux.

2. Experimental

2.1. Materials

Commercial polyamide seawater reverse osmosis membranes were purchased from Woongjin Company (CSM, South Korea), which known by commercial name of RE4040-SHF. Potassium persulfate (KPS, initiator), acrylic acid (AA, monomer) and ethylene glycol dimethacrylate (EGDMA, cross-linker) were obtained from Merck, Germany. Carboxylated multiwalled carbon nanotubes (COOH-MWCNTs) with 5-15 nm OD were provided from US Research Nanomaterials, Inc., USA. Bovine serum albumin (BSA) and sodium chloride used to measure performance of the membranes were obtained from Merck. Water used in grafting solutions and performance testing were prepared using a two-stage distillation device and its conductivity was 6-8 micro-Siemens.

2.2. Membrane surface modification by acrylic acid grafting

A redox system, included of potassium persulfate and sodium metabisulfite, was used to generate radicals. These radicals attack polymer backbone of membrane surface and initiate the graft polymerization by attachment of the monomers to membrane surface. The new polymer then grows by propagation. A cross-linker was added to the reaction solution for stabilizing grafting layer. The coverage amount of the surface increases with monomer concentration and modification time. Schematic of this reaction is shown in Fig. 1.

Fig. 1. Schematic of the modification process

Prior to modification, the commercial membrane was cut in the right size and was dipped in distilled water for 2 hours to remove any dirt. Then, the membrane was placed for 30 minutes in a 50-50 mixture of water and ethanol and then in distilled water for at least 60 minutes. Then, the membrane was clamped in a plastic frame prepared for grafting.

An aqueous solution containing acrylic acid as a monomer (AA, M) and ethylene glycol dimethacrylate as a cross-linker (EGDMA, 0.01 M) was prepared and mixed on a stirrer and then, a redox system composed of potassium persulfate and sodium metabisulfite as initiators (0.025 M, 0.025 M) were added to the above solution. After adding the initiators, the mixture was immediately poured on surface of the membrane clamped in the frame and rolled by a soft roller to eliminate any bubbles and make a uniform area. After passing of certain contact time of grafting solution with the membrane, the mixture on the membrane surface was emptied and the membrane was detached from the frame and heated at 50 °C for specific period in an oven.

For optimization of the grafting conditions, the grafting solutions with different concentrations of acrylic acid (0.25, 0.5, 0.75, 1 and 1.5 M) were prepared and contacted with the RO membrane surfaces for 3, 5 or 7 minutes. The resulted membranes were placed in an oven for 60, 80 or 100 minutes. Finally, the modified membranes were washed with distilled water for 10 minutes to eliminate additional monomer, additional products and loose homopolymers. The membranes were then placed in distilled water for 24 hours and the water was changed every 5 hours. Then, the membranes were kept in an aqueous solution of 1 wt% sodium bisulfite (to prevent microbial growth on the membranes).

2.3. Embedding nanotubes in grafting layer

First, all parameters of the grafting process were optimized without presence of the carbon nanotubes and next, presence and concentration of the carbon nanotubes in the grafting layer was investigated. For membrane modification with the COOH-MWCNTs, *in-situ* polymerization method was used [16, 17]. In this method, the nanoparticle is dispersed in monomer solution and then polymerization is done.

The COOH-MWCNTs with specified weight percentages based on the weight of monomer (0.0125, 0.015, 0.025, 0.05, 0.075, 0.1, and 0.15) were dispersed in distilled water. After adding COOH-MWCNTs to water, the mixtures were placed in an ultrasonic bath for half hour to good disperse of the CNTs. Then, the resulted aqueous suspensions were used for making grafting solutions and the procedure was same as before phase.

2.4. Membrane characterization

Fourier-transform infrared spectroscopy (FTIR) was recorded by the attenuated total reflectance (ATR) technique using Bruker-IFS 48 FTIR spectrometer (Ettlingen, Germany)

with horizontal ATR device (Ge, 45°) to obtain information about the chemical structure of the original and the modified membranes.

