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ORIGINAL ARTICLE

Modification of thin-film polyamide membrane with multi-walled carbon nanotubes by interfacial polymerization

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Abstract Polyamide thin-film composite (TFC) was fabricated on polysulfone (PS-20) base by interfacial polymerization of aqueous *m*-phenylenediamine (MPD) solution and 1,3,5-benzenetricarbonyl trichloride (TMC) in hexane organic solution. Multi-wall carbon nanotubes (MWCNT) were carboxylated by heating MWCNT powder in a mixture of HNO_3 and H_2SO_4 (1:3 v/v) at 70 °C under constant sonication for different periods. Polyamide nanocomposites were prepared by incorporating MWCNT and the carboxylated MWCNT (MWCNT–COOH) at different concentrations (0.001–0.009 wt%). The developed composites were analyzed by Fourier transform infrared spectroscopy-attenuated total reflection, scanning electron microscopy, transmission electron microscopy, contact angle measurement, determination of salt rejection and water permeate flux capabilities. The surface morphological studies displayed that the amalgamation of MWCNT considerably changed the surface properties of modified membranes. The surface hydrophilicity was increased as observed in the enhancement in water flux and pure water permeance, due to the presence of hydrophilic nanotubes. Salt rejection was obtained between 94 and 99% and varied water flux values for TFC-reference membrane, pristine-MWCNT in MPD, pristine-MWCNT in TMC and MWCNT–COOH in MPD were 20.5, 38, 40 and 43 L/m^{2}h. The water flux and salt rejection performances revealed that the MWCNT–COOH membrane was superior membrane as compared to the other prepared membranes.

Keywords Polymerization · Phenylenediamine · Membrane · Carbon nanotube · Desalination

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Introduction

Desalination of wastewater or sea water to generate freshwater is acknowledged to be one of the major significant concerns in the science and conservational engineering fields. The deficiency of freshwater can be due to the quick increase in world population and environmental contamination (Al-Sheetan et al. 2015; Potts et al. 1981; Pendergast and Hoek 2011; Kang and Cao 2012; Greenlee et al. 2009). There are several categories of membranes, for instance reverse osmosis (RO), nanofiltration, ultrafiltration and microfiltration membranes. In these membrane methods, RO is the most extensively applied process for water desalination (Lee et al. 2011; Elimelech and Phillip 2011; Nataraj et al. 2006). In short, the RO membrane method is recognized as the most effective to eliminate small-sized ions in sea water. Presently, polyamide membranes are comprehensively used in the RO methods, because they provide better salt rejection and have high water permeation flux.

There have been several efforts to develop the performance and properties of the RO membrane, such as antifouling property, water permeability, chemical stability and salt rejection (Kang and Cao 2012; Lee et al. 2011; Li and Wang 2010; Fathizadeh et al. 2011; Zhou et al. 2009).

Presently, nanocomposite polyamide membranes comprising nanomaterials such as metal oxide nanoparticles including silver, titanium, zinc, zeolite and carbon nanotube (CNT) have been established to improve the performances and properties of these membranes (Cong et al. 2007; Shawky et al. 2011; Lee et al. 2007, 2008; Lind et al. 2009; Kim et al. 2012). Among nanomaterials, carbon nanotube (CNT) that was first identified by Iijima Sumio in 1991 displays outstanding electrical, optical and mechanical properties and has been utilized in wide areas of engineering and chemistry fields. Particularly, CNT has been thoroughly studied for use in the areas of fuel cell, sensor, electrode of lithium battery, nano-probe, drug delivery, gas separation, display, energy storage, ion exchange and filters (Ajayan 1999; Nikolaev et al. 1999; Couvreur et al. 2002; Cicero et al. 2008; Gusev and Guseva 2007; Coleman et al. 2006).

CNTs have been considered for water treatment method because of their exceptional properties. The incorporation of carbon nanotube in membranes has been known to have high liquid or gas permeability and mechanical and chemical stability (Shi et al. 2013). Improved separation performances were achieved by employing those CNTs as inclusions to polymers (Qiu et al. 2009; Kim and Van der Bruggen 2010; Sahoo et al. 2010). CNTs are tubular in shape and offer the fast transport way to pass water molecules. Water molecules can go into the inside of CNT by capillary force because of the nanosized capillary structure of CNT and they can pass through the hydrophobic inner side of CNT (Iijima 1991; Hummer et al. 2001). These polymeric membranes associated CNTs having high values of water flux were attributed to the unique hydrophobic character of the CNT surfaces and uniformly aligned nanosized pores of CNT materials. There have been very few reports on the development of polymeric membranes with associated CNTs having high salt rejection and a sufficient membrane area for applied RO membrane applications.

