Effective natural organic matter removal in pond water by carbon nanotube membrane with flocculation/adsorption

Jieun Lee, Saravanamuth Vigneswaran, Yongshun Zhang, Ramireddy S. P. Raj Reddy and Zongwen Liu

ABSTRACT

A carbon nanotube (CNT) ultrafiltration (UF) membrane was applied to natural organic matter (NOM) removal in pond water treatment. The source water was pretreated by flocculation and/or adsorption prior to the UF process to alleviate permeate flux decline and improve NOM removal efficiency. The performance of a commercial polyethersulfone (PES) UF membrane was compared to evaluate that of the CNT membrane. The CNT membrane outperformed the PES-UF membrane. The permeate flux, total organic carbon and humic acid (HA) removal rate of the CNT membrane was observed to be 230 LMH/bar, 60%, and 80% when 30 mg/L poly aluminium chloride (PACl) flocculation was applied. This highlights that the permeate flux was three times higher with slightly higher rejection efficiency than the PES-UF membrane. In particular, severe permeate flux decline was completely overcome by the CNT membrane with 30 mg/L PACl coagulation. For powder activated carbon (PAC) adsorption, even though there was a severe permeate flux decline in the CNT membrane, almost complete HA removal (98%) was achieved when 0.5 g/L PAC adsorption was coupled. Based on the superior performance of the CNT membrane with pretreatment, the CNT membrane is suggested to be a robust system for a high concentration of organic matter pond water treatment without membrane flux decline.

Key words | adsorption, carbon nanotube membrane, flocculation, membrane hybrid system, natural organic matter removal, ultrafiltration membrane

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ABBREVIATIONS

MWCNT membrane	Multi-walled carbon nanotube membrane
NOM	Natural organic matter
PES	Polyethersulfone
UF	Ultrafiltration

INTRODUCTION

Natural organic matter (NOM) contained in surface water is required to be removed from drinking water for the following reasons: it generates colour, taste and odour issues and forms complexes by reacting with metals and hydrophobic organic chemicals. When it reacts with chlorine residual, it generates disinfection by-products (Joseph *et al.* 2012) and promotes bacterial regrowth in the distribution system (Jacangelo *et al.* 1995).

Processes such as coagulation, flocculation, adsorption, and membrane filtration have been adopted for NOM removal. Of those, the ultrafiltration (UF) membrane system is widely used for drinking water treatment due to its superior separation performance – improving turbidity and dissolved organic carbon (DOC) removal (Blankert *et al.* 2007). However, larger particulates in feed water than the membrane pore size often results in severe flux decline by membrane fouling. Further, NOM adsorption on the surface of and inside the membrane often results in irreversible membrane fouling and performance decline due to its comparable size to the

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membrane pore (Kennedy *et al.* 2005). In order to alleviate these problems, pretreatment such as flocculation and adsorption are used for the purpose of enhancing the permeate flux by reducing membrane fouling (Jung *et al.* 2006; Qiao *et al.* 2008). Poly aluminium chloride (PACI) is a commonly used coagulant in surface water treatment due to its high efficiency in NOM removal (Kabsch-Korbutowicz 2006). Its removal process is the sequence of charge neutralization, adsorption, and bridging or sweep flocculation (Duan & Gregory 2003). PACI is less temperature- and pH-dependent than other aluminium salts. In addition to flocculation by PACI, adsorbents have also been exploited for NOM removal prior to the UF membrane system. An adsorbent such as powder activated carbon (PAC) removes organic matter with its affinity by covalent bonding (Tomaszewska & Mozia 2002; Duan *et al.* 2003). However, a high dosage of coagulants/adsorbents generates a large volume of sludge, leading to a negative impact on the environment. Further, membrane fouling by organics still leads to a performance decline and frequent membrane cleaning even after coupling with a flocculation/adsorption system. The majority of current studies have been focused on the development of coagulant/adsorbent and its contribution to membrane fouling (Zhao *et al.* 2010; Cao *et al.* 2011; Zhao & Zhang 2011; Zhao *et al.* 2015). However, there has been little consideration of developing UF membrane material aiming to reduce sludge volume by decreasing the optimal dosage of adsorbent/flocculant. For the purpose of advancing the membrane process, the focus has been on nanomaterial incorporation into conventional polymer membranes (Lee *et al.* 2016a). For example, a nanomaterial composite membrane enhances separation performance by increasing adsorption capacity and delivering high permeate flux in comparison to conventional membranes (Yin & Deng 2015). Recently, we successfully fabricated a multi-walled carbon nanotube (MWCNT) composite membrane and verified its effective NOM removal and high permeate flux (Lee *et al.* 2016b). Such superior performance was attributed to the MWCNT/polyaniline (PANI) complex altering the physicochemical properties of the membrane.

