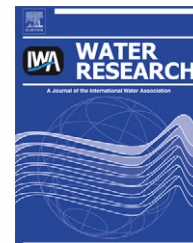




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Modification of low pressure membranes with carbon nanotube layers for fouling control

Gaurav S. Ajmani^a, David Goodwin^b, Kristofer Marsh^b, D. Howard Fairbrother^b, Kellogg J. Schwab^a, Joseph G. Jacangelo^{a,c}, Haiou Huang^{a,*}

^aCenter for Water and Health, Johns Hopkins University, Baltimore, MD 21205, USA

^bDepartment of Chemistry, Johns Hopkins University, Baltimore, MD 21218, USA

^cMWH, Lovettsville, VA 20180, USA

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ABSTRACT

Carbon nanotubes (CNTs) with different physiochemical properties were layered onto low pressure membranes and tested for antifouling properties using a natural surface water with high fouling potential. Membranes modified with the largest diameter pristine multi-walled CNTs (MWCNTs) were most effective in controlling membrane fouling, tripling the time it took for the membrane to become noticeably fouled at a CNT loading of 22 g/m². The differences in the structure of CNT layers were an important contributing factor for antifouling properties; scanning electron microscopy imaging showed that large diameter MWCNTs formed homogeneous porous layers across the membrane surface, while less effective, small diameter MWCNTs formed heterogeneous layers. Water quality analysis showed that CNT-membranes constructed with larger diameter CNTs were more effective at removing larger organic macromolecules responsible for fouling from feedwater compared to membranes made with smaller diameter CNTs. This reduced the concentration of foulants reaching the PVDF membrane and thus helped reduce membrane fouling. Beneficial for application, increased loadings of CNTs onto the membrane surface increased resistance to fouling while only slightly reducing the clean water permeability of the modified membranes. Overall, CNT layered membranes were shown to highly resist membrane fouling with potential applications in sustainable water treatment.

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1. Introduction

Access to safe drinking water is a basic necessity for all human life. The United Nations estimates that approximately 780 million people around the world are without access to safe drinking water sources (World Health Organization and UNICEF, 2012). Membrane separation has emerged as one of the most promising methods for water purification, given that it has a low environmental footprint and does not require chemical treatment of the water (Peter-Varbanets et al., 2009).

In particular, low pressure membranes (LPMs) have been gaining popularity worldwide, because of their effectiveness in removing particulate contaminants combined with very low operational costs. Indeed, the installed capacity of LPM systems worldwide has grown exponentially in the past twenty years (Furukawa, 2008). The low costs of LPMs derive from their low operational transmembrane pressures (TMPs), typically less than 1–2 bar (US-EPA, 2001; Huang et al., 2009). In contrast, reverse osmosis (RO) membranes used for fresh-water treatment typically operate at a TMP of 7–14 bar (Baker,

* Corresponding author. Tel.: +1 410 955 7706; fax: +1 410 955 9334.

E-mail address: haiouh@jhu.edu (H. Huang).

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2004). This makes LPMs a much more attractive option from a cost-benefit and energy perspective, because they can operate at filtration pressures that range from 70% to more than 90% lower than those required for RO membranes (Baker, 2004).

The sustainability of LPMs in water treatment is, however, limited by membrane fouling, which results in a loss of membrane permeability due to an accumulation of aquatic constituents on the membrane surface or within the pores themselves (Huang et al., 2009). Fouling increases the energy costs of membrane filtration, due to a higher hydraulic resistance and thus higher TMP (Kimura et al., 2004). To prevent membrane fouling from occurring, feedwaters to LPM systems are often pre-treated at great expense and with limited effect (Huang et al., 2009). LPMs are also regularly backwashed for hydraulic cleaning, but this process must be augmented by frequent chemical treatment. Commonly used cleaning agents, including acids and oxidizing agents, are usually effective in cleaning fouled LPMs, but their use interrupts the filtration process and cannot always permanently restore membrane permeability (US-EPA, 2001; Kimura et al., 2004). Therefore, the development of LPMs with a high resistance to fouling would be extremely useful, as such membranes would require less frequent chemical cleaning and exhibit a longer operational life.

To this end, the increasing production rates and rapidly decreasing costs of carbon nanotubes (CNTs) provide an opportunity to develop novel CNT layered membranes with practical real-world value (Parish, 2011). CNTs exhibit extremely high surface area-to-volume ratios and large aspect ratios, making them attractive as a new class of sorbents for removing chemicals and microbes from water (Stafiej and Pyrzynska, 2007; Brady-Estevez et al., 2008; Ji et al., 2009; Upadhyayula et al., 2009; Heo et al., 2011; Vecitis et al., 2011). Indeed, membranes containing CNTs as active components have been studied for their potential to reduce fouling and/or improve contaminant removal. Different methods of fabrication include: vertically aligned CNTs (Holt et al., 2006), CNT-polymer composites (Brunet et al., 2008; Celik et al., 2011; Shawky et al., 2011), and CNTs layered on existing membranes (Brady-Estevez et al., 2008; Vecitis et al., 2011; Rahaman et al., 2012). The first method is difficult to scale up due to existing difficulties in fabrication (Holt et al., 2006), and the second limits the active role of CNTs at the membrane/water interface because they are impregnated in the membrane polymer matrix. Therefore, the third method was employed in this

study to modify LPMs with CNTs with the goal of improving fouling resistance during natural water filtration.

The primary objective of this research was to develop a CNT layered membrane that exhibits improved resistance to fouling from organic materials in natural water compared to an unmodified membrane. As part of this study we also identified factors responsible for determining the antifouling properties of CNT layers. Finally, we considered some of the issues that must be considered if this technology were to be applied beyond a bench-scale model to a real-world water treatment system.