Scanning electron microscopy (SEM) apparatus (Tescan Vega, Czech Republic) was employed to obtain images of the membranes surface and cross-section. The membrane samples for cross-sectional images were soaked in liquid nitrogen before breaking to protect structure. Then, the samples were coated with gold and viewed at 20 kV.

The hydrophilicity of the membranes surfaces was characterized by water contact angle measurements performed using goniometer (G10, Kruss, Germany) at room temperature. In this test, a drop of distilled water is carefully placed on the surface of the membrane and the contact angles between the membrane surface and the droplet are determined.

2.5. Cross-flow test setup

Performance of the original commercial reverse osmosis membrane and the membranes modified with the acrylic acid and the carbon nanotubes were evaluated using a cross-flow system. This system contains a high-pressure pump, which feeds solution run from a feed tank to three sequential stainless steel cross-flow cells (the membranes are placed within the cells). The permeate flow exits from the cells output and the concentrate flow returns to the feed tank. The membrane effective surface area in the filtration cells is $4 \times 9 \text{ cm}^2$, the flow rate is 120 L/h and the pressure that the tests are taken is 15 bar. In addition, the feed tank temperature is kept constant during the tests at about room temperature (25 °C).

2.6. Membrane performance evaluation

For pure water flux test, the membranes were placed in the cells and the feed tank was filled with distilled water. Then, the pump was turned on and the membranes were pressed for 30 minutes at pressure of 20 bar. After compressing, the pressure slowly was reduced from 20

bar to 15 bar and water flux was measured after 90 minutes filtration by recording time required for passing 10 ml permeate through the membrane. Pure water flux (J) was obtained by the following formula:

$$J = \frac{V}{A \Delta T} \quad (1)$$

where J is pure water flux of membrane (L/m²h), V is volume of permeate (m³), A is effective surface area of membrane (m²) and ΔT is time (h).

After 90 minutes of measuring pure water flux, NaCl was added to the tank until salt concentration of solution tank was reached to 2000 mg/L. At this stage, the aim was to measure saline solution flux and salt rejection of the membranes. The permeate conductivity was measured using a conductivity meter. The observed salt rejection (R) was obtained from below formula:

$$R (\%) = \left[1 - \frac{\lambda_p}{\lambda_F} \right] \times 100 \quad (2)$$

where λ_p and λ_F are the ion conductivity in permeate and feed, respectively.

2.7. Membrane fouling test

Membrane antifouling properties were evaluated with a cross-flow system. After pure water flux test and saline solution flux test, the fouling test was done using a solution containing 2000 mg/L NaCl and 500 mg/L BSA solution. The foulant solution flux measured within 24 hours every one hour (three first hours and three last hours) by the pervious method and each time, the permeate conductivity was measured. Then, permeate flux and salt rejection were obtained from equations (1) and (2).

3. Results and discussion

3.1. FTIR analyses

FTIR spectroscopy was used to investigate carboxylated carbon nanotubes structure, the RO membrane structure and effect of graft on it. In Fig. 2, FTIR spectrum of the carboxylated carbon nanotubes was shown. In this spectrum, absorption bands in the range of 1400 cm^{-1} to 1600 cm^{-1} approve C=C double bond. A strong band at 1628 cm^{-1} is related to C=O stretching vibration of $-\text{COOH}$ functional group [18]. Strong peak at 3439 cm^{-1} is assigned to carboxylic acid O-H stretching vibration [19].

Fig. 2. FTIR spectra of carboxylated multiwalled carbon nanotubes.

ATR-FTIR spectra of the commercial reverse osmosis membrane and the membrane modified with 0.75 M AA are presented in Fig. 3. In this spectrum, adsorption bands at 1411 cm^{-1} and 1584 cm^{-1} are related to stretching vibration of aromatic ring C=C bond and adsorption band at 1666 cm^{-1} is assigned to polyamide C=O band stretching vibration. Absorption band at 3349 cm^{-1} is attributed to carboxylic acid O-H stretching vibration [20, 21].

