Modification of ultrafiltration membranes with carbon nanotube buckypaper for fouling alleviation

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Abstract. The modification of ultrafiltration membranes with carbon nanotube (CNT) buckypaper on fouling control was investigated. Two types of commercially available flat-sheet membranes were used: PS35 and PES900C/D (PES) (the PS35 membranes were hydrophilic with a molecular weight cutoff of 20 kDa, and the PES membranes were hydrophobic with a molecular weight cutoff of 20 kDa). The CNT buckypaper modified ultrafiltration membranes were prepared by filtering a CNT suspension through the flat-sheet membrane in a dead-end ultrafiltration unit. After modification, the pure water flux of PES was significantly increased, while the pure water flux of PS35 was decreased. The properties of the CNT modified membranes were also investigated. Considering the antifouling properties, pure water flux of the modified membrane, and the stability of CNT buckypaper layer on the membrane surface, ethanol solution with a concentration of 50 wt.%, multi-walled carbon nanotubes (MWCNTs) with a larger diameter (30-50 nm), and the CNT loading with $7.5 g/m^2$ was selected. The CNT buckypaper on the surface of ultrafiltration membranes can trap the pollutants in sewage effluent and prevent them reaching the surface of virgin membranes. Water quality analysis showed that the effluent quality of the modified membrane was obviously improved. The removal efficiency of humic acid and protein-like matters by the modified membrane was significant. These results indicate the potential application of the CNT buckypaper layer modified membranes in the field of wastewater reclaim.

Keywords: carbon nanotube; ultrafiltration membrane; membrane fouling; membrane modification; wastewater treatment

1. Introduction

With the rapid growth of population, development of economy and climate change, the problem of water resources is more and more serious (Vorosmarty *et al*. 2000). Low-pressure membrane filtration has been regarded as a promising technology for water treatment in the 21st century (Huang *et al*. 2007). With the decreasing cost of the ultrafiltration membrane, UF technology is gradually accepted by the developing countries compared to other low-pressure membrane technologies, and is expected to be more widely applied due to the more stringent water environment (Gao *et al*. 2011). The membrane fouling is still the most limiting factor for wider application of ultrafiltration (Gao *et al*. 2011). Pre-filtration, coagulation and anion exchange resin

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were investigated as pre-treatments for reducing fouling of ultrafiltration; but the effect was limited (Fan *et al*. 2008). Chemical cleaning efficiency of membrane for filtration of surface water (Ang *et al*. 2006, Liang *et al*. 2008, Yamamura *et al*. 2007) has been studied, but the cleaning effectiveness was highly dependent on the feed water qualities (Tian *et al*. 2010).

Therefore, membrane surface modification technologies to alleviate membrane fouling have been widely studied, such as: coating (Ulbricht and Belfort 1995, Kim *et al*. 1988), blending (Wang *et al*. 2006, Park *et al*. 2006, Leo *et al*. 2012), composite (Zhao *et al*. 2003) and grafting (Zhou *et al*. 2014, Meng *et al*. 2014, Cheng *et al*. 2013). CNTs owing to the several merits: strong antimicrobial activity, higher water flux than other porous materials of comparable size, tunable pore size and surface chemistry, and electrical conductivity, are widely used as additives for anti-fouling membranes (Liu *et al*. 2013). Most researchers focused on the use of CNTs blended with polymer matrix to prepare membranes via the phase inversion method to improve permeability and antifouling properties (Vatanpour *et al*. 2011, Celik *et al*. 2011a/b, Rahimpour *et al*. 2012, Yin *et al*. 2013, Majeed *et al*. 2012). But this method limits the active role of CNTs at the membrane/water interface because they are impregnated in the membrane polymer matrix (Ajmani *et al*. 2012). The research by Ajmani *et al*. (2012) revealed that PVDF membrane with a pore size of 0.45 μm modified with large diameter CNT layer exhibited high antifouling properties (Rahaman *et al*. 2012). The study by Gallagher *et al*. (2013) showed that the hollow fiber membranes modified by CNT mats exhibited improved fouling resistance which was sustained through multiple backwashing cycles. However, ultrafiltration membrane with small pore size loaded with CNT layer was seldom studied, and its antifouling needs further evaluation.

Buckypaper, similar with CNT layer, is a self-supported mat of entangled CNTs and could be used in water purification (Yang *et al*. 2013). In this paper, CNT buckypaper was loaded on the surface of ultrafiltration membranes. The antifouling properties and permeates of the modified ultrafiltration membranes were further investigated. Besides, factors influencing the properties of the modified membranes were systematically evaluated. Some issues that should be concerned were described and the further researches were summarized.

2. Materials and methods

2.1 Materials

Two types of commercially available flat-sheet membranes (PS35 and PES) were purchased from Sepro Corporation, USA. The PS35 membranes were hydrophilic with a molecular weight cutoff of 20 kDa and the normalized water flux was 1600 (L/m^{2}hbar), the PES membranes were hydrophobic with a molecular weight cutoff of 20 kDa and the normalized water flux was 1200 (L/m^{2}hbar), according to the manufacturer.

Multi-walled carbon nanotubes with three diameters (< 8 nm: length 0f 5-20 μm, 10-20 nm: length 0f 5-30 μm, 30-50 nm: length 0f 5-20 μm) were obtained from Beijing Nachen Tech Co. Ltd. China. According to the manufacturer, the purity of the received MWCNTs is 95%.