2. Materials and methods

2.1. Carbon nanotubes

Single-walled and multi-walled CNTs (SWCNTs and MWCNTs) with different functional groups and diameters were purchased from Cheap Tubes Inc. (Vermont, USA). To provide consistency among the CNTs under investigation, this study was restricted to this single commercial manufacturer. Important characteristics and unit costs (as reported by the manufacturer) of all CNTs used in the experiments are shown in Table 1. According to the manufacturer, the pristine CNTs were prepared using chemical vapor deposition and further purified or functionalized using plasma methods. Surfactant-modified MWCNTs were also prepared in-lab by dispersing purchased pristine MWCNTs in a surfactant solution overnight (TritonT X-100).

2.2. Activated carbon

Powdered activated carbon (PAC) was purchased from two manufacturers, Norit Americas Inc. (Texas, USA) and Calgon Carbon Corp. (Pennsylvania, USA). Granular activated carbon (GAC) was obtained from a Honespring Central Water Purifier (GE Water & Process Technologies). These activated carbons (ACs) were used in the same manner as CNTs to modify membranes, in order to compare the antifouling properties of AC mats to CNT mats.

2.3. Water samples

For the fouling studies, a natural surface water was collected from the source water of the Northern Bay Regional Water

Table 1 – CNT properties.

Type of CNT	Outer diameter (nm)	Length (μm)	Specific surface area (m^2/g)	Purity (wt%)	Unit cost ($\$/\text{g}$)
MWCNT	<8	10–30	500	>95	15
MWCNT	10–20	10–30	233	>95	10
MWCNT	20–30	10–30	110	>95	8
MWCNT	30–50	10–20	60	>95	5
MWCNT	50–80	10–20	60	>95	5
MWCNT-COOH	10–20	10–20	233	>95	18
MWCNT-NH ₂	13–18	3–30	233	>99	30
SWCNT	1–2	5–30	407	>90	110

Treatment Plant in California, USA, and shipped to Johns Hopkins overnight. This water was predetermined to possess a high fouling potential to commercially available LPMs in our preliminary studies (Huang et al., 2011). It was therefore selected in this study to provide a harsh feedwater condition for LPM filtration. Table S1 (Supplementary Material) presents the major characteristics of the natural water after being pre-filtered with a 1.2 μm glass fiber filter (Whatman, GF/C) to remove large particulate matter. The natural water was stored in the dark at 4 °C and equilibrated to room temperature (23 ± 1 °C) prior to testing. Because of variations in the fouling potential of water from different pre-filtered batches, each parameter was tested exclusively with one batch of water. Ultrapure water used for membrane cleaning and for determining clean membrane permeability was obtained from a Millipore water purification system (Milli-Q) at a resistivity of 18.2 $\text{M}\Omega\text{-cm}$.

2.4. Membrane modification

Polyvinylidene fluoride (PVDF) membrane filters with a 33 mm diameter housing and 24 mm diameter filtration area were purchased from Millipore (Millex with Durapore HVLP membrane). These filters consisted of flat-sheet membranes with an effective filtration area of 4.5 cm^2 and a nominal pore size of 0.45 μm . Prior to modification, PVDF membrane filters were cleaned by filtering with ultrapure water until the permeate registered an absorbance of zero at 254 nm on an online ultraviolet (UV) detector (Varian 2050 variable wavelength detector). Powdered CNTs and ACs were weighed using a microbalance (Mettler Toledo M5) and then suspended in 20 mL of ultrapure water. The suspension was then dispersed by sonication for 3 min using a water bath sonicator (Aqua-sonic 250HT) and immediately loaded onto a cleaned PVDF membrane by syringe-filtering the dispersion through the membrane filter, thus layering a CNT or AC layer onto the PVDF surface. In contrast, the surfactant-coated MWCNTs were loaded directly onto a cleaned PVDF membrane by filtering the solution through the membrane without additional water bath sonication. This membrane was then cleaned as before, by filtering ultrapure water through until the permeate had a UV_{254} absorbance of zero. Unless noted, a common surface loading of 10 mg was used in each experiment based on preliminary tests. This particular loading was chosen to ensure that the differences in the antifouling properties of the modified membranes could be determined during the time frame of the bench-scale testing.

2.5. Water filtration

The cleaned, modified membranes were setup on a bench-scale membrane filtration system and tested by filtering the natural surface water in direct flow, constant flux mode using a solvent delivery pump (ESA 580, Thermo Scientific). Dead-end filtration was chosen (as opposed to crossflow filtration) because this method is most commonly used in membrane water treatment (AWWA, 2005). The feedwater was pumped through the membrane and the permeate entered the online UV detector. From the outflow of the UV detector, 1.5 mL samples were collected periodically for

organic constituent analysis. A diagram of the filtration system is presented in the supporting information (Figure S1, Supplementary Material).

The TMP was monitored constantly during filtration by using a pressure sensor in the pump as a measure of membrane fouling—as the membrane fouled, the pressure increased. The filtration was conducted at a constant flowrate of 1 mL/min for 2 h or until the TMP increased by approximately 1 bar. This method of filtration, as compared to a constant pressure/declining filtration rate scenario, is similar to that employed in full-scale membrane plants (AWWA, 2005). To complement TMP measurements, the permeate's UV absorbance at 254 nm was measured by the online UV detector to monitor the removal of UV-absorbing natural organic matter (NOM) by the modified membrane. This filtration setup was used in membrane fouling tests.

2.6. CNT mass loading tests

To assess the impact of CNT loading on the clean water permeability and antifouling properties of the modified membranes, incremental masses of pristine MWCNTs were loaded onto a cleaned PVDF membrane using the method described above. Two factors were evaluated in this study. First, the relationship between CNT surface loading and the fouling resistance of CNT-modified membranes was determined in a loading range of 0, 1, 5, 10, and 50 mg. The method for antifouling tests has been described above. Second, to determine the membrane baseline permeability as a function of CNT loading, the following surface loadings were tested (in mg): 0, 5, 10, 20, 30, and 50. Ultrapure water was filtered through the modified membrane at each loading, and the TMP was recorded using a digital pressure gauge (Cecomp Electronics DPG1000B) installed between the membrane filter and the constant flow pump when the reading stabilized.