As can be seen, absorption bands related to grafting polymer have changed the modified membrane's spectrum. The acid C=O bond stretching vibration absorption peak has appeared at 1720 cm^{-1} for the modified membrane, and symmetric aliphatic C-H stretching vibration absorption peak at 2967 cm^{-1} has increased extremely for the modified membranes. These certainly prove the effectiveness of the grafting [22]. However, O-H absorption peak at 3336 cm^{-1} in the acrylic acid modified membrane has dropped. The reason for this is that there are many O-H groups on the surface of the commercial reverse osmosis membrane. Nevertheless, because of the polymerization reaction and free radical attack on these O-H groups, these bonds are broken and become part of the polymer.

Fig. 3. ATR-FTIR spectra of bare RO membrane and membrane modified with 0.75 M AA

ATR-FTIR spectra of the membrane modified with 0.75 M AA and the membrane modified simultaneously with 0.75 M AA and 0.025 wt% COOH-MWCNTs are shown in [Fig. 4](#). As it is clear in the spectrum, absorption peaks of the C=O (1720 cm^{-1}) and O-H (3336 cm^{-1}) are

increased by addition of the COOH-MWCNTs, while there is no increase in C-H (2967 cm^{-1}) absorption peak. Therefore, this increase is not related to grafting polymer and can be result of using the carboxylated carbon nanotubes [19, 23].

Fig. 4. ATR-FTIR spectra of membrane modified with 0.75 M AA and membrane modified with both 0.75 M AA and 0.025 wt% COOH-MWCNTs.

3.2. Effect of acrylic acid grafting on membrane performance

3.2.1. Monomer concentration

At each optimization stage of membrane modification, water flux and rejection tests were taken from the modified membranes to measure their performance. First, the commercial RO membranes were modified with different concentrations of acrylic acid. At this stage, 3 minutes of the grafting solution contact time and 80 minutes of membrane curing time were considered. To ensure the results, from each modification combination at least four samples were modified and tested.

In **Fig. 5**, mean values of pure water flux and mean values of saline solution flux of the modified membranes are presented. The water flux is reduced initially with acrylic acid

modifying. This could be for two reasons, first, the grafting polymer covers the surface of the membrane, increases the membrane thickness, reduces roughness and thereby, cause to reduction in water flux of the grafted membranes. Second, the grafting polymer initially attacks functional groups of the membrane surface and attaches to the surface by breaking their bonds. This phenomenon at low concentration of monomer decreases negatively charged functional groups of the surface and thereby reduces membrane surface hydrophilicity, but hydrophilicity of the polyacrylic acid bonded to the surface acts against these two factors and makes the surface more hydrophilic [8]. This theory corresponds with data from Fig. 6 related to the contact angles of membranes surface.

Fig. 5. Pure water and saline solution flux of the membranes modified with different concentrations of acrylic acid.

Polyamide membranes have ionized functional groups on the surface, such as carboxylic acid and amine groups. As a result, when soaked in water, polyamide membranes surface give usually a negative charge [9]. The functional groups on the membrane surface also absorb water molecules; so, increasing the functional groups makes the surface more hydrophilic [24].

In Fig. 6, the results of water contact angle analysis of the commercial membrane and the membranes modified with different concentrations of AA are presented. To ensure the accuracy of the results, the presented values are mean value of five analysis on each sample. With grafting of acrylic acid on surface of the membrane, the contact angle of the grafted membranes decreases that means the membrane surface has been more hydrophilic, and this reduction increases by more concentration of acrylic acid monomer.

Fig. 6. Static contact angle of the membranes modified with different concentrations of acrylic acid

At the concentration of 0.75 M AA, brush type hydrophilic polymer layer creates on the surface and this layer increases water flux by absorbing water. However, with further increase of monomer concentration in the grafting solution, the created layer on the surface gets thicker and denser and acts as a barrier against water molecules passage (increases mass transfer distance) and neutralizes the effect of increasing of the hydrophilicity; thus water flux reduces. This increase in thickness of the grafting layer can be seen in SEM images (Fig. 8).