2.2 Water samples

For the fouling resistance tests, actual sewage effluent was selected. The sewage effluent was taken from a pilot-scale sequence batch reactor (SBR) reactor. The sewage effluent was

pre-filtered with 0.45 μm micro-membrane and then stored in the dark at 4°C as the feed water. Before testing, the feed water was warmed to about 20°C. Each group of experiments was conducted with the same batch of feed water. Deionized (DI) water was used to measure the clean membrane flux and clean the fouled membrane.

2.3 Membrane modification

Prior to modification, the virgin membranes were cleaned by filtering the DI water and the pure water flux was measured under N2 with a pressure of 0.1 MPa. The CNT was suspended in 50mL ethanol solution. The suspension was dispersed by sonication for 10min and immediately filtered through the flat-sheet membrane under N2 with a pressure of 0.1 MPa in the dead-end ultrafiltration unit. Then a layer of CNT buckypaper was loaded on the virgin membrane. Immediately, 50 mL DI water was filtered through the membrane immediately to stabilize the CNT buckypaper layer on the membrane surface. After modification, this membrane was washed cleanly by washing bottle and the pure water flux was measured. The modified membrane of PES was abbreviated to CNT-PES and the modified membrane of PS35 was abbreviated to CNT-PS35.

2.4 Membrane filtration experiments

Membrane filtration experiments were performed in a 50mL stirring cell (Amicon 8050, Milli-pore, USA) with an effective filtration area of 13.4 cm^2 and operated in dead-end filtration mode. The membrane was placed at the bottom of the cell. The feed water was driven by N$_2$ at a pressure of 0.1 MPa. In each filtration experiment, the filtration volume was 200 mL. Permeate was collected by glassware on an electronic balance which was connected to a computer. The weighing date was automatically recorded every 30 seconds by the computer. Prior to filtering feed water, the pure water flux of the membrane was measured and named as J_0. The permeation flux was calculated as Eq. (1).

$$ \tag{1} $$

Where J was the permeation of the membrane for feed water (Lm^{-2}min^{-1}), Q was volume of permeate feed water, A was the effective filtration area (m^2) and T was the permeation time (min).

2.5 Water quality analysis

DOC was measured with a TOC analyzer (Elemetar, Germany). The UVA analysis was performed with a UV-3900PC spectrophotometer (Hitachi, Japan) at a wavelength of 254 nm using a 1 cm quartz cell. Fluorescence Excitation-Emission Matrix Spectroscopy (EEM) was measured using a Fluorescence Spectrophotometer (F-7000, Hitachi, Japan). Emission spectra were scanned from 300 to 550 nm at 1 nm increments and excitation spectra was scanned from 200 to 400 nm at 5 nm increments.

2.6 SEM analysis

Surface and cross-sectional images of the modified membranes were analyzed with a scanning electron microscope (SEM) (S-4300, Hitachi, Japan) at 15 keV. All specimens were dried for 24 h at 60°C before test. Cross-sections were obtained by fracturing the membranes in the presence of liquid nitrogen and then coated with a thin layer of gold to prevent charging during SEM.

3. Results and disscusion

3.1 Effect of ethanol concentration on membrane fouling

The ethanol concentration had an important impact on the dispersing of CNT and its loading effect. Effect of ethanol solution with different concentration on dispersing CNT was tested for investigating its influence on the modified membranes' properties. The ethanol concentration (wt.%) used were: 10%, 50% and 100%, and the CNT diameter was 30-50 nm with a common loading of 10 mg. Fig. 1(a) shows the effects of ethanol concentration on pure water flux of CNT-PES membrane. It could be found that the pure water flux of CNT-PES membrane was increased as the concentration of the ethanol solution increased from 10% to 50%. However, with the concentration further increased from 50% to 100%, the pure water flux of CNT-PES membrane was not increased significantly. In contrast to it, the pure water flux of the CNT-PS35 membrane was obviously decreased after its modification, as shown in Fig. 1(b). The flux was decreased by almost 35%, when the concentration of ethanol solution reached 50%. It can be speculated that the pure water flux of the CNT buckypaper was higher than the virgin PES membrane. The CNT was dispersed in the ethanol solution and adsorbed ethanol molecules, which might improve the hydrophilicity of PES original membrane after modification. On the other hand, the swelling effect of ethanol on PES membrane may also improve the flux. As a result, the flux of CNT-PES increased. Nevertheless, the original PS35 were hydrophilic, which has a high pure water flux, the CNT buckypaper could not increase the pure water flux but as a cake layer to decrease the virgin membrane's permeability.