This study aims to overcome the sludge disposal issue by reducing PACI dosage, contributing to the conservation of the environment. The MWCNT membrane flocculation/adsorption hybrid system was applied to pond water treatment. Flux decline behaviour and total organic carbon (TOC) and humic acid (HA) rejection efficiency were compared to that of the conventional polyethersulfone (PES) UF membrane.

MATERIALS AND METHODS

Materials

Water collected from a pond in Victoria Park, Sydney, was used as feed water. The feed water was filtered with 1.2 μm filter paper to remove any contaminant in the pond (rocks, leaves, etc.). MWCNT and PES-UF membranes were used. A commercial PES UF membrane (10 kDa, Stelitech) was used to evaluate the MWCNT membrane performance. Detailed information on the membranes is presented in Table 1. The flocculant was 23% PACI (Orica). This stock solution was diluted to prepare 10, 20 and 30 mg/L PACI solutions. For PAC adsorption, coal-based PAC (MDW3545CB, James Cumming & Sons PTY LTD) was used as an adsorbent. The detailed information is as follows: 19.7 μm as a mean diameter and 75.0 μm as a nominal size (80% min. finer).

Membrane preparation

The MWCNT membrane was fabricated in two steps: synthesis of 0.5 wt% MWCNT/50 wt% PANI complex by

Table 1 | Characteristics of the MWCNT membrane and PES-UF membrane

					Zeta potential (mV)		
Membranes	**UPW* permeability (LMH/bar)**	**Pore size by BET (nm)**	**MWCO** (kDa)**	**Contact angle (°)**	**pH 4.7**	**pH 7**	**pH 10.4**
MWCNTs	330	4.4–4.6	12	45.4 ± 0.1	17.12	10.9	−25
PES	86	–	10	57.6 ± 0.4	−20	−22	−39

*UPW = Ultrapure water.
**MWCO = Molecular weight cut-off.

in-situ polymerization and a fabrication of the MWCNT membrane by the phase inversion method (Lee *et al.* 2016b). A solution of 3 mM aniline monomer and 0.8 mM APS was prepared in 1 M HCl and 99.5% *N*-methyl-pyrrolidone (NMP). MWCNTs were dispersed in 99.5% NMP solution. Three substances (Aniline, APS and MWCNTs) were mixed for 48 h at 4 °C for chemical oxidation. In the second step, the MWCNT/PANI complex was blended with 15% PES polymer dissolved in NMP for 7 h. The casing solution was cast onto a glass plate with 300 μm gap height. The glass plate was immersed in deionized (DI) water at room temperature. All prepared membranes were stored in a DI water bath for 1 day in order to remove residual solvents.

Flocculation/adsorption optimization

Optimal flocculation dosage was determined by jar test. An amount of 500 mL of raw water was put in 1 L beakers, and PACI of 2.175, 4.345 and 6.520 mL was added in the beakers to prepare 10, 20 and 30 mg/L PACI concentrations, respectively. The raw water samples were first mixed vigorously at 120 rpm for 2 min to react for uniform mixing/dispersion, and mixed at a reduced speed of 20 rpm for 15 min to facilitate flocculation. After flocculation, samples were settled for 1 hour and the supernatant was taken, and filtered through a 0.45 μm syringe filter to remove flocs completely. For PAC adsorption, optimal adsorption dosage was also determined by jar test. 0.1–0.5 mg/L of PAC (based on feed water volume) was added to the pond water.

Performance evaluation

The UF membrane filtration test with water treated with flocculation/adsorption was carried out in dead-end filtration under 2 bar with 0.00146 m^2 of effective membrane area for 3 hours. The pressure was constantly applied in the filtration test using a compressed nitrogen gas cylinder. The permeate flux data were continuously recorded using an electronic balance connected to a computer. A schematic of UF coupled with flocculation/adsorption systems is shown in Figure 1. Rejection behaviour was determined by measuring DOC via TOC analyser (Shimadzu) and HA concentration via UV absorbance at $UV_{254\,nm}$ (UV spectrophotometer UV-2450, Shimadzu).