Consequently, several polymeric membranes comprising disseminated CNTs in the support layers were established and the performances of membranes were evaluated. Nevertheless, when these membranes comprising scattered CNTs were utilized for the NaCl separation methods, many of them displayed relatively high salt rejection values. We consider that the high salt rejection values attained from these nanocomposite membranes comprising CNTs would be affected by the CNTs' better distribution in the polymer matrix.

Nevertheless, very few studies have described carbon nanotubes employed in the RO membrane. At present, we employed multi-walled carbon nanotubes (MWCNT) in the polyamide thin film of an interfacial polymerization composite membrane for water desalination. The MWCNT–polyamide membrane might considerably produce enriched performance of RO membrane because of its quick mass transport (Falk et al. 2010). Initially, water molecules seem to move alongside the MWCNT nano channel, ensuing in an energy-saving desalination method (Zhang et al. 2011). Subsequently, current various simulations on passage of water through CNTs have recommended that not only water filled the channels and also the water passage ratio would be accelerated through that channels (Corry 2008). If the MWCNT is embedded with few hydrophilic groups such as –OH and –COOH (Zhang et al. 2011), it might develop the hydrophilicity of membranes and improve their performance.

In this study, we developed nanocomposite polyamide membrane with MWCNT through interfacial polymerizations of 1,3-diaminobenzene (MPD) and benzene-1,3,5-tricarbonyl chloride (TMC) in hexane organic solution. The developed composite membranes were characterized by TEM, SEM, FTIR-ATR and contact angle measurement, determination of water permeate flux and salt rejection capabilities. The surface morphological studies displayed that the amalgamation of MWCNT considerably improved the surface properties of the modified membranes. The surface hydrophilicity had increased water flux and pure water permeance, due to the presence of hydrophilic nanotubes. Salt rejection was obtained between 94 and 99% and the water flux for TFC-reference membrane, pristine-MWCNT in MPD, pristine-MWCNT in TMC and MWCNT–COOH in MPD was 20.5, 38, 40 and 43 L/m^2h.

Experimental section

Materials

Materials and chemicals used in this study for all tests were of analytical grade as shown below: multi-walled carbon nanotubes, OD: 3–10 nm and length: 10–30 µm (KNT M31, MWCNT, Grafen Chemical Industries Company), sodium carbonate anhydrous (>99%, Scharlau, Spain), polysulfone supports (PS-20, Sepro, USA), *n*-hexane and *m*-phenylenediamine (MPD) (99%, Sigma Aldrich, USA), 1,3,5-benzenetricarbonyl trichloride (TMC) (98%, Sigma Aldrich, USA), and ultrapure deionized water (DI) (Millipore Milli-Q system, Germany).

Methods

Carboxylation of multi-walled carbon nanotubes (MWCNTs)

MWCNT was carboxylated by immersing MWCNT powder (0.5 g) in a mixture of H_2SO_4/HNO_3 at 3:1, v/v (80 ml) of the acid mixture solution was placed in a 100 or 250 mL round-bottom flask equipped with a magnetic stirring bar

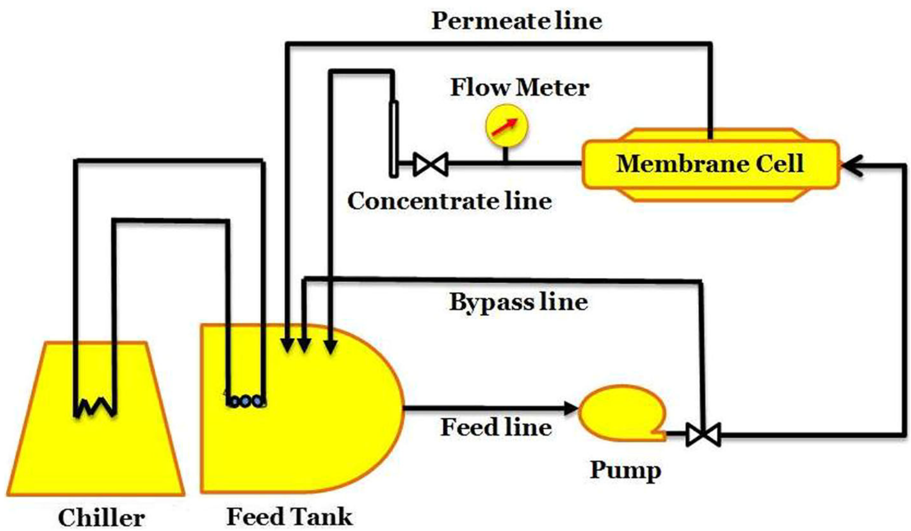


Fig. 1 Schematic illustration of a forward cross-flow filtration system

and the mixture was sonicated for 30 min. The flask was then placed in an oil bath and heated to 70 °C for different periods of time as required for experimental purposes under continuous sonication. A black solid mass was attained after filtration. It was washed numerous times with distilled water and dried at 80 °C in a vacuum oven for 8 h. The resulting MWCNT mass was found to contain the –COOH group attached to the MWCNT molecule (i.e., MWCNT–COOH), which was detected using various analytical tools by Kim et al. (2014).