2.7. Membrane imaging

CNT layered membrane surfaces were imaged using a cold cathode field emission scanning electron microscope (SEM) (JEOL 6700F) with a 1.0 nm resolution at 15 keV. Samples were imaged on either a 25 mm diameter PVDF membrane or a 13 mm PVDF membrane scaled to maintain the same mass per area loading of 22 g/m^2 . Top views were taken of both the uncoated membrane and CNT coatings on the membrane at various magnifications. To take cross-sectional images, the MWCNT-layered PVDF membranes were first cryo-snapped in the presence of liquid nitrogen and then sputter-coated with platinum to prevent charging of the PVDF. These samples were then mounted vertically to the side of a sample stub for imaging at various magnifications.

SEM images were analyzed using the Analyze Particle function of ImageJ, (National Institute of Health, version 1.45) by maximizing the color contrast between the actual CNTs and nanopores. The pores were then analyzed by the software to determine the Feret's diameters of each pore (Dumée et al., 2010; Gribble et al., 2011), with the minimum Feret's diameter taken as relevant for its effective sieving ability.

2.8. Size fractionation of dissolved organic carbon

To assess the relationship between the ability of different CNT layers to reduce membrane fouling and filter out organic materials, size exclusion chromatography with organic carbon detection (SEC-OCD) analysis was performed on the filtered natural water. Samples were collected after 10 min in the size (diameter) testing experiments because this time was less than the time required to produce a measureable increase in TMP pressure for any of the CNT-membranes (an indication of filter clogging or membrane fouling). Consequently, analysis of the permeate after this time interval provides a means to directly compare different CNT layers in terms of their particle filtration capabilities. SEC-OCD was used to determine the size fractionation of dissolved organic carbon (DOC) in the permeate samples. The SEC column (TSK-gel G4000PW_{XL}, 7.8 mm inner diameter, 30.0 cm length) separates materials in water samples based on their size, with larger particles coming through before smaller ones. Subsequently, the OCD (General Electric, Sievers 900 portable total organic carbon analyzer) measures the organic carbon concentration in the elutant of the SEC column. The SEC-OCD system was setup and operated based on previous methods for the system setup (Lee et al., 2004) and mobile phase chemistry (Huber et al., 2011).

3. Results and discussion

3.1. Effects of CNT surface chemistry on membrane fouling

Pristine MWCNTs, surfactant-coated MWCNTs, amine functionalized MWCNTs ($-\text{NH}_2$), and carboxylated MWCNTs ($-\text{COOH}$) of similar diameters (ca. 10–20 nm), as well as SWCNTs, were tested separately for antifouling properties after being loaded onto a PVDF membrane at a common loading of 10 mg. Comparisons were made between the filtration times needed to observe a noticeable increase in TMP, which was taken as an indication of the onset of fouling. As shown in Fig. 1, all CNT-modified membranes outperformed the uncoated PVDF membrane except for the membrane modified by surfactant-coated MWCNTs. The pristine MWCNTs, MWCNT- NH_2 , and SWCNTs exhibited comparable antifouling properties and all were better than the MWCNT- COOH . However, pristine CNTs should not be dispersed in surfactant prior to membrane modification because, as shown in Fig. 1, they appeared to decrease the membrane's baseline permeability, either through pore blocking or through the formation of a dense, nonporous cake layer. This increased the modified membrane's initial TMP to 1 bar and decreased its resistance to membrane fouling during filtration of the natural surface water. Thus, in a broader sense the poor performance of the surfactant modified CNTs highlights the need to use aggregated CNTs which are too large in size to pass through and clog the membrane pores and not well-enough dispersed to form a dense cake when creating CNT layers on top of existing membranes.

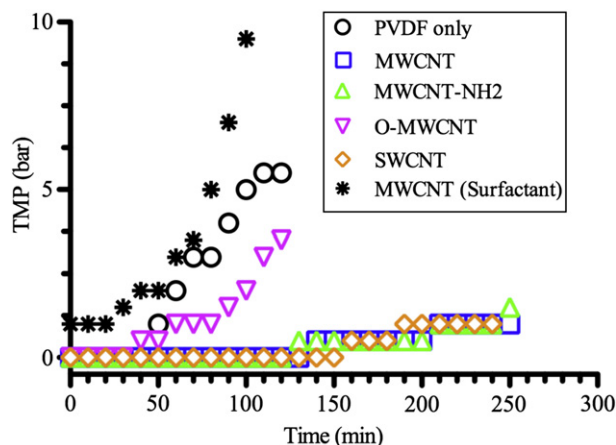


Fig. 1 – Increase of TMP as a function of filtration time for MWCNTs of similar diameters (ca. 10–20 nm) but with different surface chemistries and SWCNTs.

Flowrate = 1 mL/min, temperature = 23 ± 1 °C.

3.2. Effect of CNT diameter on membrane fouling

Pristine MWCNTs with different diameters were also tested on the PVDF membrane for their ability to reduce membrane fouling. Pristine MWCNTs were chosen because they offered the best performance value based on their cost and resistance to membrane fouling (Fig. 1). The diameters used were (in nm) : <8, 10–20, 20–30, 30–50, and 50–80, with a common loading of 10 mg. All CNTs were found to improve the membrane's antifouling properties, shown by the extended filtration time before TMP increases were observed in coated membranes relative to an uncoated membrane (Fig. 2). The largest diameter MWCNTs (50–80 nm) performed best—they were able to filter water for the longest period of time before a noticeable increase in TMP. In contrast, the smallest diameter MWCNTs (<8 nm) were least effective in reducing fouling. MWCNTs with intermediate diameters performed slightly worse than the largest diameter CNTs but noticeably better than the smallest diameter CNTs.