The effect of ethanol concentration on fouling control was also studied. As shown in Fig. 2, all the modified membranes presented high antifouling performance, especially for CNT-PS35. Relatively, the influence of ethanol concentration on fouling control of CNT-PES was more obvious. With the decrease of ethanol concentration, the antifouling efficiency of both the CNT-
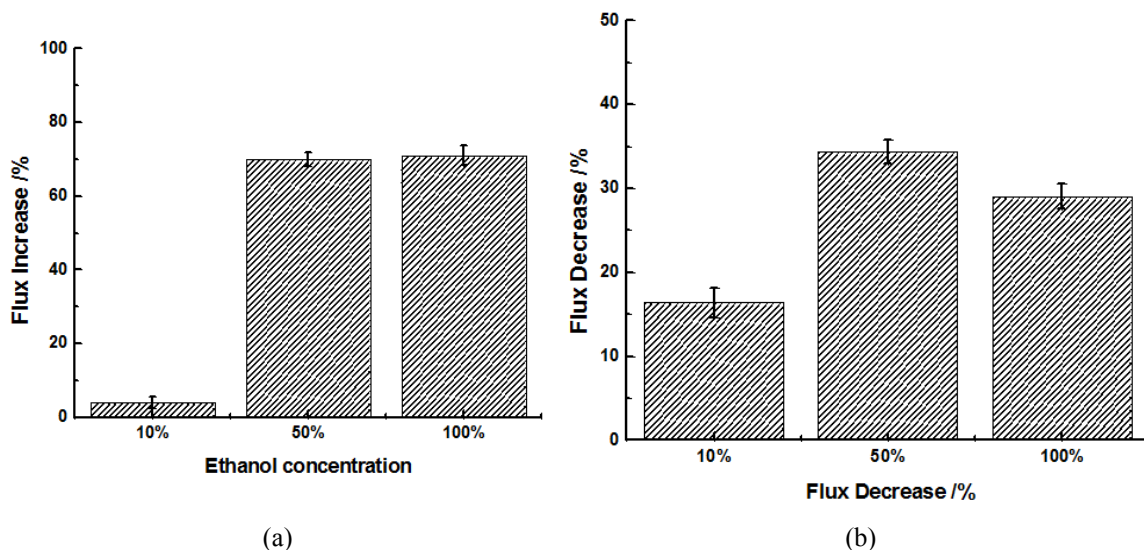

(a)   (b)

Fig. 1 Effect of ethanol concentration on the pure water flux of the CNT modified membranes:
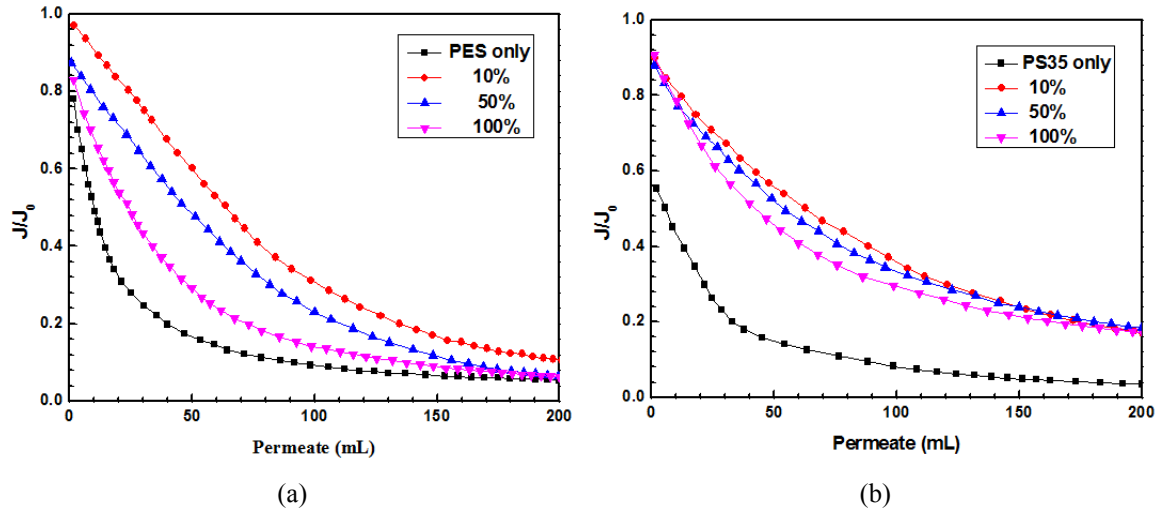(a) CNT-PES; (b) CNT-PS35

(a)   (b)

Fig. 2 Effect of ethanol concentration on fouling control: (a) CNT-PES; (b) CNT-PS35

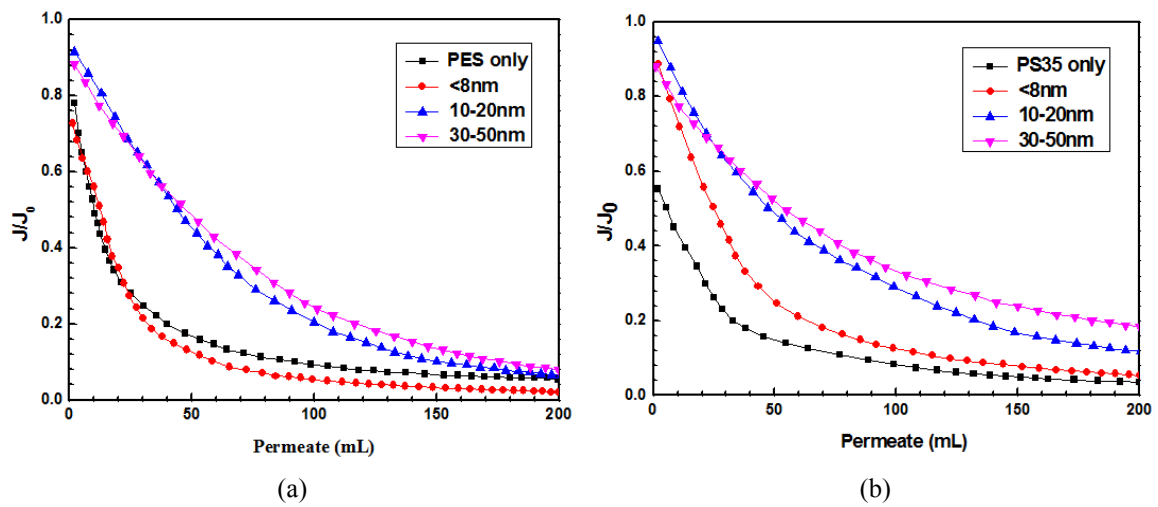(a)   (b)