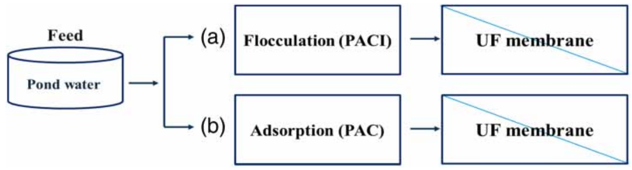

Figure 1 | Schematic of UF coupled with (a) flocculation (PACI) and (b) adsorption (PAC) systems.

RESULTS AND DISCUSSION

Comparison of membrane characteristics

The physico-chemical properties of the membrane significantly contribute to membrane performance. To evaluate different membrane performances under the same type of water filtration, a reliable approach to benchmark the system has been made (Yangali-Quintanilla *et al.* 2016). As suggested in the reference, the physico-chemical properties of the membranes were compared after careful membrane characterization. As shown in Table 1, the MWCO and pore size of the MWCNT membrane were measured to be 10 kDa and 4.4–4.6 nm. As explained above for membrane preparation, the MWCNT/PANI complex was blended with a PES casting solution, and then the MWCNT/PANI/PES composite UF membrane was fabricated. Thus, the commercial PES-UF membrane with the similar MWCO was selected. Due to the incorporation of the MWCNT/PANI complex into the PES matrix, the MWCNT membrane became more hydrophilic (45.4°) and its surface charge changed to be positive (10.4 mV at pH 7); in comparison the contact angle of the PES-UF membrane is 57.6°, and it is negatively charged (−22 mV) at pH 7 (Lee *et al.* 2016b). Such changes in the membrane characteristics greatly influenced the water permeability of the MWCNT membrane (PES matrix) as shown in Table 1 (330 LMH/bar).

Effect of flocculation/adsorption on organic matter removal

Table 2 shows the removal efficiency of pretreatments such as PACI flocculation and PAC adsorption on the pond water treatment. The TOC and UV absorbance at 254 nm wavelength were measured. After flocculation by PACI, TOC in pond water decreased by 37.6%. As the dosage of PACI increased to 30 mg/L, TOC removal increased to 45.4%.

Table 2 | Results of flocculation/adsorption

		Flocculation by PACl				Adsorption by PAC		
	Raw pond water	10 mg/L	20 mg/L	30 mg/L	Raw pond water	0.1 g/L	0.3 g/L	0.5 g/L
TOC (mg/L)	11.58	7.23	7.60	6.32	11.54	10.13	7.68	5.73
Removal rate (%)	–	**37.56**	**34.37**	**45.42**	–	**12.22**	**33.45**	**50.35**
$UV_{254\,nm}$ (cm^{-1})	8.56	3.87	3.75	3.43	10.47	4.32	2.58	1.66
Removal rate (%)	–	**54.79**	**56.19**	**59.93**		**58.74**	**75.36**	**84.15**

Meanwhile, slightly higher removal at $UV_{254\,nm}$ was observed. A proportion of 55.0% of HA in the feed water was removed by 10 mg/L PACl flocculation. It increased to 60% when PACl was increased to 30 mg/L.

As shown in Table 2, the TOC removal rate by PAC adsorption was around 50%, similar to that of PACl flocculation (45.4%). However, PAC adsorption was more effective at removing HA than TOC. As seen in Table 2, PAC adsorption exhibited a much enhanced HA removal efficiency, reaching 75–84% with increased dosage (0.3–0.5 g/L). This is mostly due to the fact that PAC adsorption has a much-enhanced removal efficiency for hydrophobic fractions such as HA (Shon *et al.* 2008).

UF membrane coupled with PACl flocculation system

Effect of the MWCNT membrane with PACl flocculation system on flux enhancement

The effect of flocculation prior to UF membrane filtration on the permeate flux was examined under dead-end filtration with the MWCNT membrane and commercial PES-UF membranes for 3 hours. Figure 2 shows the permeate flux pattern after flocculation of the MWCNT and PES membranes.