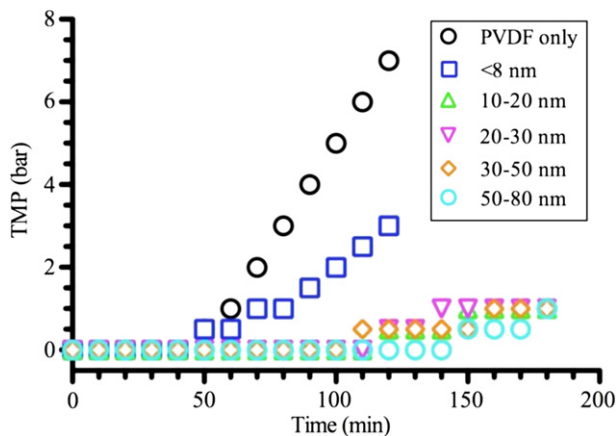


Fig. 2 – Increase of TMP as a function of filtration time for pristine MWCNTs of different diameters. Flowrate = 1 mL/min, temperature = 23 ± 1 °C.

Overall, in comparing all the CNTs tested (Figs. 1 and 2), membranes composed of the 50–80 nm diameter pristine MWCNTs layers were the most effective in preventing membrane fouling. A 1 bar increase in TMP was observed after 180 min, compared to only 60 min for the uncoated membrane and 70 min for the <8 nm diameter MWCNTs. These results are promising for practical implementation, as the costs of larger diameter MWCNTs are lower than those of smaller diameter MWCNTs (Table 1).

3.3. SEM imaging of CNT layered membranes

To better understand how the interactions between CNTs and the PVDF membrane influenced the antifouling properties of

the CNT modified membranes studied, SEM images were taken of an uncoated PVDF membrane (Figure S2, Supplementary Material) and of several PVDF membranes coated with different CNTs at a lower (Fig. 3a, c, e) and higher magnification (Fig. 3b, d, f). The images show markedly different surface structures based upon the CNT used. Pristine MWCNTs with diameters 50–80 nm formed a uniform CNT layer on top of the PVDF membrane (Fig. 3a, b). A homogeneous structure was also observed for SWCNTs (Fig. 3e, f), which appeared to form bundles that acted akin to a larger-diameter multi-walled CNT. On the other hand, the MWCNTs with diameters <8 nm formed a rough, heterogeneous layer on top of the membrane with large aggregates of CNTs (Fig. 3c, d). Indeed, close analysis of Fig. 3c reveals that

