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Preparation of high-flux thin film nanocomposite reverse osmosis membranes by incorporating functionalized multi-walled carbon nanotubes

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ABSTRACT

To enhance the water flux of reverse osmosis membranes, thin film nanocomposite reverse osmosis membranes are prepared by incorporating functionalized multi-walled carbon nanotubes (MWNTs). The functionalized MWNTs are obtained by the treatment of pristine MWNTs with the mixed acid of H_2SO_4 and HNO_3 (3:1 v/v). The MWNTs are analyzed by Fourier transform infrared spectrometry (FTIR). The surface morphology and structure of membrane are characterized by scanning electronic microscopy (SEM), transmission electron microscopy (TEM) and contact angle measurement, respectively. Those results show that modified MWNTs yielded some hydrophilic groups, such as -COOH and -OH, which make acidified MWNTs disperse more evenly in the aqueous solution. The SEM and TEM results demonstrate that the functionalized MWNTs penetrated through the polyamide layer, and might play the role of water channel. Compared with the bare polyamide membrane, the MWNT-polyamide thin film nanocomposite membranes have more hydrophilic surface, and the water flux of MWNT-polyamide membranes improve dramatically. For 2000 ppm NaCl, the water permeability increases from 26 l/m^2h without MWNTs to 71 l/m^2h at the acidified MWNTs loading of 0.1% (w/v), while NaCl rejection of MWNT-polyamide membranes decreases obviously compared to bare polyamide membrane. However, for 200 ppm purified terephthalic acid (PTA) solution, the pure water flux increases from 19 l/m^2h up to 49 l/m^2h, while PTA rejection is all higher than 98%. The experimental results reveal that the modified MWNTs well dispersed in the polyamide thin film layer, and hence improve the water permeation.

Keywords: Multi-walled carbon nanotube; Acidulation; Polyamide film; Reverse osmosis nanocomposite membrane; Desalination; Terephthalic acid

1. Introduction

Carbon nanotubes (CNTs) have been studied as a molecular sieve for pervaporation, gas separation, ion-exchange, and fuel cell applications [1–3], and better separation performances were obtained using those CNTs as additions to polymers [4–5]. Carbon nanotubes have the seamless and tubular structure [6], and the hydrophobic channel for water passing through [7]. It is believed that in carbon nanotubes, hydrated salt ions [8] are "size-excluded" through the innermost tube and the interstitial voids between the graphitic sheets, while smaller water molecules are able to pass through. However, to our best knowledge, no open literature has been reported on the carbon nanotubes used in reverse osmosis (RO) membrane.

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Here we embed multi-walled carbon nanotubes (MWNTs) throughout the polyamide thin film of an interfacial composite RO membrane for desalination. The MWNT-polyamide film might offer much improved membrane performance for reverse osmosis because of its rapid mass transport behavior [9–10]. First, water molecules appear to flow along the nanochannel of MWNTs, resulting in an energy-saving desalination process [11]. Second, recent numerous simulations on water transport through carbon nanotubes have suggested that not only water occupied the channels, but also the rate of water transport would increase through that channels [7,12]. Third, if the MWNTs can be grafted with some hydrophilic groups such as -COOH and -OH, it might improve the hydrophilicity of membrane and for better membrane performance.

In the present study, we have prepared MWNT-polyamide nanocomposite membranes. The MWNT-polyamide membranes have been characterized by scanning electron microscope (SEM) and transmission electron microscopy (TEM). The membrane separation performance including water flux, rejection of NaCl solution and purified terephthalic acid (PTA) solution have also been evaluated as a function of MWNTs concentration.

2. Experimental

2.1. Materials

The pristine multi-walled carbon nanotubes (MWNTs), 95.0% purity, were manufactured by Shenzhen Nanotech Port Co., Ltd. China. Concentrated sulfuric acid (H_2SO_4, 98.0%), concentrated nitric acid (HNO_3, 65.0%), analytical grade dimethyl formamide (DMF) were purchased from Shanghai Reagent Company, China. PSF ultrafiltration membranes were obtained from National Engineering Research Center for Liquid Separation Membrane, Hangzhou, China. M-phenylenediamine (MPD, >99.0%) and trimesoyl chloride (TMC, >99.0%) were bought from Sigma-Aldrich Company.