Fig. 3 Effect of CNT diameter on fouling control: (a) CNT-PES; (b) CNT-PS35

PES and CNT-PS improved. However, low concentration of ethanol solution could not guarantee the stability of CNT buckypaper layer on the membrane surface. It was found that CNT buckypaper could be washed away in the backing step with ethanol concentration of 10%, even with a higher value of 30%. As reported by Ajmani *et al.* (2012), CNTs dispersed in ultrapure water (0%) modified on membrane surface was easy to washed away. Because the high concentration of ethanol solution could improve the dispersion of the CNTs, leading to reduction of CNT agglomerates, which can enhance the uniformity and stability of the CNT buckypaper layer on membrane surface. Considering the impact of ethanol concentration on modified membrane (including the flux, antifouling performance and stability), the ethanol concentration of

50% was selected.

3.2 Effect of CNT diameter on membrane fouling

To investigate the impact of CNT diameter on the properties of the modified membranes, pristine MWCNTs with three diameters (< 8, 10-20, and 30-50 nm) were tested. The CNT was dispersed in ethanol solution with a concentration of 50%, and the loading was 10 mg. Fig. 3 shows that all CNTs presented antifouling performance except for the smallest diameter (< 8 nm). The CNT with larger diameter (30-50 nm) performed better antifouling property. It was speculated that the larger diameter CNT formed a uniform CNT buckypaper layer on the membrane surface, which could effectively trap the pollutants and prevent them reaching the virgin membrane surface to cause fouling.

To evaluate the stability of the CNT buckypaper on the membrane surface, the surface images of the modified membranes were observed. As the surface images of CNT-PS35 and CNT-PES were similar, only CNT-PES was taken as example. As shown in Fig. 4, it revealed that the CNT buckypaper formed by the smaller diameter CNT (< 8 nm) showed the lowest stability and could be easily washed away in the backwashing step (Figs. 4(b1) and (b2)), while the CNT buckypaper formed with the diameter of 30-50 nm presented good stability on the membrane surface and could bear backwashing and hydraulic washing in all directions using wash bottle (Figs. 4(a1) and (a2)). It was speculated that the small diameter CNT can easily agglomerate together to form larger clusters and loosely loaded on the membrane surface. Overall, the CNT buckypaper formed by the large diameter (30-50 nm) CNT was the most effective on fouling alleviation and had a higher stability.

3.3 Effect of CNT loading on membrane properties

The effect of CNT loading on membrane permeability and fouling control was studied. In this test, the 30-50 nm diameter CNT was selected and dispersed in ethanol solution with a concentration of 50%. The CNT loadings chosen were: 5, 10, 20 and 30 mg. The relationship between the CNT loading and the pure water flux of the modified membrane was obvious. As shown in Fig. 5, the pure water flux of both the CNT-PES and CNT-PS35 membrane were almost linearly declined as the CNT loading multiply increased. This may due to the enhancement of
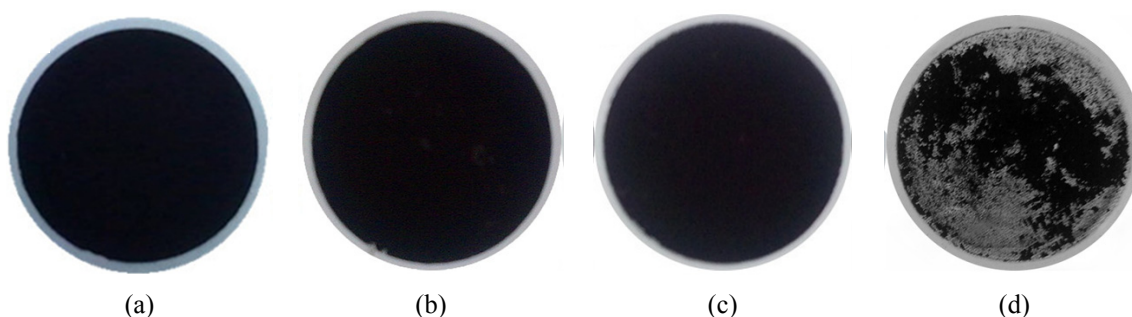