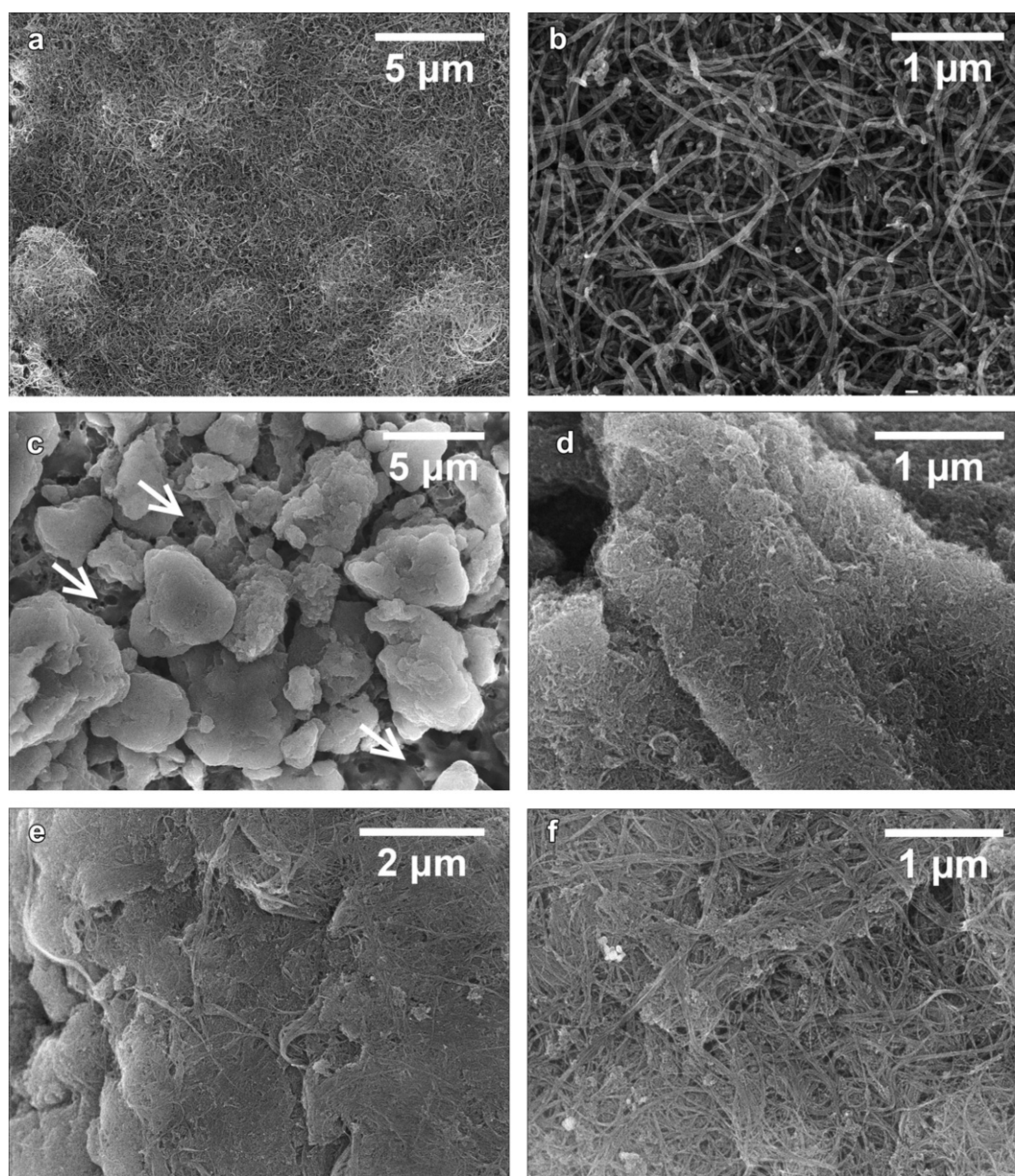


Fig. 3 – SEM images of a) 50–80 nm MWCNTs on PVDF (5,000 \times); b) 50–80 nm MWCNTs on PVDF (30,000 \times); c) <8 nm MWCNTs on PVDF (5,000 \times) with arrows pointing at exposed PVDF; d) <8 nm MWCNTs on PVDF (30,000 \times); e) 1–2 nm SWCNTs on PVDF (15,000 \times); f) 1–2 nm SWCNTs on PVDF (30,000 \times). All CNT loadings were the same based on the ratio of CNT mass added to the membrane's two-dimensional surface area.

there are some regions, indicated by arrows, where the underlying PVDF membrane is still visible. MWCNTs having diameters between 10 and 50 nm formed porous layers with structures more homogenous than <8 nm and less homogenous than 50–80 nm MWNTs (data not shown). Thus, MWCNTs showed increasing homogeneity with increasing diameter. This observation suggests that the larger diameter MWCNTs and SWCNTs exhibit stronger attractive interactions with the PVDF membranes compared to the smaller diameter MWCNTs.

SEM image analysis with ImageJ software (Figure S3, Supplementary Material) helps confirm two key observations regarding the 50–80 nm MWCNT layer. First, the average pore size of this CNT layer was small, on average less than one-third the average size of the PVDF membrane pores. Second, the CNT layer pore size distribution was almost entirely within a very narrow range, whereas the PVDF membrane's pore size distribution was far more spread-out. This confirms the observation that the large diameter MWCNTs formed a homogeneous layer, which was likely better able to trap fouling materials in the source water, and could explain their stronger antifouling properties. In contrast, the more heterogeneous CNT layers formed by <8 nm MWCNTs likely allowed fouling materials to pass through the gaps between the agglomerates and reach the membrane surface. Overall, the performance of the CNTs showed that the ones that formed a more homogeneous porous layer were most effective in preventing membrane fouling.

Cross-sectional SEM images were also taken of the best performing CNT layer: 50–80 nm MWCNTs on a PVDF membrane (Fig. 4). To image the cross section, the MWNT–PVDF membrane was first cryo-snapped. The image in Fig. 4c was taken with the layered membrane at an angle, in order to show more of the surface in addition to the cross-section. Interestingly, the 50–80 nm MWCNTs were the only ones that remained on the PVDF through this process, demonstrating that they had the strongest interaction with the PVDF at low temperature in liquid nitrogen. Other CNT layers were cryo-snapped but no longer remained on the PVDF when placed in liquid nitrogen. The cross-sectional images highlight the clear separation between the CNT layers and the underlying PVDF membrane as well as the relative uniformity of the layer's thickness and coverage across the PVDF membrane.

3.4. Size fractionation of DOC in filter permeate

Membrane fouling is typically ascribed to high molecular weight biopolymers present in feedwater (Howe and Clark, 2002; Gabelich et al., 2004; Kimura et al., 2004; Huang et al., 2009). To highlight the differences in organic removal, the results for permeate samples from the worst (pristine MWCNT <8 nm diameter) and best (pristine MWCNT 50–80 nm diameter) performing CNTs in terms of membrane fouling are presented in Fig. 5. As a comparison, the permeate that passed through the unmodified PVDF is also shown. The permeate from the unmodified PVDF membrane shows that it was easily the worst of the three membranes at removing both medium and high molecular weight organic molecules (Fig. 5). Comparing the permeates from the two CNT-modified membranes, the 50–80 nm MWCNTs were better than the <8 nm MWCNTs at removing the fraction corresponding to large biopolymers relevant to membrane fouling (Fig. 5b), but the smaller diameter MWCNTs were better at removing the fraction of medium molecular weight organics (Fig. 5a). These observations provide a rationale for the larger 50–80 nm diameter CNTs' superior fouling retarding performance, as they can form dense and uniform layers with nanopores inside (average diameter ca. 77 nm, Figure S3) and are therefore more effective at trapping the larger sized organics (diameter ca. 80 ± 40 nm) (Huang and O'Melia, 2008) responsible for membrane fouling within these pores compared to the smaller (<8 nm) CNTs where the non-homogeneous coverage of the CNT layers means that some of the larger organics can reach the PVDF membrane directly (Fig. 3). Consequently, the larger diameter CNTs have a greater capability to reduce fouling of the substrate PVDF membrane. On the other hand, the nanopores in the 50–80 nm CNT layers are much larger than medium molecular weight organics (diameter ca. 1 nm) (Huang and O'Melia, 2008). Therefore, the removal of medium molecular weight organics is primarily due to adsorption. The smaller MWCNTs have a greater specific surface area than do the larger MWCNTs (Table 1) so they are more effective in removing the medium molecular weight organics through adsorption. Past work has demonstrated the greater adsorption capacity per gram of smaller diameter MWCNTs compared to larger diameter MWCNTs, possibly as a result of the greater specific surface area of the smaller CNTs (Apul et al., 2012). These differences in the