Modified membrane preparation

The polyamide (PA) thin-film composite (TFC) membrane was fabricated by interfacial polymerization on a PS-20 support. The PS-20 was fixed on a glass plate to prevent any probable penetration of liquid into its back from the sides. Then, it was drenched in deionized water (DI) for 1 min. At the end, the PSF support on the glass plate was eliminated to get rid of the excess water on its top surface by positioning it vertically under ambient conditions. The following polyamide TFC membranes were produced:

1. The pristine-CNT disperse during the preparation of membrane was carried out by using the procedure from Kim et al. (2014).
2. The TFC-reference membrane was obtained by immersing PS-20 in a 2% MPD/H_2O solution for 2 min (the surplus MPD solution was removed by pressing a rubber roller). It was then immersed in 0.1% TMC/hexane solution for 1 min.
3. The modified TFC membrane (MWCNT/MPD) was prepared by immersing PS-20 in a 2% MPD/H_2O solution for 2 min in the presence of different amounts of MWCNT (0.001–0.009 wt%). It was then immersed in 0.1% TMC/hexane solution for 1 min.
4. The modified TFC membrane (MWCNT/TMC) was obtained by immersing PS-20 in a 2% MPD/H_2O solution for 2 min. It was then immersed in 0.1% TMC/hexane solution for 1 min in the presence of different amounts (0.001–0.009 wt%) of MWCNT and then rinsed with 0.2% Na_2CO_3, washed with DI water and finally stored in a refrigerator at 4 °C in DI water till use. The same procedure was implemented for the preparation of all the other membranes.

Characterization and instrumentation

The following instrumentation techniques were used to characterize the developed membranes.

Scanning electron microscopy (SEM)

The microstructure and surface morphology of the developed nanocomposite membrane were investigated by scanning electron microscopy (SEM, Nova NanoSEM-600, Netherlands). This was used to examine the roughness and surface morphology of the synthesized membranes.

Transmission electron microscopy (TEM)

TEM was executed on a JEOL JEM 1101 (USA). The specimen for TEM was made by positioning the specimen on a carbon copper grid and drying out for 6–8 h at 70–80 °C in an oven.

Fourier transform infrared-attenuated total reflection (FTIR-ATR)

FTIR attached with ATR plate (Perkin Elmer, USA) was used to trace out the chemical compositions of the membrane. The surface layer of the polyamide membrane samples was placed facing the crystal surface. The FTIR-ATR spectra were estimated over a range of wave numbers from 4000 to 600 cm^{-1} at a resolution of 4 cm^{-1}.

Goniometer

Contact angle study was executed using a ramé-hart Model 250 Standard Goniometer/Tensiometer with drop image (Ramé-hart Instrument Co., Succasunna, NJ, 07876 USA). A water drop was positioned on a dry uniform membrane surface and the contact angle between membrane and water drop was assessed until no more variation was noticed. The average distilled water contact angle was obtained in a sequence of eight different measurements for every membrane surface.

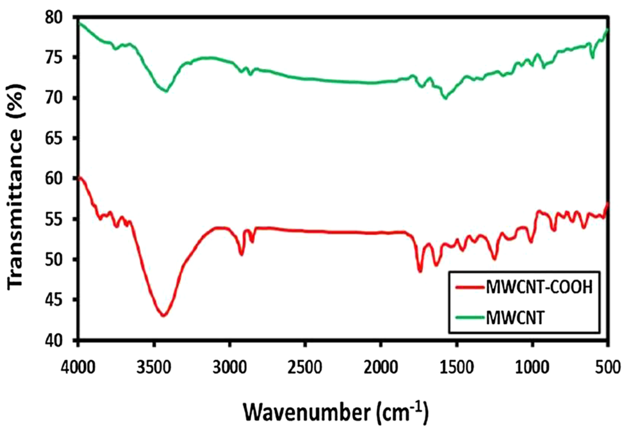


Fig. 2 FTIR image of MWCNT and MWCNT–COOH

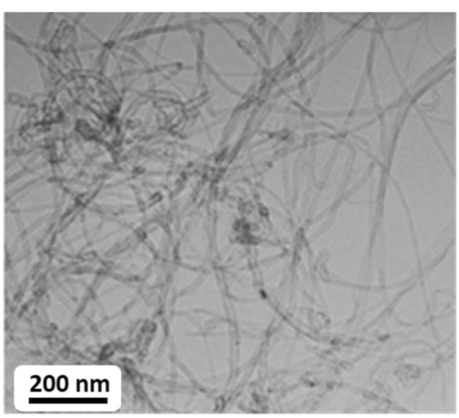


Fig. 3 SEM image of MWCNT

Cross-flow (water flux and salt rejection)