| (a) | (b) | (c) | (d) |

Fig. 4 Images of PES membranes modified with different diameters CNT buckypaper before and after backwashing: (a1) before backwashing 30-50nm, (a2) after backwashing 30-50nm, (b1) before backwashing <8nm, (b2) after backwashing <8nm
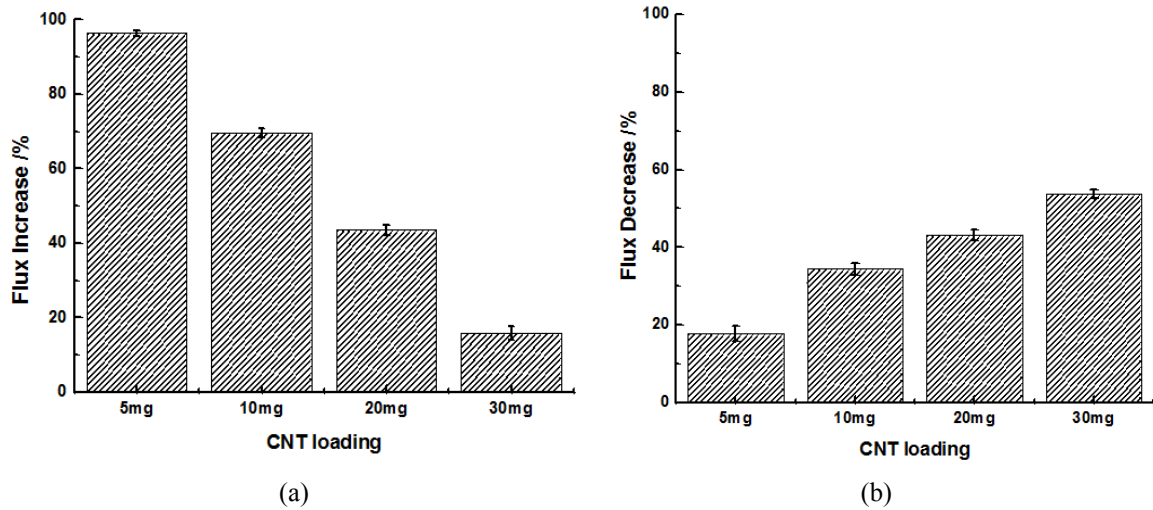
Fig. 5 Effect of CNT loading on pure water flux: (a) CNT-PES; (b) CNT-PS35

the cake layer pollution on the membrane surface, which caused by the increase of the CNT buckypaper' thickness. However, as for the CNT-PES, with the CNT loading increased to 30 mg (about 22.5 g/m^2), the pure water flux was also increased by almost 15% compared with the original membrane. As shown in Fig. 6 the antifouling ability of the modified membrane was obviously enhanced as the CNT loading increased. The retention of the pollutants was enhanced with the increasing of the adsorption capacity of the CNT buckypaper. Considering the economic factors and the volume of water sample, in this research, the loading amount of 10 mg (7.5 g/m^2) was chose.
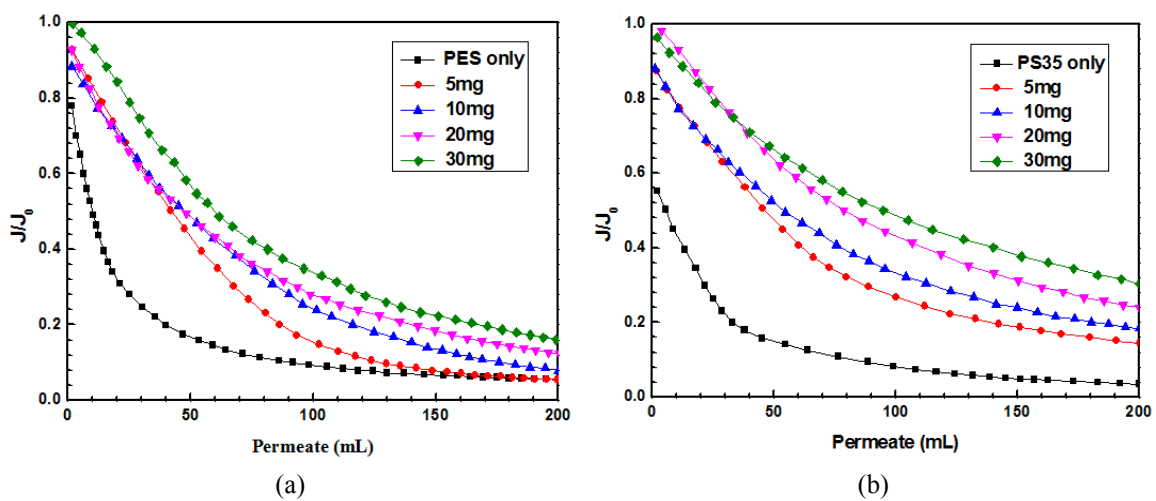

Fig. 6 Effect of CNT loading on fouling control: (a) CNT-PES; (b) CNT-PS35

3.4 SEM imaging of CNT modified membrane

The surface images of the membrane modified with 30-50 nm CNT buckypaper and < 8 nm CNT buckypaper were further investigated with SEM. The SEM images of the CNT modified membranes were shown in Fig. 7. Only CNT-PES was taken as example. Obviously, the CNT buckypaper constructed with 30-50 nm diameter CNT formed a uniform layer on membrane surface (Figs. 7(a) and (b)). The diameter < 8 nm CNT showed a very serious agglomeration phenomenon, which formed a compact buckypaper layer on membrane surface (Figs. 7(c) and (d)). The dense buckypaper layer is easier to cause cake fouling by larger molecule pollutants and lead to rapid decrease flux. Therefore, the membrane modified with the 30-50 nm CNT was more effective on fouling alleviation (Fig. 3).