2.2. Preparation of acidified MWNTs

Since MWNTs are generally seriously bundled, pristine MWNTs were first dispersed in mixed acid (H_2SO_4/HNO_3 = 3/1 by volume), then treated by ultrasonic agitation at 80°C for 6 h in order to make MWNTs much shorter and homogeneously dispersed in desired polymer matrices. After that, MWNTs were diluted by deionized water and vacuum-filtered through PTFE membrane (pore size: 0.2 μm) until the pH of filtrate was neutral. MWNTs were then dried in vacuum drying oven at 70°C for 24 h to yield MWNT-COOH as shown in Fig. 1.

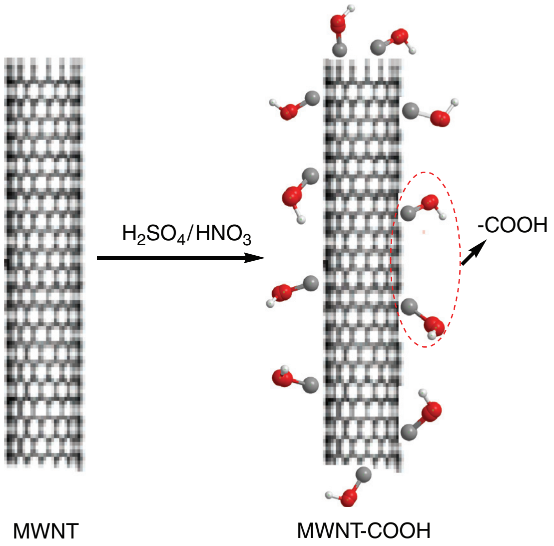


Fig. 1. Modification process of multi-walled carbon nanotubes.

2.3. Characterization of MWNTs

The morphology of pristine MWNTs and acidified MWNTs were directly observed by transmission electron microscopy (TEM) (JEOL JEM-1230, Japan). Functionalization of the MWNTs was confirmed with Fourier transform infrared spectra (FTIR) (Bruker Tensor 27, Germany) and Ultra-visible spectra (Ultrospec 3300 pro, USA), respectively.

2.4. Fabrication and characterization of MWNT-polyamide membrane

A PSF ultrafiltration membrane was taped to a glass plate, and then 2% (w/v) MPD aqueous solution containing MWNTs nanoparticles and 0.2% (w/v) TMC solution in hexane was immersed on the surface of PSF membrane to produce polymerized membrane by interfacial polymerization. After the reaction, the resulting MWNT-polyamide membranes were heated in an oven at 60°C for further polymerization. The conceptual illustration of MWNT-polyamide membrane was shown in Fig. 2. Finally, the membranes were rinsed with deionized water and stored in 1% $NaHSO_3$ solution. Nanocomposite MWNTs dispersion were made by dispersing 0.005% – 0.2% (w/v) of MWNTs in the water-MPD solution, and then, the ultrasonic bath, agitating the mixture for 1h at room temperature immediately before interfacial polymerization.

The morphology of thin film surface was observed with scanning electron microscopy (SEM) (FEI SIRION-100, Netherlands) and TEM (JEOL JEM-1230, Japan), respectively. The hydrophilicity of membrane surface was characterized by contact angle goniometer

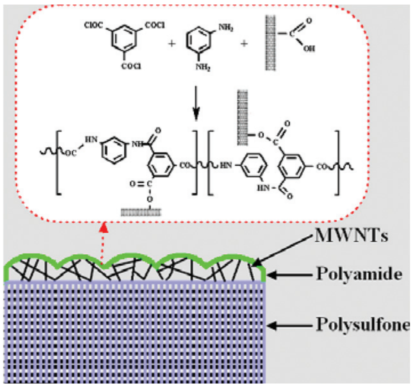


Fig. 2. Conceptual illustration of MWNT-polyamide membrane structures.

(Dataphysics OCA20, Germany). The contact angles of samples were measured by 1 µl water at room temperature, and the average of at least six measurements at different locations of the sample was observed.

2.5. Characterization of membrane performance

Separation performance of the nanocomposite membranes was tested with 2000 ppm NaCl solution and 200 ppm purified terephthalic acid (PTA) solution (pH = 9) at 25°C with the apparatus of a cross-flow type. As an important organic raw material of synthesizing polyester fibers, coatings, films and engineering plastics, PTA is usually degraded from the polyester fabric produce process, and it has been recognized as the main component of wastewater alkaline reduction in textile printing and dyeing industry. Therefore, it is a very important practical application in purifying PTA from aqueous solutions.