Overall, an enhanced permeate flux pattern was observed when the flocculation system was coupled with membrane filtration (both the membranes). In a raw pond membrane filtration test, the MWCNT membrane exhibited lowest permeate flux and severe flux decline. The permeate flux decreased nearly two-fold in the initial filtration period (30 min), indicating the need for pre-treatment such as the flocculation system. However, when flocculation with 10 mg/L PACl was carried out, the permeate flux increased from 50 LMH/bar to nearly 100 LMH/bar. There was, however, an enhancement in flux decline (1.5-fold) in the initial filtration period although the initial permeate flux was the same as the one without flocculation. When PACl dose was increased to 20 mg/L, initial permeate flux increased to almost 200 LMH/bar; PACl flocculation still did not overcome the permeate flux decline (1.3-fold). However, when PACl dose was increased up to 30 mg/L, four-fold higher permeate flux was achieved without any flux decline.

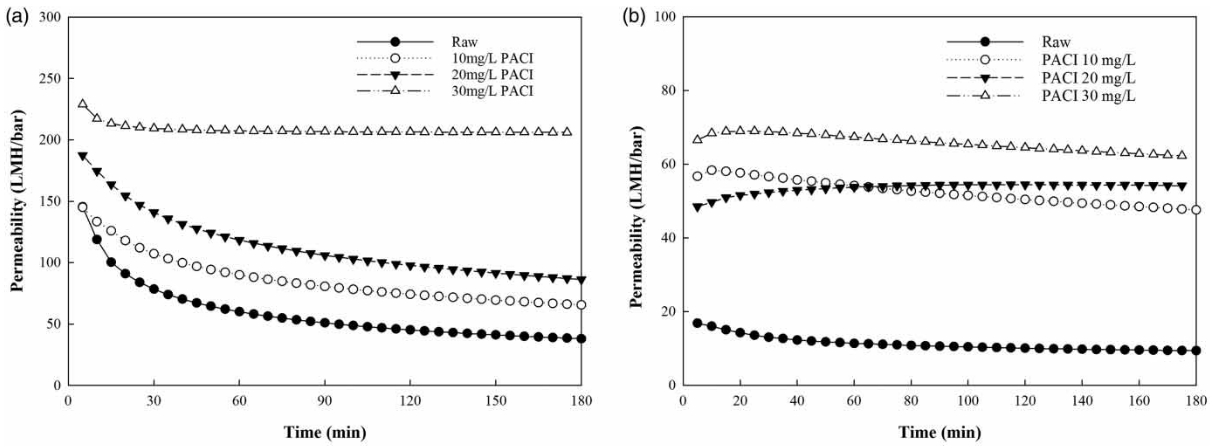

Figure 2 | Comparison of flux behaviour between (a) MWCNT membrane and (b) PES-UF membrane with PACl flocculation.

In comparison, PES-UF membrane filtration showed a different trend in permeate flux enhancement and its decline. Even though extremely low permeate flux (10 LMH/bar) was observed compared to the ultra-pure water permeate flux (86 LMH/bar) in raw pond water filtration, severe permeate flux decline did not occur in PES-UF membrane filtration. Compared with MWCNT membrane filtration, a higher ratio of permeate flux enhancement appeared when 10 mg/L PACI flocculation was applied. More than 2.5-fold flux enhancement occurred without any flux decline in the initial filtration period. With 20 mg/L PACI flocculation, initial permeate flux decreased slightly, but was nearly same as that with 10 mg/L PACI flocculation at the later stage. As 30 mg/L PACI was dosed, almost three-fold permeate flux (70 LMH/bar) was achieved without much flux decline at the initial stage. The effect of PACI flocculation on permeate flux enhancement was considerably high, but the difference in PACI dosage was minimal, compared with that of the MWCNT membrane filtration. Overall, the MWCNT membrane outperformed the PES-UF membranes in the presence of PACI flocculation and the raw pond water filtration.

Such a superior performance is mainly due to the synergetic effect of the increased hydrophilicity and porosity in the MWCNT membrane. The insertion of the MWCNT/PANI complex into the PES matrix improved the membrane structure delivering the high permeate flux, increased hydrophilicity, porosity and enhanced finger-like structure as presented in the previous study (Lee *et al.* 2016b).

The performance of the MWCNT membrane (10 kDa) with the PACI flocculation system can be compared to previous research. The enhancement in permeate flux decline and higher permeate flux was achieved due to the increased hydrophilicity of the membrane and PACI coagulation.