In Fig. 7, surface SEM images of the original membrane and the modified membranes with different concentrations of AA are presented. The surface of the reverse osmosis membranes usually has a nodular morphological pattern (hills and valleys), which this morphology is the nature of interfacial polymerization [7]. As can be seen in the images, the nodular morphology of the surface of modified membranes remained unharmed even with the highest concentration of the grafting monomer and there is no defect in the surface of the modified membranes. However, in Fig. 7e and 7f related to high concentrations of acrylic acid can be seen that the valleys of the commercial membranes were filled with the grafting polymer (polyacrylic acid). By increasing the concentration of acrylic acid monomer, this phenomenon increases and the membrane surface get smoother and roughness decreases, which roughness reduction could lead to fouling decrease [8, 25].

Fig. 7. SEM images of the membranes modified with different concentrations of acrylic acid

In [Fig. 8](#), images obtained from SEM analysis of cross-sectional part of the original and the modified membranes with different concentrations of AA are illustrated. In these images, sponge-like polysulfone (PSf) support layer and a thin film polyamide layer deposited on the PSf can be observed. The polyacrylic acid grafted layer is clearly seen and at higher concentrations of acrylic acid monomer, the layer thickness increases. By increasing the monomer concentration, the created layer on the surface gets thicker and acts like a barrier against water molecules diffusion. For high concentrations of acrylic acid monomer, the thickness of the grafting layer is high that neutralizes the hydrophilic effect of the layer and decreases water flux of the membranes as shown in [Fig. 5](#).

Fig. 8. Cross-sectional SEM images of the membranes grafted with acrylic acid

The favorite morphology of the grafting layer is a condensed polymeric brush on the surface of the membrane, since the hydrophilic polymer brushes can greatly absorb water and swell up, such a structure can alter the absorption properties of the surface, while high flux of polyamide layer is maintained [8]. The membranes grafted with 0.75 M AA monomer had the permeate flux more than the original reverse osmosis membrane.

In [Fig. 9](#), mean salt rejection of the modified membranes with various concentrations of acrylic acid monomer is exhibited. It is clear that initially by acrylic acid modifying, the salt rejection decreases. The reason is that the grafting polymer coats on the surface and reduces surface charge of the membrane [8]. In addition, the grafting monomer initially attacks functional groups of the membrane's surface and breaks their bonds to the surface. This phenomenon at low concentration of monomer decreases functional groups of the surface and reduces salt rejection of the membrane because of reducing the Donnan effect. By increasing concentration of acrylic acid in the grafting solution, functional groups of the grafting polymer increases in the membrane surface and the more negative charge creates on the surface, and thus, the NaCl salt rejection of the membranes rises again [11].

Fig. 9. Mean salt rejection of the modified membranes with various concentrations of acrylic acid monomer

For the concentration of acrylic acid monomer in which water flux of the modified membrane was optimum, still salt rejection is less than the commercial reverse osmosis membrane. With further addition of the concentration of acrylic acid in the grafting solution, salt rejection of the modified membrane increases by increasing negative charge of the membrane surface.

At concentration of 1.5 molar of acrylic acid, high number of molecules attack to the membrane surface for reaction, which probably caused some defects in the membrane surface and the defects filled with grafting solution and as a result water flux and salt rejection of the modified membrane is reduced.

3.2.2. Effect of contact time of grafting solution with membrane surface

In the next stage, the monomer concentration in the grafting solution was kept constant at two different acrylic acid concentrations of 0.75 M and 0.5 M; and 80 minutes of membrane curing time in the oven to eliminate effect of them. The membranes were contacted with the grafting solutions for different times and the resulted membranes were tested to measure their performance. To ensure the results, at least four samples were tested. In Fig. 10, mean values of water flux, brine solution flux and salt rejections of the modified membranes with a

grafting solution containing 0.5 M of acrylic acid with different contact times (1, 3 and 5 min) are presented. In addition, in Fig. 11, these results are exhibited for 0.75 M of acrylic acid grafting solution.