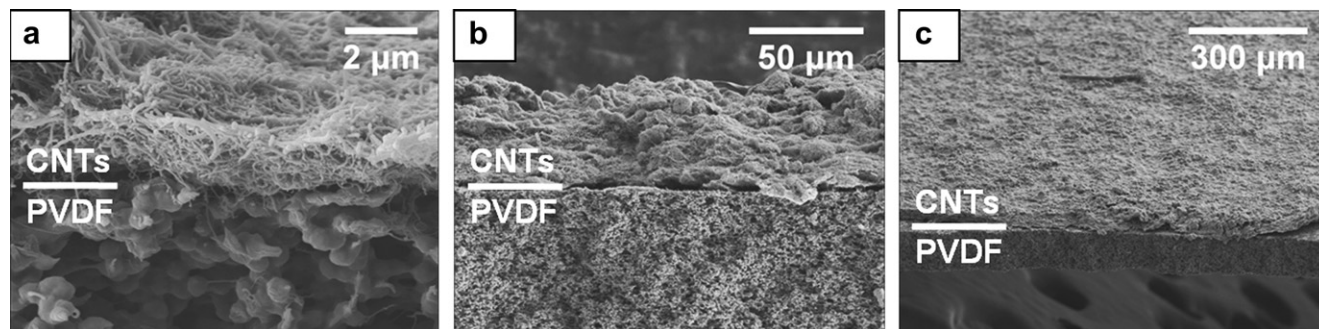


Fig. 4 – Cross-sectional SEM images of the 50–80 nm pristine MWCNTs on PVDF. Magnifications for the images were a) 10,000 \times ; b) 650 \times ; c) 110 \times .

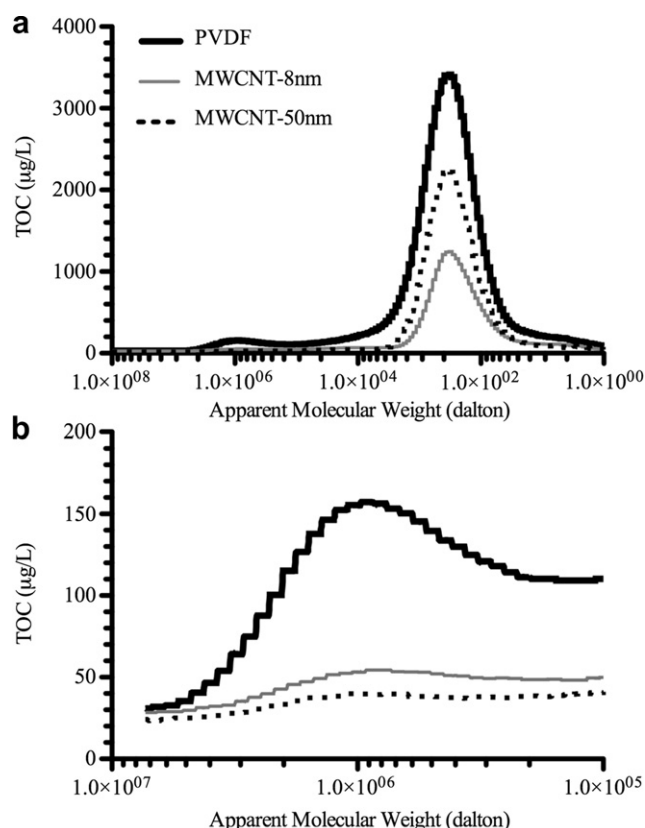


Fig. 5 – SEC-OCD results from permeate that passed through three different membranes; an unmodified PVDF membrane and membranes modified by <8 nm and 50–80 nm MWCNTs layers. Differences in the concentrations of medium molecular weight organics (humic substances) and high molecular weight organics (biopolymers) are highlighted in (a) and (b), respectively.

removal efficiency of different organic size fractions by the <8 nm and 50–80 nm CNT layered membranes is an indication of differences in removal mechanisms (filtration by CNT nanopores for the larger sized macromolecules, but sorption dominating for the medium molecular weight organics).

3.5. CNT adhesion to the PVDF membrane surface

A key issue with loading CNTs onto a membrane surface is the adhesion properties of the CNTs to the membrane, and stability has been found to be a concern for membranes modified by nanoparticles (Kim and Brugger, 2010). Because a principal method of cleaning membranes in LPM filtration facilities is periodic backwashing of the membrane, the CNTs must have a strong adhesion to the membrane surface, or they will be removed during backwashing. To study this qualitatively, CNT layered membranes which had been fouled from the filtration experiments were backwashed by pushing 10 mL of permeate collected during the filtration run at a roughly constant flowrate through the fouled modified membrane from the PVDF side. Two CNT membranes were used in this study: PVDF coated with <8 nm pristine MWCNTs

and PVDF coated with 50–80 nm pristine MWCNTs. Images were taken of the membranes before and after the backwash. For comparison, an uncoated, used PVDF membrane is also shown. As can be clearly seen in Fig. 6, the 50–80 nm MWCNTs exhibited stronger adhesion to the PVDF membrane than did the <8 nm diameter MWCNTs. Thus, the PVDF membranes coated with 50–80 nm MWCNTs looked similar before and after backwashing, while the membranes coated with <8 nm MWCNTs displayed a noticeable change in CNT coverage after backwashing. This behavior is also consistent with the difference in the structure of the CNTs observed in Fig. 3. These results are promising, because the 50–80 nm MWCNTs were most resistant to fouling and their ability to adhere more strongly to the PVDF membrane will help to integrate them into a water treatment system. However, some of the 50–80 nm MWCNTs did detach from the PVDF membrane surface during permeate backwash and were observed during the backwash. Therefore, future studies are warranted to enhance the adhesion of CNTs to LPM surfaces.