To better understand the interactions between the CNT buckypaper and the PES base membrane, the cross-section images of the membranes modified with CNT diameter of 30-50 nm and < 8 nm were further analyzed with SEM. It could be found that the 30-50 nm diameter
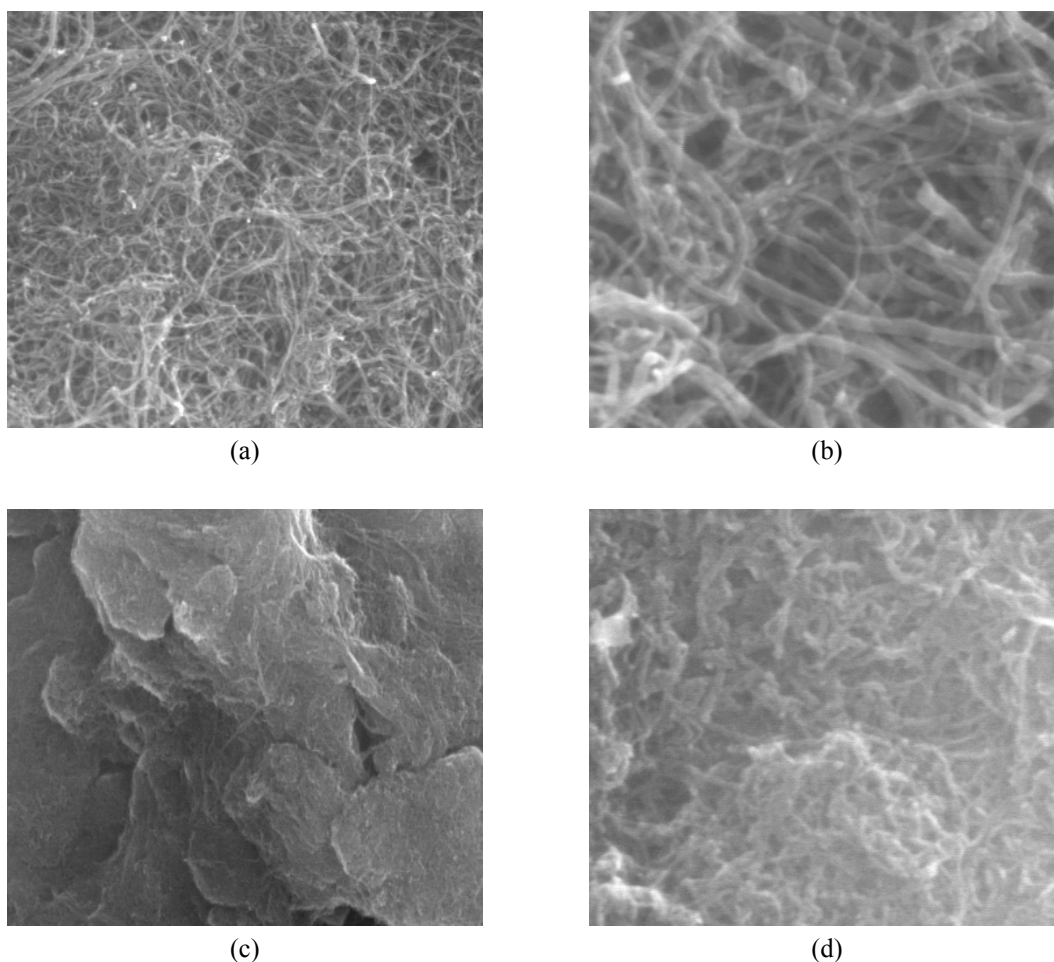

(a)   (b)

(c)   (d)

Fig. 7 SEM images of CNT on PES: (a) 30-50 nm (10,000x); (b) 30-50 nm (40,000x); (c) < 8 nm (10,000x); (d) < 8 nm (40,000x)
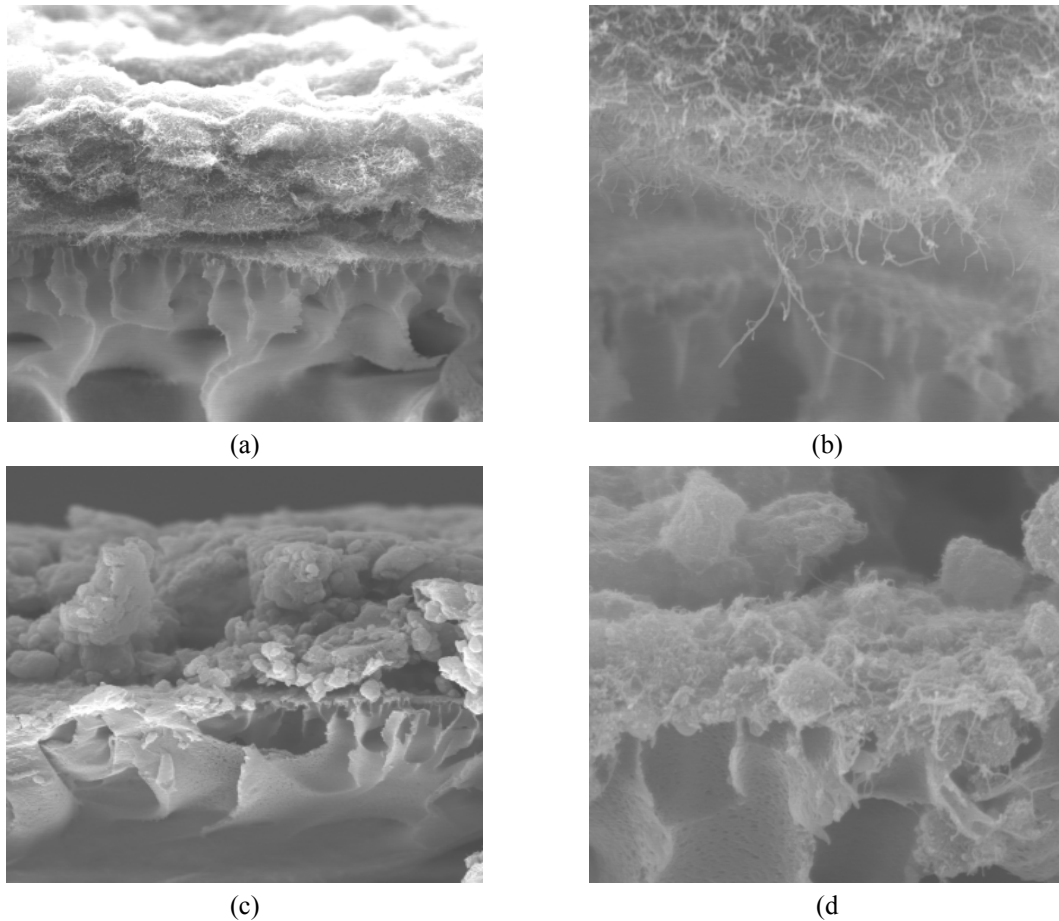
Fig. 8 Cross-sectional SEM images of CNT on PES: (a) 30-50 nm (1,000x); (b) 30-50 nm (10,000x); (c) < 8 nm (1,000x); (d) < 8 nm (10,000x)