As can be seen in both figures, at one minute contact time, both flux and rejection are lower than the membranes prepared by 3 min contact time. However, by increasing contact time to 5 min, the flux extremely reduces but the rejection increases. By increasing the reaction time, more polyacrylic acid is formed on the surface causes to increase of membrane thickness and decrease of the fluxes and improvement of salt rejection.

Fig. 10. A) Pure water flux and saline solution flux and B) salt rejection of the modified membranes with different contact times of solution containing 0.5 M AA

One minute time is not enough to attract and complete adsorption of acrylic acid on the surface. By slight attack of acrylic acid molecules, the surface charge of the membrane reduces and thus, the water flux and the salt rejection of the modified membranes decrease. By increasing contact time to 5 minute, the AA can more diffuse in the membrane porosity due to having enough time and a thicker barrier layer is formed on the membrane surface that this causes to reduce in water flux and increase in salt rejection of the modified membrane. The membranes fabricated by 3 minutes contact time showed the best results and this contact time is enough to create a suitable thin polymer layer on the membrane surface.

Fig. 11. A) Pure water flux and saline solution flux and B) salt rejection of the modified membranes with different contact times of solution containing 0.75 M AA

3.2.3. Effect of curing time

In the final stage of grafting layer optimization, the membranes prepared by 0.75 M AA concentration and 3 minutes contact time were putted in the oven for different curing times. **Fig. 12** shows the water flux, brine solution flux and salt rejection results. It is illustrated that 80 minutes of time in the oven at 50 °C is suitable to complete the grafting modification process. At 60 minutes curing time, because of incomplete polymerization process of the monomer, the membrane homopolymers that not fully bonded to the surface or not completely crosslinked, are separated from the membrane surface by washing [11]. This inadequate grafting process decreases the functional groups of the membrane surface and reduces surface hydrophilicity and surface charge and thereby, the water flux and salt rejection of the membrane are reduced. In addition, with increasing curing time of the membrane to 100 min, some damages are made to the surface and cause defects in the membrane surface, cause to increase in water flux and extremely reduce in salt rejection.

Fig. 12. A) Pure water flux and saline solution flux and B) salt rejection of the modified membranes with different curing times at 50 °C for solution containing 0.75 M AA

3.3. COOH-MWCNTs blended grafting layer

After finalizing the modification process and achieving the optimum conditions of acrylic acid grafting, the carboxylated carbon nanotubes were added to the grafting solution. For this purpose, different weight percentages of the COOH-MWCNTs were mixed to the optimum grafting solution formula. [Fig. 13](#) presents the mean values of water flux, brine solution flux and salt rejection of the modified membranes with different weight percentage of COOH-

MWCNTs in the acrylic acid solution. By adding low amounts of the carboxylated carbon nanotubes, the flux was increased. This behavior can be related to the passing water molecules through the nanotubes and increasing efficiency of acrylic acid polymerization [23] and more increasing hydrophilicity of the membrane surface (carboxylated carbon nanotubes induce their functional groups to the membrane surface).

The carbon nanotubes can contribute in different ways to transfer water molecules through the grafting layer: water molecules pass directly through the grafting layer or pass directly through the carbon nanotubes in linear arrangement. In addition, interaction of carboxyl groups on the carbon nanotubes with the water molecules helps their passage through the active layer of the membrane [26].

However, by loading higher concentrations of the COOH-MWCNTs, the fluxes are reduced, although the rejections are increased. The COOH-MWCNTs increase yield of the polymerization by providing more sites for acrylic acid monomer [23] and make more acrylic acid monomers attaching to the surface and make membrane surface more hydrophilic (see Fig. 14). Nevertheless, in more high concentrations of the carboxylated MWCNTs (more than 0.075 wt%), the rejections decrease.