Effect of the MWCNT membrane with PACI system on NOM removal

The difference of NOM removal efficiency in both MWCNT and PES-UF membranes coupled with PACI flocculation was examined by measuring TOC concentration and HA concentration in the feed water and permeate. As shown in Figure 3, the MWCNT membrane had enhanced TOC and HA removal compared with the PES-UF membrane. The MWCNT membrane removed only 50% of TOC in raw pond water, without any more flocculation. However, the removal efficiency increased to 70% when 30 mg/L of PACI was in the flocculation system. However, the removal rate for the PES-UF membrane remained only 50% even at 30 mg/L PACI flocculation, indicating that the PES-UF membrane was not able to remove low molecular weight organic matter which cannot be removed by PACI flocculation. Moreover, both MWCNT and PES-UF membranes exhibited higher removal efficiency in HA removal rate according to the absorbance at $UV_{254\ nm}$. While only 60% of HA in pond water was removed by the MWCNT membrane itself, the removal efficiency increased up to 80% as the 30 mg/L PACI flocculation system was used. Removal by the PES-UF membrane increased slightly (50% → 65%) as the PACI flocculation system was coupled.

The considerably enhanced NOM removal efficiency may be due to the increased adsorption capacity for NOM of the MWCNT membrane. The MWCNT/PANI complex altered the surface charge of the membrane to be positive, leading to increased electrostatic interaction between the positively charged membrane and negatively charged NOM due to hydroxyl and carboxylic functional groups (Lee *et al.* 2016b). It should be noted that the majority of NOM size (<350 Da) is much smaller than the MWCO of UF membranes (10–350 kDa) (Kennedy *et al.* 2005; Zularisam *et al.* 2007). Thus, the commercial PES-UF membrane (10 kDa) with negative surface charge may not have enhanced adsorption capacity, in comparison with that of the positively charged MWCNT membrane.

UF membrane coupled with PAC adsorption system

Effect of the MWCNT membrane with PAC adsorption on flux enhancement

The effect of PAC adsorption on the permeate flux was examined under dead-end filtration in the MWCNT and PES-UF membranes for 3 hours. Figure 4 presents the permeate flux behaviour in both MWCNT and PES-UF membranes. Compared with PACI flocculation prior to UF filtration, relatively decreased permeate flux was observed in the MWCNT membrane. Moreover, there was no flux enhancement even when the PAC dosage increased

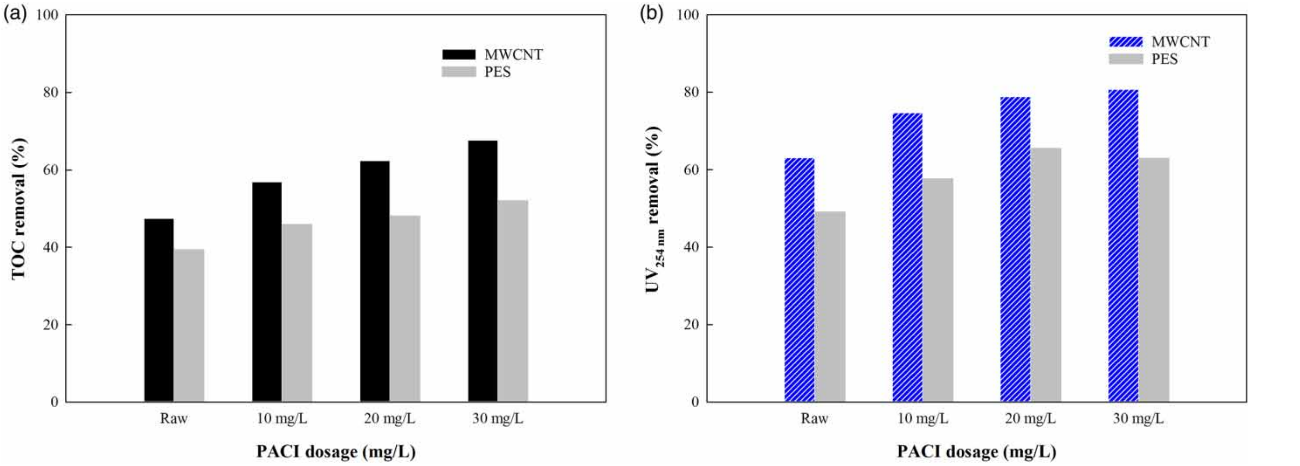

Figure 3 | Comparison of organic matter removal of the MWCNT and PES-UF membranes with PACl flocculation: (a) TOC removal rate (%) and (b) HA ($UV_{254\,nm}$) removal rate (%).

to 0.5 g/L. As shown in Figure 4(a), severe flux decline was observed at the initial stage of filtration (0.5 hours). Nearly 70% of flux decreased within 0.5 hours even when PAC adsorption was coupled. In comparison, permeate flux in the PES-UF membrane was enhanced (50%) when PAC adsorption was added. However, the increasing amount of PAC dosage did not contribute to the flux enhancement. Although there was a slight enhancement in the permeate flux, it was still lower than that of the MWCNT membrane.