The pure water flux was measured after the membranes were compressed for 1 h at 1.6 MPa. The water permeation flux F (l/m^{2}h) and the solute rejection R (%) of the membrane were obtained as follows:

$$F = \frac{V}{St} \tag{1}$$

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

where V was the volumetric flow rate of permeate (L), t was the time (h). S was the effective area of membrane (m^2), and in this case the membrane area was 38.46 cm^2. C_f and C_p were the concentrations of the feed solution and permeate solution, respectively. All membrane samples were prepared and tested in at least duplicate with a total of six membrane tests for RO performance, and the results were averaged.

3. Results and discussion

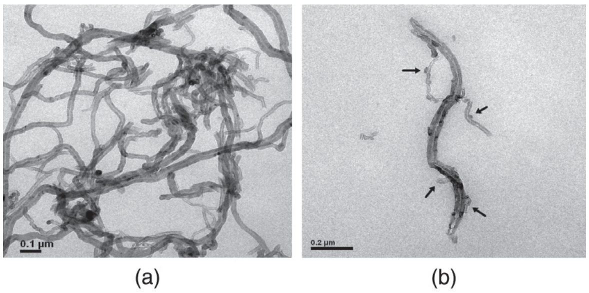
3.1. Characterization of MWNTs

3.1.1. TEM

Fig. 3 displays the typical TEM images of the pristine and acidified MWNTs. It is observed that the pristine MWNTs are curled and entangled in the aqueous solution, and it is difficult to observe a single one. After functionalization, the MWNTs are well dispersed in the aqueous solution, shows a loose morphology, and they are much shorter than their original one after the treatment of ultrasonic and mixture acid as shown in Fig. 3(b).

3.1.2. FTIR and ultra-visible spectroscopy

Fig. 4 shows the FTIR spectra of pristine MWNTs and acidified MWNTs. FTIR spectrum of pristine MWNTs exhibits weak sp^2 C-H and sp^3 C-H stretching bands, which is attributed to the defects at both the sidewalls and open ends of MWNTs. The defects provide sites for the electrophilic substitution reaction. The peaks at



(a) (b)

Fig. 3. TEM pictures of (a) pristine MWNTs and (b) acidified MWNTs.

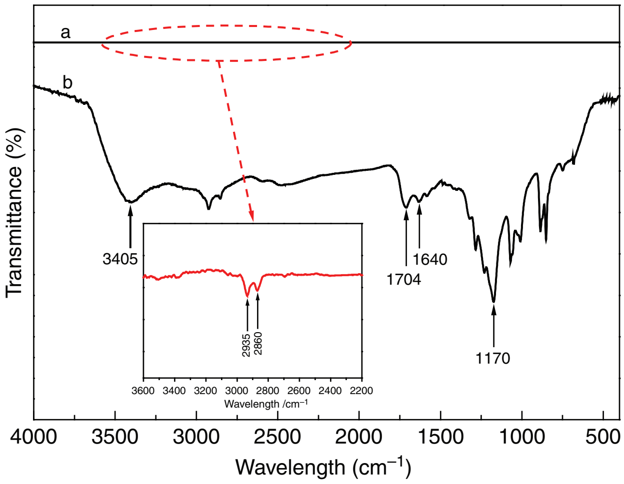


Fig. 4. FTIR spectra of pristine MWNTs (a) and acidified MWNTs (b).

1170 and 1704 cm^{-1} of MWNT-COOH correspond to C = O, C-O stretching vibration, respectively, while the band at 3405 cm^{-1} is the characteristic peak of -OH group. Those bands indicate the carboxyl group has been grafted on the MWNTs [13].

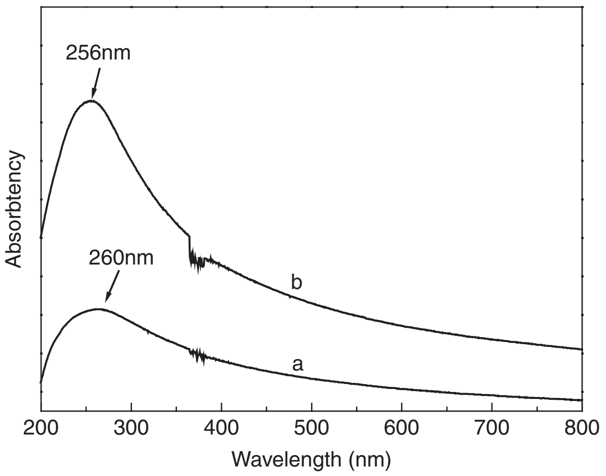


Fig. 5. Ultra-Visible spectra of pristine MWNTs (a) and acidified MWNTs (b) in aqueous solution.