Fig. 13. A) Pure water flux and saline solution flux and B) salt rejection of the modified membranes with grafting solutions containing different weight percentages of COOH-MWCNTs

Fig. 14 shows the contact angle tests of the modified membranes with different weight percentages of the COOH-MWCNTs. As can be seen, by addition of the COOH-MWCNTs to the grafting solution (except high loading), the contact angle reduces (relative to the membrane modified with the optimum concentration of the acrylic acid). It can be connected to this fact that the carboxylated carbon nanotubes increase efficiency of the polymerization of acrylic acid by providing more surfaces for acrylic acid monomer to attack [23]; which cause more attachment of acrylic acid to the surface and make the modified membrane surface more hydrophilic. However, more adding of COOH-MWCNTs leads to extreme compressing of the grafting layer and making it too stiff and thereby, reduces wettability and hydrophilicity and finally reduces contact angle of the membrane surface. Also, the surface morphologies of the 0.1 and 0.15 wt% embedded membranes are changed as presented in Fig. 15 by SEM images and it seems to be more smoother rather than the other membranes. Therefore, their contact angle is little more than the others. It well known the rougher surfaces causes to lower contact angle [27].

Fig. 14. Contact angle the membranes modified with 0.75 M AA and different weight percentages of COOH-MWCNTs.

In Fig. 15, the SEM images of the modified membranes surface with different weight percentages of COOH-MWCNTs are displayed. Due to low concentration of carbon nanotubes and good dispersion of them, the carbon nanotubes do not observed. By adding of the COOH-MWCNTs to the grafting solution, the hills and valleys of surface reduce, but adding more of them cause extreme compressing of the grafting layer and make the membrane surface too stiff. In addition, thickness of the grafted layer enhances by increasing of the carbon nanotubes weight percentages (cross-sectional SEM images are not shown).

Fig. 15. Surface SEM images of the membranes modified with 0.75 M AA and different weight percentages of COOH-MWCNTs.

Comparing SEM images specially 0.05 wt% with 0.075 wt%, shows that new nodular groups created on the surface due to agglomeration of acrylic acid polymer chains and carbon

nanotubes in dry condition. Similar results have been observed for commercial RO membrane surface modification by grafting carbodiimide along with polyethylene glycol derivatives [28 , 29].

3.4. Fouling behavior

After testing water flux and salt rejection of the modified membranes, the modified membrane with optimal acrylic acid grafting layer and the membranes modified with all weight percentages of the COOH-MWCNTs were conducted to BSA/salt foulant solution test.

In Fig. 16, normalized graph of mean values of the foulant solution flux is presented. The fouling of membrane modified with 0.75 M of acrylic acid is less than the commercial reverse osmosis membrane, which can be result of more hydrophilic surface and increase in negative charge of the surface after modifying the membrane [28]. BSA molecules have negative charge of the surface after modifying the membrane [28]. BSA molecules have negative charge in water in neutral pH [29]. Meanwhile, functionalized groups of the MWCNT and acrylic acid exist in surface of membranes are also negatively charged at pH 7 due to dissociation. The prepared polymer brushes created by the grafting prevent fouling agents from sticking to the membrane surface [30].

Fig. 16. Normalized flux of the foulant solution

The fouling is even less with adding the carboxylated carbon nanotubes to the grafting solution. It can be due to improving efficiency of the polymerization by using carbon nanotubes. Another reason could be improvement of compression resistance using the carbon nanotubes [15]. The test data indicated that the best amount of the carboxylated carbon nanotubes for adding to the grafting solution is 0.025 wt%. In this concentration, the lowest flux decline is observed.