The severe permeate flux decline in the MWCNT enhanced membrane is presumably due to the effect of the NOM fractions (hydrophobic and hydrophilic) on the membrane fouling potential.

As discussed above, PAC adsorption mostly contributed to hydrophobic removal while PACl flocculation removed hydrophilic fractions of NOM. It is noted that hydrophilic fractions of NOM have higher fouling potential than the hydrophobic one probably due to adsorption on the hydrophilic membrane surface and inside the pores (Kennedy *et al.* 2005). Such fouling accelerated severe permeate flux decline. For this reason, the more hydrophilic MWCNT membrane with PAC adsorption was found to be more vulnerable to permeate flux decline at the initial stage of filtration due to the hydrophilic fractions in the feed water after PAC adsorption.

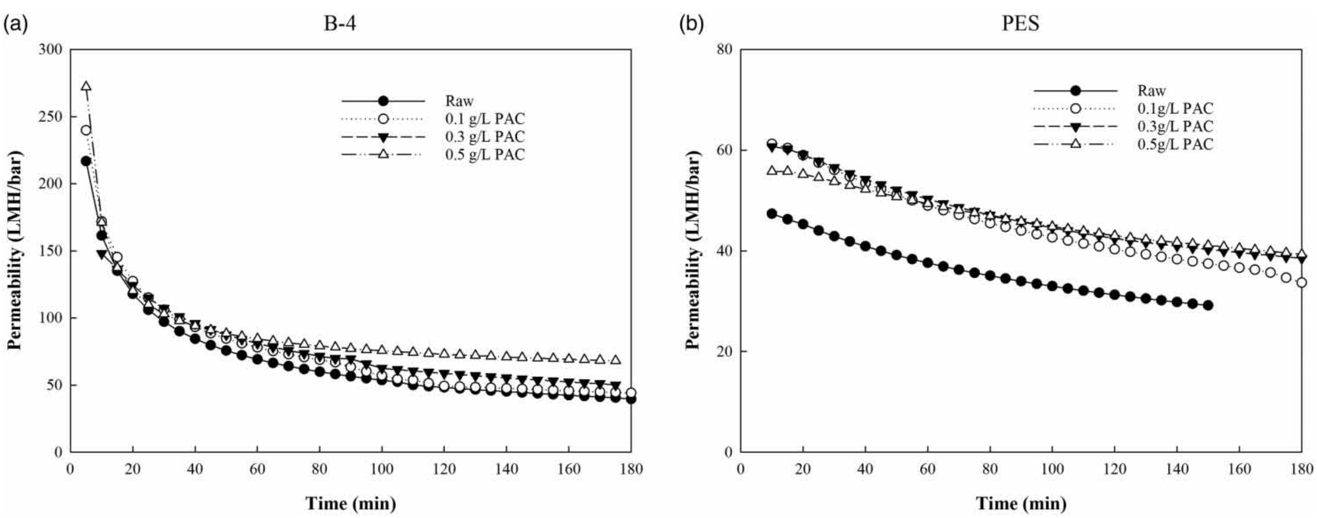

Figure 4 | Comparison of flux behaviour between (a) MWCNT membrane and (b) PES-UF membranes with PAC adsorption.

Effect of the MWCNT membrane with PAC adsorption on NOM removal

The NOM removal efficiency in both the MWCNT and PES membranes was investigated by the measurement of TOC concentration and HA concentration in the feed water and permeate. Figure 5 shows the TOC removal rate and the HA removal rate by UV absorbance at 254 nm wavelength. Similar TOC removal efficiency was observed in MWCNT filtration compared to PACI flocculation. The TOC removal rate increased to 53% when 0.1 g/L PAC adsorption was coupled and remained 60% as the PAC dosage increased up to 0.5 g/L. In comparison with TOC removal, there was a great enhancement in HA removal in both the MWCNT and PES membranes. As can be seen in Figure 5(b), the HA removal rate increased nearly two-fold (38.6% →75%) as PAC adsorption was coupled. Compared to PACI flocculation, PAC adsorption prior to UF filtration greatly contributed to the much-enhanced HA removal efficiency. Figure 5(b) indicates that the HA was almost completely removed (98.2%) when 0.5 g/L PAC adsorption was coupled with MWCNT membrane filtration.