The developed membrane performance of water flux and salt rejection was examined through a cross-flow system (CF042SS316 Cell, Sterlitech Corp., USA). The membrane area in this method was 42 cm^2. The temperature of the feed water was 25 °C with pH adjusted at 6–7 for 2000 ppm feed solution of NaCl and at 1 gal/min feed flow rate. The filtration was performed at the pressure of 225 psi. The salt rejection and water flux measurements were estimated after 30 min of water filtration tests to confirm stable conditions. A cross-flow filtration system schematic diagram is shown in Fig. 1.

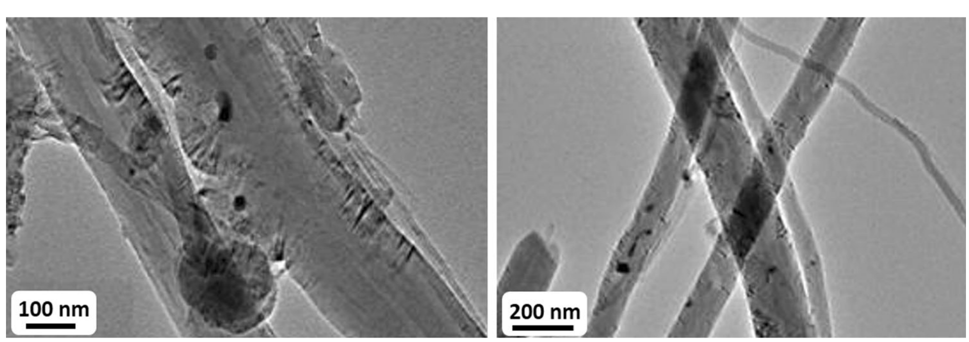
Results and discussion

Characterization of multi-walled carbon nanotubes (MWCNT)

FTIR spectroscopy

Figure 2 demonstrates the FTIR spectra of MWCNT and MWCNT–COOH. The FTIR spectrum of MWCNT displays weak sp^3 C–H and sp^2 C–H stretching bands at 2940 and 2850 cm^{-1}, respectively. They are originated from the defects on MWCNT at sidewalls, which convey abundant reaction sites. The FTIR spectrum of MWCNT–COOH displays characteristic peaks of OH at 3405 cm^{-1}, C=O at 1717 and 1580 cm^{-1}, and $-CH_2$ at 1208 cm^{-1}, indicating the appearance of the carboxyl group grafted on MWCNT.

