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OZONE CLEANING OF FOULED POLY(VINYLIDENE) FLUORIDE/CARBON NANOTUBE MEMBRANES

Jono Suhartono[1,2], Chedly Tizaoui[2]

[1]Chemical Eng. Department, Institut Teknologi Nasional, Jl. PHH. Mustafa No.23, Bandung, 40124 Indonesia

[2]Systems and Process Engineering Research Centre, College of Engineering, Bay Campus, Swansea University, Swansea, SA1 8EN, UK.

jonosuhartono@yahoo.com; c.tizaoui@swansea.ac.uk

Abstract

This research demonstrates for the first time that ozone is an effective cleaning agent for polyvinylidene fluoride (PVDF) membranes fouled by natural organic matter (NOM). Bare PVDF membranes as well as PVDF impregnated with CNTs (pristine (CNTs–P) and oxidized (CNTs–O)) at 0.3 %mass membranes were used. Three different methods were investigated for cleaning the fouled membranes including; A: 10min cleaning by pure water, B: 5min water followed by 5min ozonated water, and C: 10min fully ozonated water. It was found that the application of fully ozonated water for 10 minutes was very effective to reinstate the flux to almost its original value of un-fouled membrane. The CNTs–P/PVDF membrane exhibited the highest fouling with a total fouling ratio of 81% whilst for the bare PVDF and the CNTs–O/PVDF membranes, the fouling ratios were 76% and 74%, respectively. The full ozonated water cleaning method gave the highest removal of fouling leaving the lowest irreversible fouling on the membrane as compared to the other cleaning methods. On the other hand, the highest removal of NOM fouling was obtained for CNTs–O/PVDF membranes indicating that fouling on CNTs–O/PVDF membrane was less bound than the other membranes. Contact angle measurements of the fouled membranes showed that all membranes exhibited increased contact angles due to the NOM deposition but after cleaning, particularly with ozonated water, the membrane contact angles returned to almost their original values. FTIR analysis of the membranes corroborated the results obtained.

Keywords: Ozone; PVDF membrane; carbon nanotubes; membrane fouling; membrane cleaning.

1. Introduction

Membrane fouling leads to operational failure where the permeate flow constantly decreases due to the adherence of different foulants to the membrane surface. Amongst membrane foulants, organic fouling is a serious problem in membrane-based water treatment. Organic fouling can occur via adsorption at molecular level, deposition or cake formation of organic colloids, and pore restriction or blocking by molecules that penetrate into the membrane (Schäfer et al., 2005). Among many potential organic foulants, natural organic matter (NOM) is one of the most common and problematic foulants in surface water (Zazouli et al., 2008). The amount and the physical and chemical properties of NOM greatly vary with climate and the hydrological regime as well as a number of other environmental factors (Sharp, Parsons and Jefferson, 2006). The presence of NOM in surface water is hence inevitable and may generate problems in water treatment plants all the way to consumers (Metsämuuronen et al., 2014).

Appropriate membrane selection, pre-treatment process, applied operating design and conditions are all recognized as methods to control membrane fouling (Vatanpour et al., 2011). However, all the above efforts cannot prevent fouling and cleaning methods will always be employed in practice (Mulder, 1996). The most important cleaning methods use chemicals where a number of individual chemicals or in combination at given concentrations are used to clean the membrane. Chemicals such as scale inhibitors, biocides, and surfactants are used to clean and control fouling in membranes. These chemicals can be expensive, have adverse effects on the quality of water, reduce membrane life time, and difficult to remove from within the pores and membrane surface.

Commonly, sodium hydroxide solutions are applied to remove organic and microbial foulants (Liu et al., 2001) but certain membrane types such as cellulose or polyvinylidene fluoride membranes might react with caustic resulting in degradation of the membrane's active layer. Cellulose based membranes have to be used under a limited pH range to prevent their hydrolysis (Liu et al., 2001) whilst in the presence of a base, especially sodium hydroxide, PVDF membranes

dehydrofluorinate which results in large membrane defects and crazing (Bottino, Capannelli and Comite, 2006).

The properties of polymeric membranes could be enhanced by the addition of fillers such as carbon nanotubes (CNTs).   CNTs have low density, high aspect ratio, and extraordinary mechanical properties which make them particularly attractive as reinforcements in composite materials (Spitalsky et al., 2010). The presence of CNTs in polymeric materials also increases membrane fluxes and improves membrane rejection of water solutes (Suhartono and Tizaoui 2015). Although, impregnation of CNTs into polymeric membranes provides useful membrane properties, membrane fouling remains an issue.

With the above issues in mind, there is clearly a need for new cleaning agents that provide efficient removal of organic foulants whilst being benign towards selected membrane materials. A promising chemical agent in cleaning NOM fouled membranes is ozone, which is a well-known oxidant being used effectively in water treatment for over a century now. In this study, ozone cleaning of different types of PVDF membranes was for the first time studied. This study is significant as it provides a novel and effective cleaning method for fouled PVDF membranes.