3.6. Effects of CNT surface loading on membrane fouling and permeability

To appropriately scale this technique to a full-scale membrane plant level, the suitable surface loading of CNTs in the layered membranes needs to be determined. The 50–80 nm diameter MWCNTs were selected for these experiments because they had the greatest antifouling properties of all CNTs tested. Two factors were evaluated in this study. The first was the relationship between CNT surface loading and the fouling resistance of CNT-modified membranes. As shown in Fig. 7, a clear relationship between CNT loading and fouling resistance was found, with higher loadings exhibiting a greater resistance to membrane fouling. This trend may be explained by enhanced removal of fouling materials (e.g., biopolymers) from the natural water by thicker CNT layers.

The second factor considered was the decrease in membrane permeability due to the CNT loading. As shown in Fig. 8, increased CNT loading produced a linear decrease in the membrane's permeability when ultrapure water was flowed through the membrane (as measured by an increasing TMP), suggesting relatively uniform pore structure inside the CNT layers, regardless of the thickness. However, these pressure increases were very small even at the highest CNT surface loading of 50 mg, much lower than the 1–2 bar range where most LPMs operate. Thus, a much higher dose of CNTs could have been loaded onto the membrane without increasing the operational membrane pressure beyond normal levels for LPMs. The standard 10 mg loading used in most of the experiments led to a TMP increase of only 0.0121 bar. This loading corresponds to a mass per area loading of 22 g/m². If the same pressure-loading relationship can be extrapolated to higher CNT loadings, nearly 1 kg/m² of these large pristine MWCNTs could be loaded onto a membrane while only increasing the TMP by 0.5 bar.

3.7. Economic and practical considerations

Because of the common use of more traditional ACs in conjunction with membrane treatment (Stoquart et al., 2012),

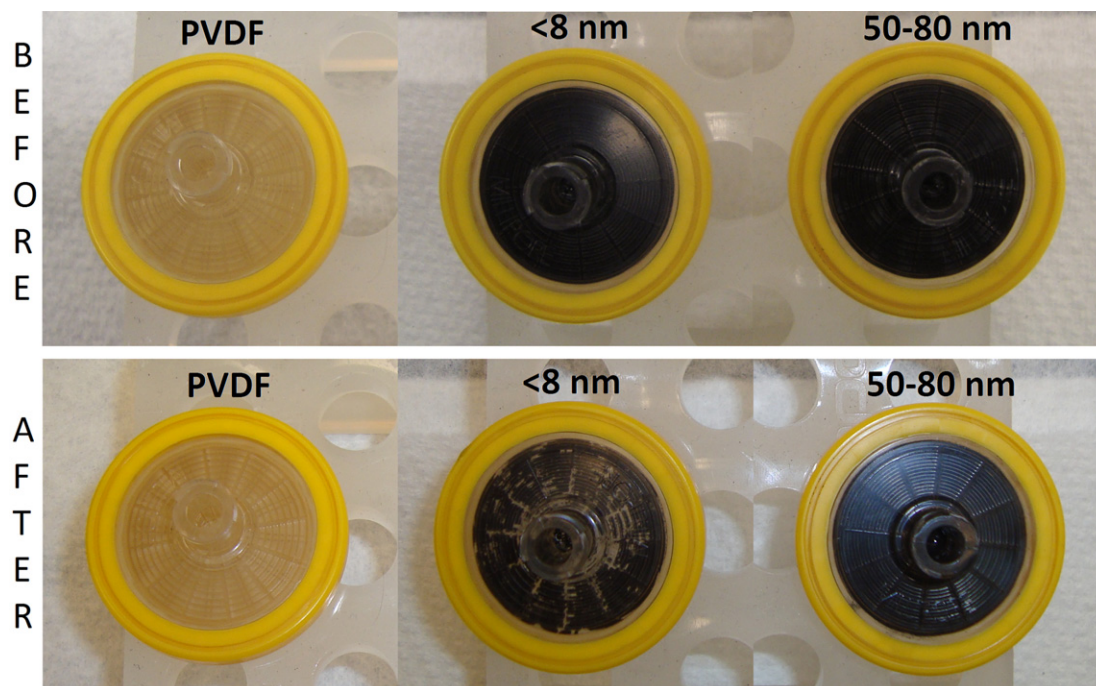


Fig. 6 – Images of uncoated and CNT layered membranes before and after backwashing with 10 mL of permeate.

the antifouling properties of ACs were tested under the same conditions as were CNTs. Filtration studies were conducted with PAC massed at 10 mg and GAC massed at 50 mg (a higher dose of GAC was needed to achieve complete membrane coverage). The data (Fig. 9) show that membranes layered with PAC and GAC offered no antifouling benefit compared to a virgin PVDF membrane, justifying the use of CNTs in this antifouling application.

Amongst the various CNTs evaluated in this study, the pristine MWCNTs exhibited antifouling properties that were at least comparable to those of surface functionalized CNTs of the same diameter. This is a promising sign for economic

development of novel membranes, because the costs of pristine CNTs are much lower than for functionalized CNTs and SWCNTs (see Table 1). Furthermore, amongst the pristine MWCNTs tested, the larger diameter and least expensive CNTs were the most effective. Industrial MWCNTs can now be purchased for <\$ 1000/kg and the cost of 50–80 nm MWCNTs used in this study is \$ 600–\$ 700/kg if purchased in large quantities, which equals approximately \$ 13–\$ 15 per m² of membrane surface area at the common surface loading used in this study. This cost is comparable to the manufacturing

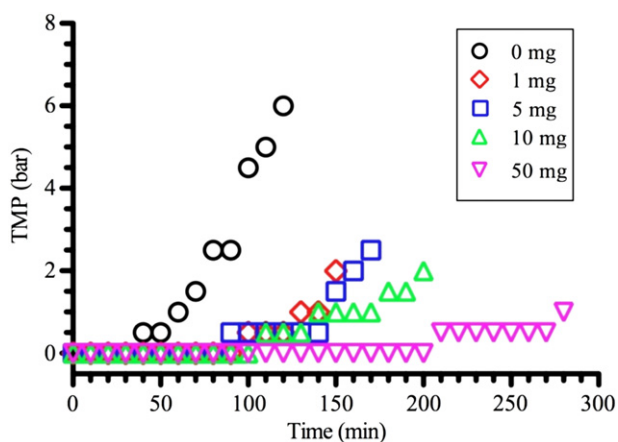


Fig. 7 – Increase of TMP as a function of filtration time for CNT layered membranes at different loadings. The 50–80 nm MWCNTs were used in these tests. Flowrate = 1 mL/min, temperature = 23 ± 1 °C.