Since the hybridization of carbon atoms in MWNTs is mainly in the form of sp^2, each carbon atom can spare one electron in p-orbit to form delocalized bonds which can be excited transition of $\pi \rightarrow \pi^*$ in ultraviolet radiation. Fig. 5 shows the Ultra-visible spectra of MWNTs in an aqueous solution. Both the pristine MWNTs and the acidified MWNTs have corresponding peaks at around 256 nm resulting from the transition of $\pi \rightarrow \pi^*$. Compared with pristine MWNTs (260 nm), there is a blueshift to the acidified MWNTs (256 nm), which means the side walls of acidified MWNTs have been modified with carboxyl group and hydroxyl group.

3.2. Characterization of MWNT-polyamide thin film nanocomposite membrane

The surface morphologies of polyamide membranes containing MWNTs are shown in Fig. 6. The surface of polyamide membrane with different loading of MWNTs exhibits the familiar "hill and valley". With the addition of acidified MWNTs, the membrane surface becomes rougher. As shown in Fig. 6, further addition of MWNTs in the membranes makes the surface of polyamide film closely and neatly packed together. The micrographs

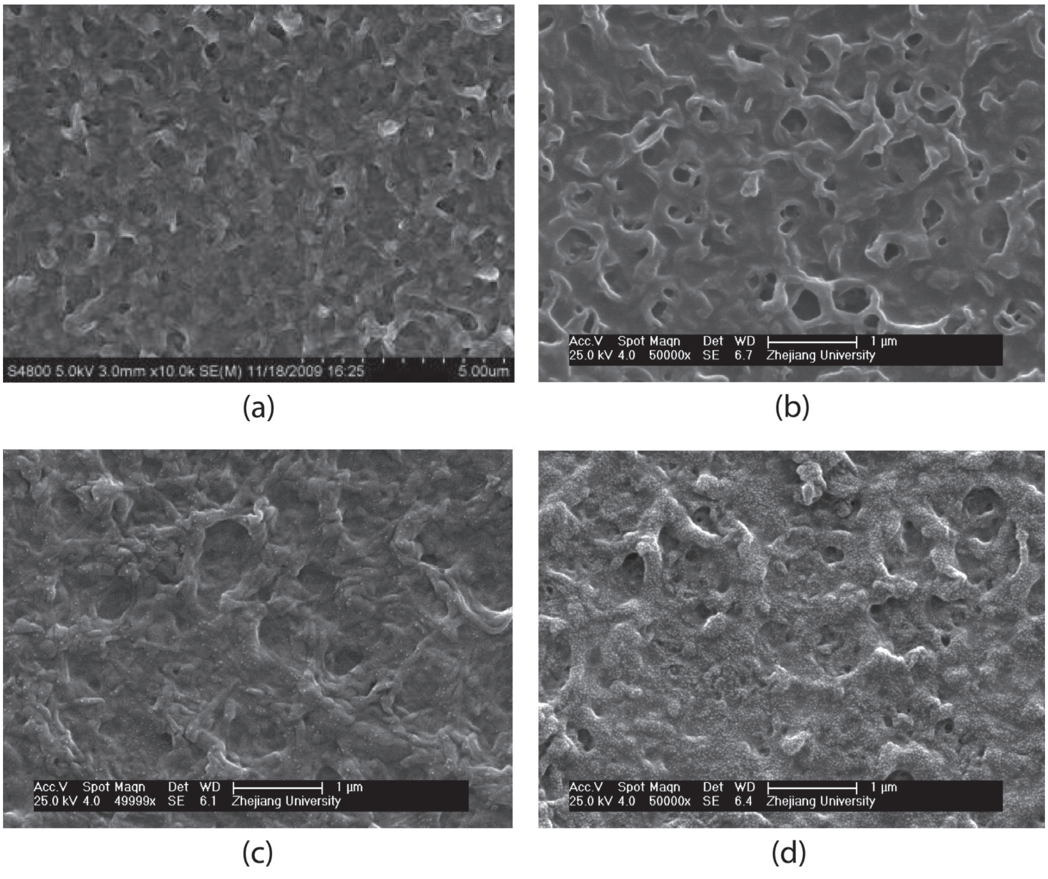


Fig. 6. SEM images of surface morphology of MWNT-polyamide membranes. MWNTs loadings are (a) 0.0%, (b) 0.005%, (c) 0.05%, and (d) 0.1% (w/v).

of MWNTs-polyamide membranes with 0.05 and 0.10 % (w/v) MWNTs content display short-strip surface morphology. Those differences of MWNTs-polyamide composite surface morphologies may be related to the modified MWNTs with hydrophilic functional groups, which result in the nodular structure and rough surface formed on the polyamide membrane [13].