In Fig. 17, permeation flux diagram of fouling tests of the three membranes i.e. commercial bare RO and two modified membranes with the best performances are presented. The membrane modified with 0.75 M acrylic acid solution without the COOH-MWCNTs shows the highest flux in the first hours of the test. However, in the final hours of the test, the membrane modified with acrylic acid solution containing 0.025 wt% carboxylated MWCNTs presents the best flux. This suggests that over time, the use of membranes modified with acrylic acid solution containing 0.025 wt% MWCNTs is effective and efficient.

Fig. 17. Foulant solution flux of the membranes with the best performance and unmodified membrane

It should be noted that in early hours of the test, salt rejection of the membrane modified with 0.75 M AA was over 90 percent, and for other membranes was above 96%. In the final hours of the test, for the membrane modified with 0.75 M AA, the rejection was over 94% and for other membranes was above 98.5%.

4. Conclusion

The purpose of this research was to modify a commercial polyamide reverse osmosis membranes with grafting of the hydrophilic acrylic acid monomer and simultaneously by embedding carboxylated multiwalled carbon nanotubes to reach the membranes with more fouling resistance, meanwhile flux and rejection maintains constant. This project seeks to optimize modification of the membrane to reach the best membrane performance.

FTIR analysis proved the effectiveness of the grafting procedure and creating a thin layer of acrylic acid on the surface of membrane and showed the possibility of carbon nanotubes sitting on the membrane for modified membranes. SEM images showed a layer of acrylic acid was formed on the surface of the modified membranes.

Modifying the membranes with acrylic acid increased the water flux, but reduced their salt rejection. With increasing concentration of acrylic acid in the grafting solution, the barrier layer created on the surface of the membrane got thicker and water flux decreased. The best acrylic acid concentration in the grafting solution was 0.75 molar, which the modified membranes had the highest flux and reduction in salt rejection was minor.

Adding the COOH-MWCNTs initially increased flux of the modified membranes, but with further increase, caused in reduction of the flux. However, salt rejection was increased. Membranes modified with grafting solution containing 0.025 wt% of COOH-CNTs showed the best performance.

It was concluded from membrane fouling test that membranes grafted with acrylic acid had less fouling in comparison to the original membranes and this difference become more by adding the COOH-MWCNTs to the grafting solution.

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Figure's Captions

Fig. 1. Schematic of the modification process

Fig. 2. FTIR spectra of carboxylated multiwalled carbon nanotubes.

Fig. 3. ATR-FTIR spectra of bare RO membrane and membrane modified with 0.75 M AA

Fig. 4. ATR-FTIR spectra of membrane modified with 0.75 M AA and membrane modified with both 0.75 M AA and 0.025 wt% COOH-MWCNTs.

Fig. 5. Pure water and saline solution flux of the membranes modified with different concentrations of acrylic acid.

Fig. 6. Static contact angle of the membranes modified with different concentrations of acrylic acid

Fig. 7. SEM images of the membranes modified with different concentrations of acrylic acid

Fig. 8. Cross-sectional SEM images of the membranes grafted with acrylic acid

Fig. 9. Mean salt rejection of the modified membranes with various concentrations of acrylic acid monomer

Fig. 10. A) Pure water flux and saline solution flux and B) salt rejection of the modified membranes with different contact times of solution containing 0.5 M AA

Fig. 11. A) Pure water flux and saline solution flux and B) salt rejection of the modified membranes with different contact times of solution containing 0.75 M AA

Fig. 12. A) Pure water flux and saline solution flux and B) salt rejection of the modified membranes with different curing times at 50 °C for solution containing 0.75 M AA

Fig. 13. A) Pure water flux and saline solution flux and B) salt rejection of the modified membranes with grafting solutions containing different weight percentages of COOH-MWCNTs

Fig. 14. Contact angle the membranes modified with 0.75 M AA and different weight percentages of COOH-MWCNTs.

Fig. 15. Surface SEM images of the membranes modified with 0.75 M AA and different weight percentages of COOH-MWCNTs.

Fig. 16. Normalized flux of the foulant solution

Fig. 17. Foulant solution flux of the membranes with the best performance and unmodified membrane