CNT buckypaper is very neatly and compactly spread on the membrane surface (Figs. 8(a) and (b)). The CNT buckypaper seems to be binding on the membrane surface. While the < 8 nm diameter CNT shows serious agglomeration phenomenon and massively loaded on the membrane surface (Figs. 8(c) and (d)). It seems to be loosely and can easily fall off from the membrane surface. These findings support the former suspicion that the buckypaper formed by the small diameter CNT can easily agglomerate together to form larger clusters and this agglomeration phenomenon seriously influenced the stability of buckypaper on the membrane surface.

3.5 Water quality of CNT modified membrane

CNTs have the potential to serve as superior adsorbents for removal of both organic and inorganic contaminants from water systems (Liu *et al*. 2013). In this test, the removal efficiency of organic matter by the modified membrane was investigated. The 30-50 nm diameter CNT was chosen and dispersed in 50% ethanol solution to prepare CNT-PES and CNT-PS35 with a loading of 10 mg. During each filtration test, permeate from the beginning to the end of filtration was

Table 1 The DOC and UV_{254} of the feed water and the permeate

Water samples	Feed water	PES		CNT-PES		PS35		CNT-PS35	
		Value	Rejection (%)	Value	Rejection (%)	Value	Rejection (%)	Value	Rejection (%)
DOC (mgC/L)	8.507	7.058	17.03	6.767	20.45	7.751	8.89	7.297	14.22
UV_{254}	0.24	0.227	5.42	0.185	22.91	0.227	5.41	0.207	12.75

collected and analyzed. DOC and UV_{254} of the feed water and permeate of the CNT modified membrane was shown in Table 1. It could be found that the modified membrane was more effective on the removal of organic matter in sewage effluent. After modification, the removal efficiency of DOC by PES was just increased from 17.03% to 20.45%, while the rejection of UV_{254} was increased from 5.42% to 22.91%. Comparing the removal efficiency of the DOC with UV_{254} by the modified membranes, the CNT buckypaper was more effective at trapping the larger sized organic matter which contains unsaturated double bond responsible for UV_{254}.

The fluorescence EEM spectra of permeate from different membranes are shown in Fig. 9. Peak C is related to humic acid-like organics and Peak T corresponds to protein fluorescence for which soluble microbial by-product-like is an important component (Chen *et al.* 2003). It could be found that after modification, the intensity of peak T and peak C dramatically decreased, especially for the CNT-PS35 (Figs. 9(c1) and (c2)). The PES original membrane was very efficient on removal of humic acid-like and protein-like matters (Fig. 9(b1)), but after modification, the intensity of peak T and peak C was also decreased. These results suggested that the modified membranes were more efficient on removal of humic acid-like organics and protein-like matters compared with the original membranes. As previously reported that the CNT buckypaper exhibited excellent removal of HA (Yang *et al.* 2013), and the BSA adsorption on C/P composite membranes was high than the PES bare membrane (Celik *et al.* 2011a/b). Therefore, after the membrane was modified, the removal efficiency of humic acid and protein-like matters was significantly improved, especially for the PS35 membrane. The biopolymers (polysaccharides and proteins) and humic acid-like organics are the main pollutants caused membrane fouling during ultrafiltration (Kim and Dempsey 2013, Haberkamp *et al.* 2008). Thus the CNT buckypaper on the membrane surface could effectively alleviate the membrane fouling by preventing those large molecules from reaching the virgin membrane surface to cause cake layer pollution. And this result was consistent with the result in Table 1.