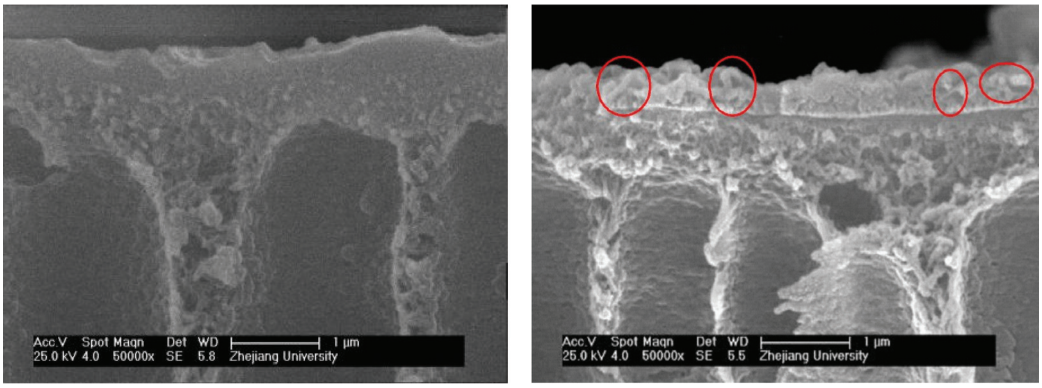
SEM images of cross-section morphology are presented for pure polyamide membranes in Fig. 7(a) and for MWNT-polyamide membranes in Fig. 7(b). From the cross-section images, it can be seen that the polyamide thin film layer of bare polyamide membrane was approximately homogeneous. While for the MWNT-polyamide membranes, it indicates that most MWNTs are entirely incorporated into the polyamide layer.

Transmission electron microscope images are presented for bare polyamide membranes and MWNT-polyamide membranes as shown in Fig. 8. Compared with homogeneous thin film of bare polyamide membrane, the MWNTs nanoparticles in MWNT-polyamide membrane appear considerably darker than the polymer and are clearly strip-sharped located in the thin film as well as at the interface.

Measured values of MWNT-polyamide membrane water contact angle are plotted in Fig. 9. It is found that as MWNTs loading increases, the contact angle decreases from about 70° for the bare polyamide to about 25° for the MWNT-polyamide membrane with the highest MWNTs of 0.2%, showing that the MWNT-polyamide membranes become much more hydrophilic. Therefore, the decease of contact angle is attributed to, on one hand, incorporating acidified MWNTs with hydrophilic groups such as -COOH and -OH; on the other hand, the increase of surface roughness.

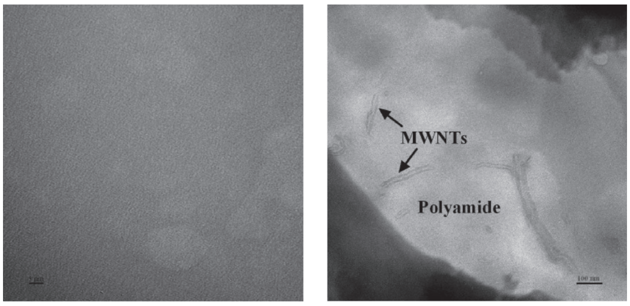
3.3. Separation Performance of MWNT-Polyamide Membrane

Fig. 10 shows the effect of acidified MWNTs loading on the pure water flux and rejection of resulting MWNT-polyamide membranes. With the increase of MWNTs content, the water permeation of MWNT-polyamide membranes are improved dramatically. For 2000 ppm NaCl, the pure water permeability increases from 261/m^{2}h without MWNTs to 71 l/m^{2}h by using the acidified MWNTs loading of 0.1% (w/v), while the NaCl solute



(a) (b)

Fig. 7. SEM images of cross-section morphology of MWNT-polyamide membranes. MWNTs loadings are (a) 0.0%, (b) 0.05% (w/v).