Fig. 4 TEM images of MWCNT



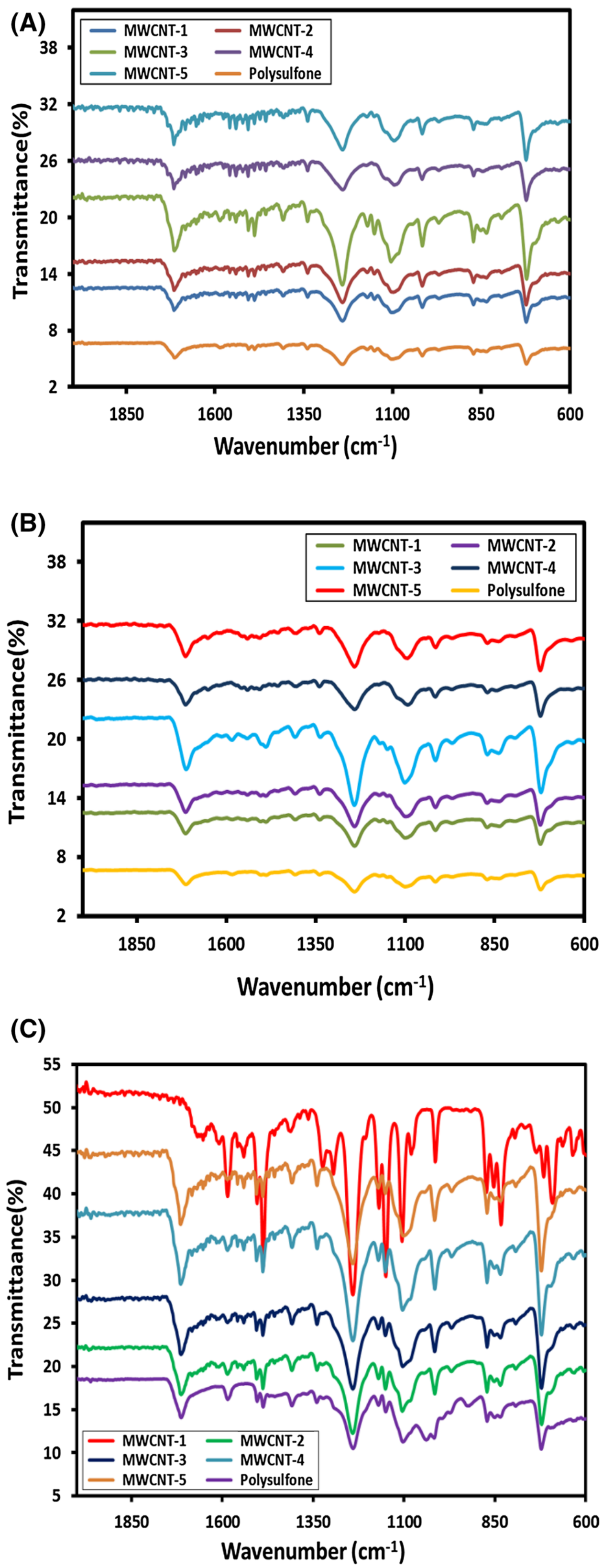


Fig. 5 ATR-FTIR spectra of TFC and modified membranes with **a** pristine-MWCNT in MPD, **b** pristine-MWCNT in TMC and **c** MWCNT–COOH in MPD

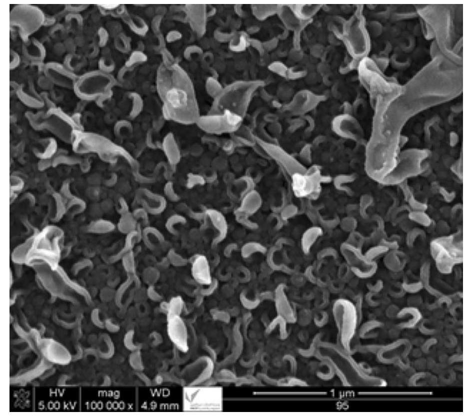


Fig. 6 SEM images of TFC

SEM analysis of carbon nanotube

The procured nanotubes were examined under scanning electron microscope (SEM) to evaluate their physical status. SEM pictures of MWCNT were taken, as displayed in Fig. 3 and revealed that the P-MWCNTs were present as bundle, surfaces were found with an average diameter of 10–20 nm and there was no amorphous carbon present in these samples, indicating lower level of defects in the production process of MWCNT and they had long length and smaller diameter.

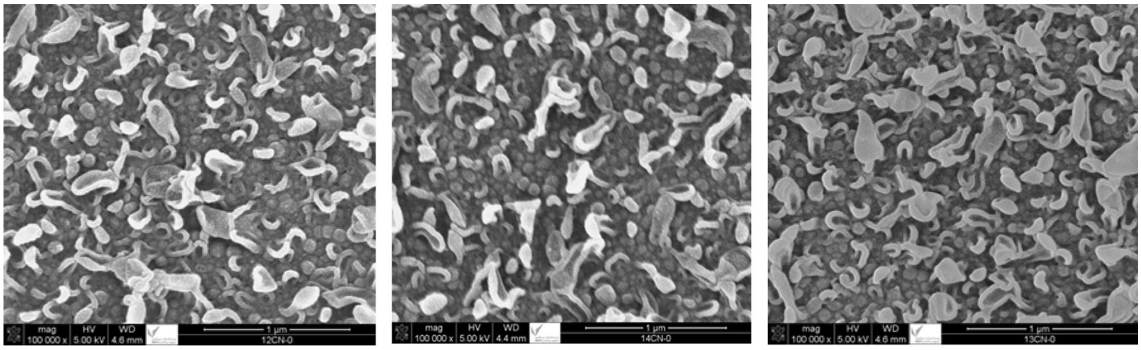
TEM analysis

In the TEM method an electron beam is transferred through an ultrathin specimen and it interacts with the sample as it passes through it. TEM analysis of P-MWCNT were taken like SEM analysis and the TEM images are as shown in Fig. 4. It shows that MWCNTs are present as bundles. It also displays that the tube surface is smooth and clean with a diameter of 10–20 nm. MWCNTs are not amorphous and, thus, have lower level of defects and have longer length.