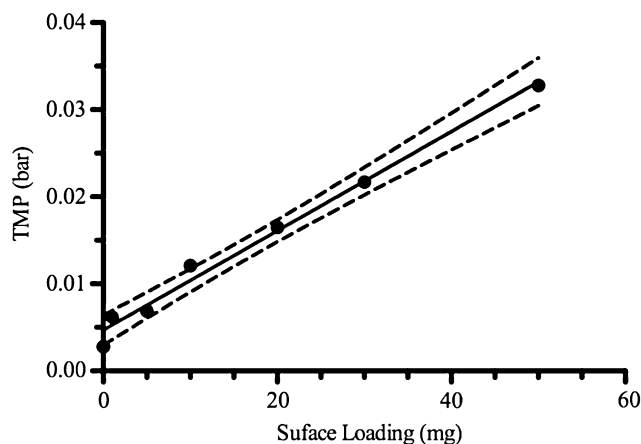


Fig. 8 – Increase of baseline TMP for clean CNT layered membranes at different CNT loadings. The tests were conducted with ultrapure water at a constant flowrate of 1 mL/min and a temperature of 23 ± 1 °C. The solid and dashed lines represent the linear regression line and 95% confidence lines, respectively.

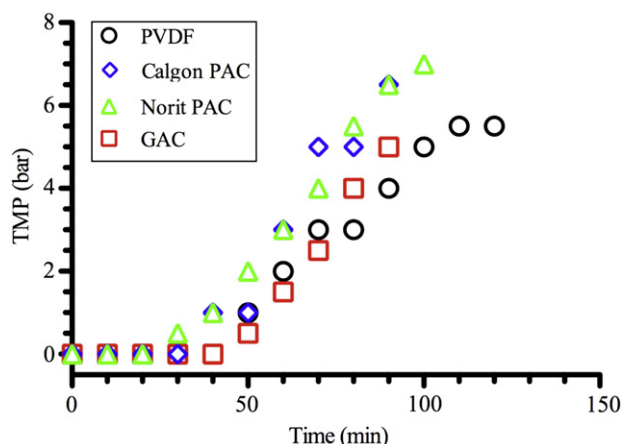


Fig. 9 – Increase of TMP as a function of filtration time for PAC (two manufacturers) and GAC. Flowrate = 1 mL/min, temperature = 23 ± 1 °C.

costs of hollow fiber LPMs (\$ 10–50/m²) or flat-sheet membranes (\$ 5–100/m²) (Baker, 2004). Additionally, CNT layered membranes could lower costs by lowering operational TMPs for membrane systems, reducing or eliminating pretreatment of water, reducing the frequency of backwash cleaning, and extending membrane life before replacement is needed due to irreversible fouling (US-EPA, 2001).

The minimal effect that CNT layers have on membrane permeability (Fig. 9) also means that the practical surface loading of CNTs in a layered membrane will be determined by antifouling requirements rather than any decreases in clean water permeability caused by the addition of CNTs. Therefore, the antifouling properties of CNT layered membranes can be tailored to the fouling potential of the source water to control manufacturing costs and optimize the cost-benefit. The ability to use pristine CNTs for reduced membrane fouling will also reduce the use of toxic and corrosive chemicals (e.g. strong acids) required for surface functionalization in the preparation of functionalized CNTs (Rosca et al., 2005). This will further reduce the manufacturing costs associated with waste disposal and simplify the manufacturing process. However, it should be noted that functionalized CNTs may be more effective than pristine CNTs for contaminant removal, so their usage will be important in the future. The backwashing of CNT layered membranes will have to be studied further to assess the practical implications of CNTs entering backwashed water and ending up at the head of the water treatment plant, where they could pose problems during pretreatment of water.

4. Conclusion

This study investigated the ability of CNT layered membranes to reduce membrane fouling and considered their practicality for sustainable drinking water treatment. The following conclusions can be drawn from the study's findings:

(1) CNT layered membranes have the ability to resist membrane fouling for extended periods of time, with all

modified membranes except that layered with surfactant-coated CNTs resisting fouling to a greater degree than an unmodified PVDF membrane. Larger diameter pristine MWCNTs were particularly effective in reducing fouling, an effect correlated with their stronger adherence to the membrane surface during backwashing compared to smaller diameter MWCNTs.

- (2) CNTs forming homogeneous porous layers on membrane surfaces resisted fouling to a greater degree than those forming heterogeneous layers, as they were able to more effectively remove fouling materials from the water before they could reach the membrane.
- (3) CNT layered membranes show practical promise because increased loading was linearly associated with increased resistance to fouling and baseline TMP, but the per area masses used in this experiment did not sufficiently raise the TMP beyond normal LPM operational levels.
- (4) Future studies will continue to explore the capabilities of different types of CNTs to remove other waterborne contaminants, potentially leading to the development of multilayered, multifunctional membranes tailored to remove specific aquatic contaminants. The antifouling properties of these membranes will ensure the sustainability of these treatment processes.

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Appendix A. Supplementary material

Supplementary material related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2012.07.059>.

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