Such an enhancement in NOM removal is found to be superior to that in previous research which exhibited nearly 50% DOC removal (45% of $UV_{254\,nm}$ removal) (Zhang *et al.* 2015). Particularly, for HA removal rate, the effluent concentration of the MWCNT membrane ($0.007\ cm^{-1}$) is lower than that ($0.11\ cm^{-1}$) of the PAC/UF filtration system in the previous research, considering that the raw pond water has much higher NOM ($0.274\ cm^{-1}$) than the raw water from the drinking water source ($0.187\ cm^{-1}$). Therefore, the MWCNT membrane with PAC adsorption can be a robust system for high concentration of NOM removal.

CONCLUSION

The study aimed to improve UF membrane performance for NOM removal in pond water by designing a nano-engineered membrane. The MWCNT membrane was coupled with PACI flocculation and/or PAC adsorption to alleviate flux decline and enhance NOM removal efficiency. Overall, the MWCNT membrane system outperformed the commercial PES-UF membrane system in terms of high initial permeate flux and enhanced organic carbon removal efficiency while the PES-UF membrane exhibited more stable permeate flux than the MWCNT membrane. For PACI flocculation, great flux enhancement in MWCNT membrane filtration was achieved when 30 mg/L PACI was used in the pretreatment step. Further, severe flux decline in raw water filtration and that at low amount of PACI dosage was completely overcome. For PAC adsorption prior to MWCNT membrane filtration, severe flux decline at the initial filtration stage was not overcome by pretreatment. However, considerable enhancement in HA removal was achieved when 0.5 g/L of PAC adsorption was coupled, and by comparison there was no significant difference in TOC removal by both adsorption and flocculation prior to UF membrane filtration. It is suggested that the MWCNT membrane had enhanced NOM removal efficiency and high permeate flux without flux decline in pond water treatment when a low amount of flocculant was applied.

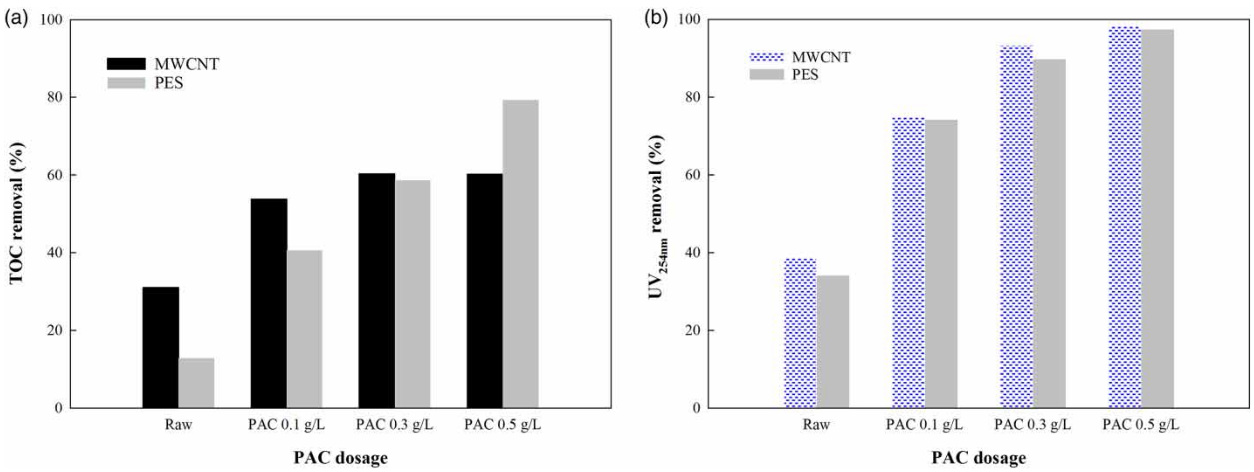

Figure 5 | Comparison of organic matter removal of the MWCNT and PES-UF membranes with PAC adsorption: (a) TOC removal rate (%) and (b) HA ($UV_{254\,nm}$) removal rate (%).

To provide a fair tool to compare the newly developed MWCNT membrane performance in pond water treatment, future work will be focused on a more careful study in a bench-scale fouling system with the scoring of TMP development, permeability recovery, required membrane cleaning and its fouling rate.

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