Characterization of PA membranes with carboxylated MWCNT (MWCNT–COOH)

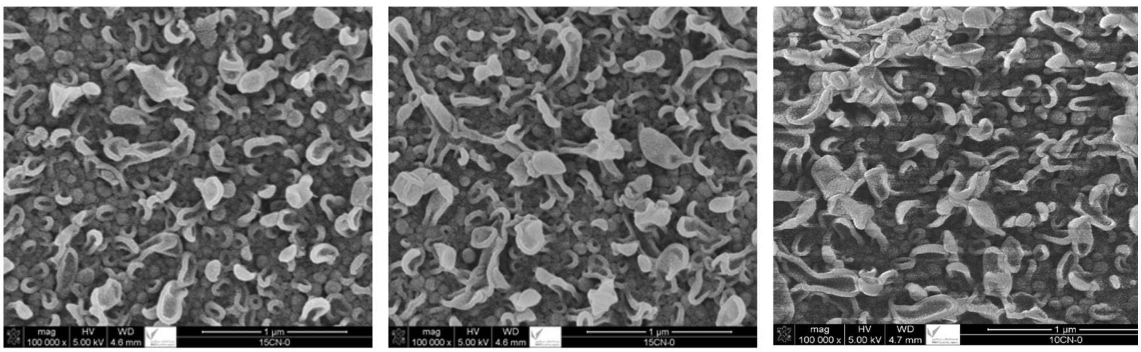
FTIR-ATR spectroscopy of the modified membrane

FTIR-ATR analysis was undertaken with both thin-film composite (TFC) and TFC/MWCNT membranes were taken to evaluate the extent of interfacial polymerization with polyamides (MPD/TMC) and that with the incorporated MWCNT spectra. The pristine-MWCNT and MWCNT–COOH were termed as MWCNT-1 to MWCNT-5 [different amounts of MWCNT (0.001–0.009 wt%)] and



0.001 Wt.% 0.005 Wt.% 0.009 Wt.%

Fig. 7 SEM images of MWCNT in MPD



0.001 Wt.% 0.005 Wt.% 0.009 Wt.%

Fig. 8 SEM images of MWCNT–COOH in MPD

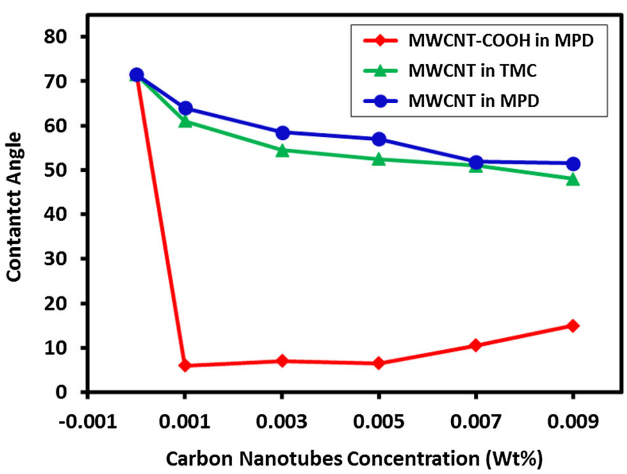


Fig. 9 Contact angle of modified membranes with MWCNT

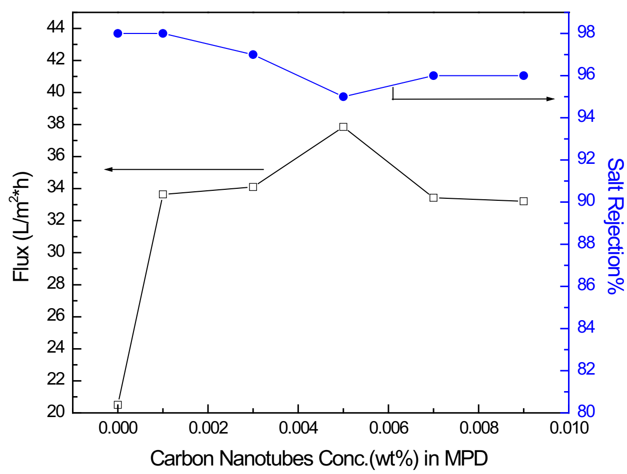


Fig. 10 Permeate flux and salt rejection of pristine-MWCNT in MPD solution

the number increases with the increase of the acid content in the reaction mixture as shown in Fig. 5a–c.

From the above spectra, it is revealed that identical peaks are observed with both types of PA samples, i.e., TFC and TFC/MWCNT, indicating that interfacial polymerization has ensued in all of the membranes. A band at 1670 cm^{-1} represents the amide I band, which is representative of the C–O bands of an amide group. In addition to this, further bands are also noticed at 1550 cm^{-1} to indicate amide II band and NH in plane bending and at 1610 cm^{-1} to represent C–C ring stretching vibrations.