(a) (b)

Fig. 8. Characterization of hand-cast thin film properties by TEM for bare polyamide membrane (a) and MWNT-polyamide membrane (b).

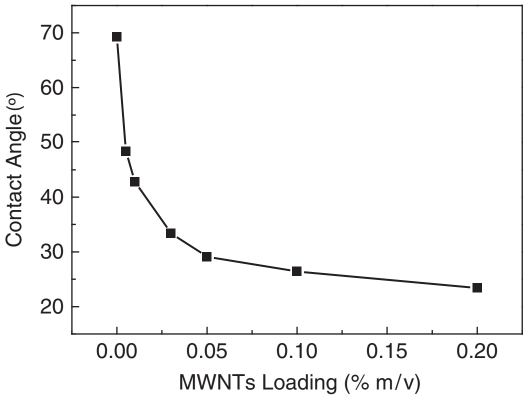


Fig. 9. Contact angle of MWNT-polyamide membranes.

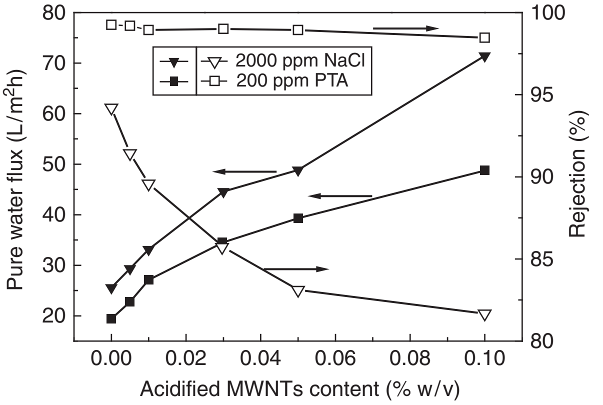


Fig. 10. Effect of acidified MWNTs loading on separation performance of MWNT-polyamide membranes. (25°C, 1.6 MPa)

rejections of hand-cast membranes decrease significantly. However, PTA molecular weight is 166, and pKa1 = 3.54, pKa2 = 4.46 (25°C), and for 200 ppm PTA, the pure water permeability increases from 19 l/m^2h up to 49 l/m^2h, meanwhile, PTA rejection is still higher than 98%.

The above result demonstrates that (i) the MWNTs in the polyamide thin film play a role as hollow nanochannel for the fast transport of water as shown in Fig. 2. The water transport route reduces because long MWNTs can penetrate across polyamide thin film along a certain direction, where water can enter into part of MWNTs instead of just passing through the high density polyamide film. (ii) The aggregation of MWNTs might lead to a formation of intact MWNTs network interconnected with other pores in membrane, resulting in the observed sharp increase of water flux for the polyamide composite membrane [5]. (iii) The hydrophilicity effect of acidified MWNTs with carboxyl group and hydroxy group might play an active role in water permeation through thin film nanocomposite membranes [14]. Nevertheless, there maybe some molecular-scale voids between MWNTs and polymer for MWNT-polyamide membrane compared with bare polyamide membrane [9], and thereby the hydrated salt ions, such as Na^+ of 0.72 nm, and Cl^- of 0.66 nm in diameter, are able to pass through some voids [8]. As a result, the NaCl rejection decreases substantially as shown in Fig. 10. In contrast, the MWNT-polyamide membranes prepared in this work show good rejection to PTA solutes, and there are no significant differences in PTA rejections as the MWNTs loading increases as also shown in Fig. 10, due to the relatively larger molecular size of PTA compared with that of the NaCl, and also because of electrostatic interaction between PTA and membrane surface.

4. Conclusions

Acidified MWNTs are synthesized from pristine MWNTs, and used successfully in the formation of MWNT-polyamide nanocomposite thin films by interfacial polymerization. The results show that modified MWNTs grafted some hydrophilic groups (such as -COOH and -OH), and thereby has better dispersion in the aqueous solution. Compared with the bare polyamide membrane, the MWNT-polyamide membrane has rougher and more hydrophilic surface. The water flux of MWNT-polyamide membranes is found dramatically improved, which might be owing to the preferentially flow of water molecules through the MWNTs, meanwhile, the NaCl rejection decreases obviously, but PTA rejection is still higher than 98%. This MWNT-polyamide thin film nanocomposite reverse osmosis membrane will have a potential application in separation of organic aqueous solution.

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