The CNT buckypaper has a strong adsorption of pollutants. Simple washing methods cannot recover the flux of the modified membrane effectively. Once the adsorption capacity of CNT buckypaper tends to saturation or the CNT buckypaper is seriously polluted by the cake layer pollution, the antifouling property of the modified membrane will become worse. It means that the recycle times of the modified membrane are seriously limited by the CNT buckypaper. Actually, we have tried three cycle times test, the results showed that the modified membrane can effectively alleviate the membrane fouling in the first two cycles; but in the third cycle, the modified membrane did not show superiority of fouling control compared with the original membrane. Nevertheless, our recent study showed that some pretreatment methods (such as ozonation), on feed water could effectively improve the recovery rate of the flux for the modified membrane; but the mechanism was under investigation.
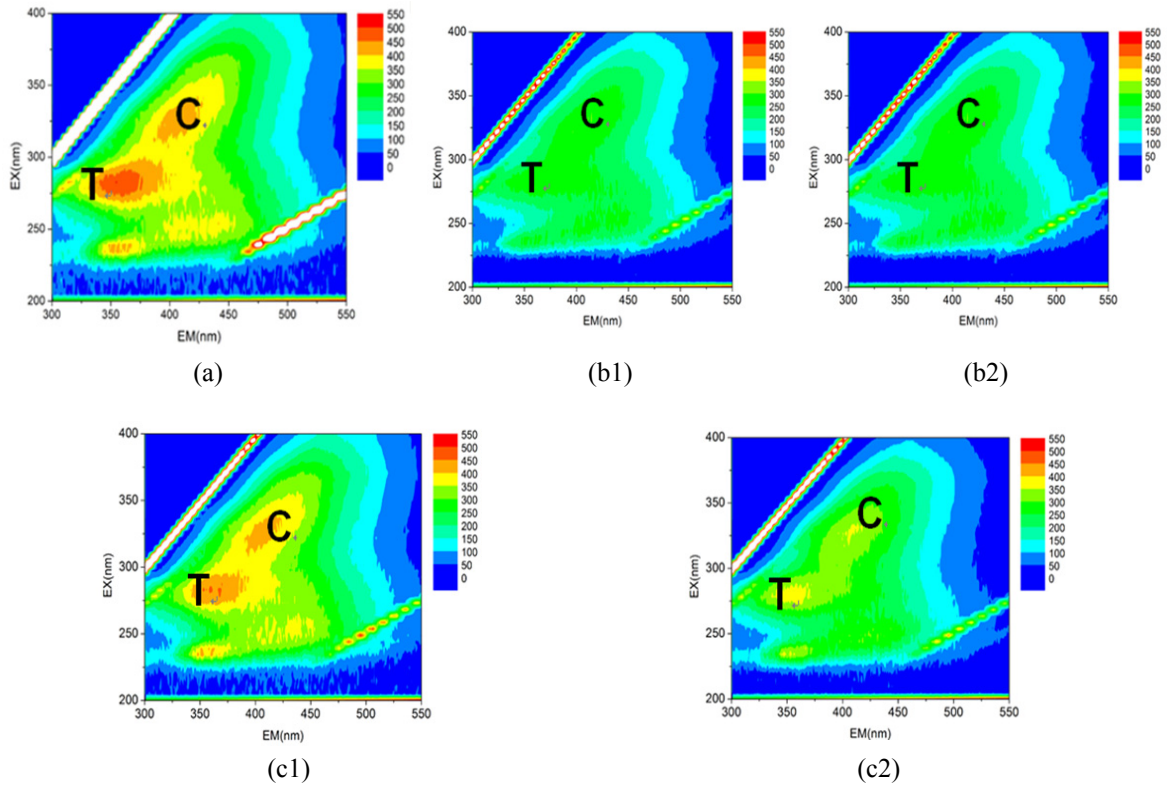
Fig. 9 Fluorescence EEM spectra of permeate from different membranes: (a) feed water; (b1) PES; (b2) CNT-PES; (c1) PS35; (c2) CNT-PS35

Our future research will continue to study the antifouling mechanism of the modified membrane to search the method that can effectively improve the backwash efficiency, and explore the removal efficiency of some specific aquatic contaminants by the modified membrane.

4. Conclusions

The flat-sheet ultrafiltration membranes modified with CNT buckypaper were prepared by filtering a CNT suspension through the membranes in a dead-end ultrafiltration unit. The CNTs were dispersed in ethanol solution without any surfactant added. The antifouling property of the modified membrane was investigated by filtering actual sewage effluent. The following conclusions can be drawn:

(1) The concentration of ethanol for dispersing CNT, the CNT diameter, and the CNT loading were three important factors affecting the properties of the CNT modified membrane.

(2) Considering the antifouling properties, pure water flux of the modified membranes and the stability of CNT buckypaper layer on the membrane surface, the ethanol solution with a concentration of 50% was optimal. The pure water flux of modified membrane was almost linearly declined as the CNT loading multiply increased. While the antifouling ability was

greatly improved as the CNT loading increased.

(3) The buckypaper layer formed by large diameter (30-50 nm) CNT was more efficient on fouling control and showed better stability after backwashing. The SEM imaging showed that the buckypaper layer formed by large diameter CNT displayed a homogeneous porous structure.

(4) The effluent quality of the modified membrane was obviously improved. The removal efficiency of humic acid-like and protein-like organics by the modified membrane was significant.

Acknowledgments

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