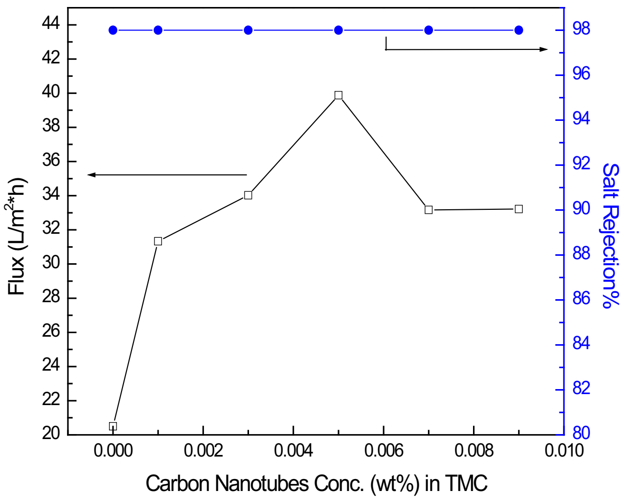


Fig. 11 Permeate flux and salt rejection of pristine-MWCNT in TMC solution

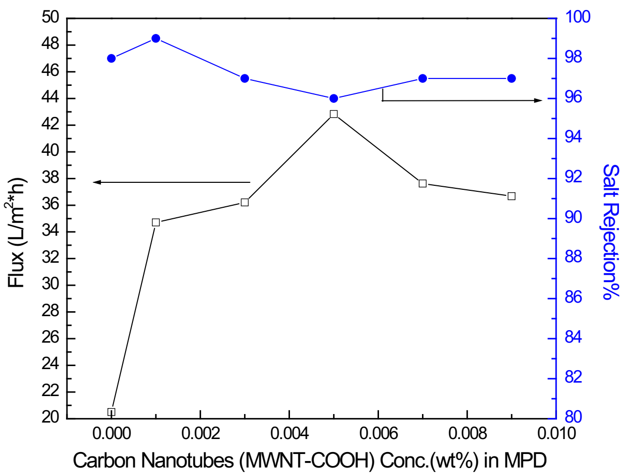


Fig. 12 Permeate flux and salt rejection of MWCNT–COOH in MPD solution

SEM analysis of the modified membrane

SEM analysis was conducted with TFC (Fig. 6), TFC/MWCNT in MPD at different concentrations (Fig. 7), and TFC/MWCNT–COOH in MPD at different concentrations (Fig. 8) to evaluate the surface morphologies of all these membranes. The addition of pristine-MWCNT shows that the membrane surface becomes rougher. On the other side, the insertion of MWCNT–COOH in the membranes forms the surface of polyphenylene diamine (PMD) film precisely and closely packed together. The appearance of MWCNT–COOH on the surface of the membrane indicates that some parts of the tube are not completely carboxylated, which causes decrease in salt precipitation.

Contact angle results

Contact angles of water droplets on the surfaces of different RO membranes containing different concentrations of pristine-MWCNT in TMC and in MPD as well as with MWCNT–COOH in MPD were determined and are shown in Fig. 9.

With increase of MWCNT concentration in RO membranes containing either TMC or MPD, the contact angles are found to decrease and membrane hydrophobicity also decreases. On the other hand, the contact angle drops sharply in the presence of 0.001 wt% of MWCNT–COOH in MPD. As the concentration of MWCNT–COOH increases, the contact angles slowly increase until it reaches an inflexion state. The MWCNT incorporation can also obstruct the establishment of dense cross-linked polyphenylene diamine structure, contributing to the enrichment of water flux. Nevertheless, when the quantity of MWCNT in aqueous phase is high enough (0.009 wt%), the dispersion of MWCNT becomes worse, leading to non-uniform dispersion and forming cluster and agglomeration of MWCNT in the solution. MWCNT packages have slighter particular surface area and lesser adsorption activity with membrane surface. Accordingly, with a high concentration of MWCNT in the aqueous phase, it may increase in hydrophilicity of the modified membrane and thus increase in water rate. It is observed here that our results are in agreement with those achieved by other investigators (Kim et al. 2014; Zhao et al. 2014; Amini et al. 2013).

The contact angle values of MWCNT-membranes in TMC and MPD are shown in Fig. 9, decreased by the addition of functionalized carbon nanotubes loading in the rejection layer. The outcomes of contact angle values of membranes containing functionalized MWCNT suggest that the incorporation of MWCNT–COOH has not established nano channels on the surfaces and, thus, does not allow expansion of water droplets on the surface easily (Choi et al. 2006). In addition, the COOH-functionalized MWCNT-membranes increase hydrophilicity with increased amount of MWCNTs above 0.002 wt%, at which point there is little effect on the contact angle of the modified membrane.

Permeate flux and salt rejection

Permeate flux and salt rejection ability performances were carried out with aqueous sodium chloride salt solution using three types of polyamide thin-film composites, which contained different amounts (0.001–0.009 wt%) of pristine-MWCNTs in MPD, pristine-MWCNT in TMC and MWCNT–COOH in MPD. The results are shown in

Table 1 A brief summary of previous studies

Carbon nanotubes type	Method	Measuring conditions	Modified membrane properties	Salt rejection (%)	Flux L/m^2h	Refs.
Multi-walled carbon nanotubes (MWCNT)	IP (MPD/TMC). MWCNTs in TMC/heptane	Feed water temperature was 25 °C, pH at 6–7 for 2000 ppm feed solution of NaCl, pressure of 225 psi	Surface hydrophilicity was increased, with enhancement in water flux and salt rejection	99	43	[a]
Multi-walled carbon nanotubes (MWCNTs)	IP (MPD/TMC). MWCNTs in TMC/hexane	Operation pressure of 0.6 MPa with 5 mmol/L Na_2SO_4 aqueous solution	Water flux increased, salt rejection decreased slightly, and better antifouling and antioxidant properties, increased hydrophilicity	>90	28.05	Wu et al. (2013)
Amine-functionalized multi-walled carbon nanotubes (F-MWCNTs)	IP (MPD/TMC). MWCNTs in MPD	Pressure of 375 kPa and 20 mM NaCl as feed solution	Increased hydrophilicity, increased surface roughness, decreased contact angle	89.3	37.7	Amini et al. (2013)
Multi-walled carbon nanotube (MWCNT)	IP (MPD/TMC). MWCNTs in MPD	2000 ppm NaCl aqueous solution, pH 7, 225 psig (15.5 bar) feed pressure	Enhanced the chlorine resistance and improved physical properties	92.5	13.6	Park et al. (2010)
CNT/polyamide nanocomposite membrane	IP (MPD/TMC) CNTs in MPD	2000 ppm of NaCl feed solution, 15.5 bar of feed pressure	Enhanced chlorine resistance, high water flux and salt rejection	97.5	34.8	Kim et al. (2014)
Multi-walled carbon nanotubes (MWNTs)/polyamide membrane	IP (MPD/TMC). MWNTs in TMC/hexane	2000 ppm NaCl solution, and 200 ppm purified terephthalic acid solution (pH 9) at 25 °C	Improved water permeation and salt rejection increases	98	49	Zhang et al. (2011)

[a] Current study

Figs. 10, 11 and 12. The effect of loading MWCNT on the pure water flux and salt rejection of ensuing MWCNT-membranes (MWCNT-membranes untreated) in the state of the TFC-reference membrane (flux, 20.5 L/m^2h) is shown. With the rise of MWCNTs content in the range of 0.001–0.009 wt%, the water permeation of MWCNT-membranes/MPD is improved at lower concentrations and varies at higher concentrations dramatically (flux, 38 L/m^2h). Moreover, while the permeate flux was improved with slight change of salts, rejection resulted within 2%. As seen in Figs. 11 and 12, the pure water permeability nearly changed likely in the state of MWCNT/TMC (flux, 40 L/m^2h) as in MWCNTs/MDP (flux, 38 L/m^2h), while the salt rejection remained unchanged at all concentrations of MWCNTs. The water flux of MWCNT–COOH membranes found dramatically improved till 0.005 W% of MWCNTs (flux, 43 L/m^2h) and decrease again as shown in Fig. 12, which might be due to the favorably water flow molecules through the MWCNT, while slightly change of salts rejection result within 2%. It is observed here that our outcomes are in agreement with those results acquired by other researchers. Zhang et al. (2011) found water permeability increases from 26 L/m^2h with increases of MWCNTs till 71 L/m^2h at 0.1% (w/v), while decrease in salt rejection from 94 to 82%. Wu et al. (2013) found the water permeability increases from 10.8 to 21.2 L/m^2h at a concentration of 0.5 mg/mL and then decreases with increase of MWCNTs concentration, while salt rejection (Na_2SO_4) slightly changes. The MWCNT-membranes will have a prospective application in the desalination of the aqueous solution. Finally, the two membrane types have nearly the same salt rejection and different flux values.

Summary of properties of modified RO membranes of previous studies

There are several scientific reports concerning the performance of interfacially polymerized cost-effective TFC polyamide and aromatic TFC polyamide membranes on the desalination properties through membranes based on TMC and MPD. The transport properties of the prepared membranes were compared to those of the membranes reported in Table 1.

Conclusion

Three types of TFC membranes were developed containing pristine-MWCNT in TMC solution, pristine-MWCNT in MPD solution and MWCNT–COOH in MPD. All of them showed high salt rejection ability from 94 to 99%, but varied flux values were exhibited for TFC-reference membrane, pristine-MWCNT in MPD, pristine-MWCNT in TMC and MWCNT–COOH in MPD of 20.5, 38, 40 and 43 L/m^{2}h, the highest being for MWCNT–COOH membrane, i.e., 43 L/m^{2}h. Based on their performance capability, high salt rejection and improved flux ability were noticed with MWCNT–COOH membrane as compared to the developed membranes.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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