2. Materials and methods

Poly(vinylidene) fluoride (PVDF) was chosen as the membrane material due to its high compatibility to ozone. PVDF (Kynar[®] 761) powder was a gift from Arkema, Ltd. and its properties are provided in Table 1.

<p align="center">*Table 1: Physical properties of Kynar$^{®}$ 761*</p>

Material Form	Powder
Material Colour	White
Melt Viscosity, 232°C (Kps)	27
Solution Viscosity, 20°C (cps)	400
Specific Gravity, 23°C	1.77 – 1.79
Water Absorption, Immersion/24h (%)	0.01 – 0.03
Melting Temperature (^{o}C)	162 – 172

Pristine multiwalled carbon nanotubes (CNTs-P) were purchased from Sigma Aldrich, UK whilst plasma oxidized multiwalled carbon nanotubes (CNTs-O) were kindly supplied by Haydale, Ltd. Both of the CNTs were used as received without any further treatment. Properties of both CNTs are shown in Table 2.

<p align="center">*Table 2: Physical properties of CNTs*</p>

Physical Properties	CNTs-P	CNTs-O
Carbon Content (%)	> 95	96.08
Outer Diameter (nm)	6-9	~13-16
Length (μm)	5	~1
Bulk Density (g/cm^3)	0.22	~0.19
Oxygen Content (%)	NA	3.5 – 4

N-methyl-2-pyrolidone (NMP, C_5H_9NO) was chosen as the polymer solvent due to its high ability in dissolving PVDF polymer and also being effective in dispersing carbon nanotubes. Analytical grade NMP was purchased from Sigma Aldrich, UK (99% purity, 99.13 g/mol) and used without any further purification. Humic acid (HA) representative of NOM was purchased from Sigma Aldrich UK. Deionised (DI) water from a Milli-Q water purification system (Millipore, UK) was used for all experiments.

Membrane fabrication was described elsewhere (Suhartono and Tizaoui, 2015). Briefly, the method involved: CNT dispersion in NMP, homogenization of PVDF/CNT matrix, and fabrication of PVDF/CNT membrane by the immersion precipitation method.

Three different membrane types, pure PVDF, 0.3 %mass CNTs-P/PVDF and 0.3 %mass CNTs-O/PVDF, were fabricated and used in this study. Membrane fouling was made by filtering a 1 g/L HA solution at pH 7 for approximately seven hours and before each fouling experiment, the membranes were tested for their initial pure water flux. The Transmembrane Pressure (TMP) and retentate flowrate were set at 3.85 bar and 1 L/min respectively.

Membrane cleaning was performed using three different methods: (A) membrane cleaning with 10 L of DI water only, (B) membrane cleaning with 5 L of DI water followed by 5 L of ozonated DI water (3 mg O_3/L) and (C) membrane cleaning with 10 L of ozonated DI water (3 mg O_3/L). The membrane cleaning operation was operated at similar TMP and retentate flowrate as the membrane fouling operation. Ozone concentration for membrane cleaning was set at 3 mg/L and monitored with a Dissolve Ozone System (Analytical Technology, Inc., Collegeville, USA). The membrane cleaning performances were evaluated by calculating membrane flux using the following sequence of equations:

$$J_{w,i}, J_s \text{ or } J_{w,ac} = \frac{V}{At} \tag{1}$$

Where $J_{w,i}$, J_s, and $J_{w,ac}$ are the initial pure water flux, solute flux, and water flux after membrane cleaning (L/m².h). V is volume of permeate (L) at each stage, A is membrane area (m²) and t is the operating time (h). The membrane flux recovery ratio (RR) and fouling indicators were calculated using:

$$RR(\%) = \frac{J_{w,ac}}{J_{w,i}} \times 100\% \tag{2}$$

$$R_t = \left(\frac{J_{w,i} - J_S}{J_{w,i}}\right) \times 100\% \tag{3}$$

$$R_r = \left(\frac{J_{w,ac} - J_S}{J_{w,i}}\right) \times 100\% \tag{4}$$

$$R_{ir} = \left(\frac{J_{w,i} - J_{w,ac}}{J_{w,i}}\right) \times 100\% \tag{5}$$

where R_t is total fouling ratio, R_r is reversible fouling ratio, and R_{ir} is irreversible fouling ratio.

NOM concentrations were measured by a UV–Vis spectrophotometer (Agilent 8453, Agilent Technology, UK) using a pre-determined calibration curve at a wavelength of 254 nm. The membrane wettability was determined by contact angle measurements with a DAT 1100 (Fibro System ab, Sweden) using 4 µL of DI water as the wetting liquid. The measurement of the contact angle was made 12s after the wetting liquid was dropped on the membrane surface and the values were presented as averages of five readings. The molecular structure of the clean and fouled membrane surface was determined by a universal sampling attenuated total reflectance (ATR) combined with Fourier Transform Infrared (FTIR) spectroscopy (Frontier FTIR spectrometer, PerkinElmer, UK).

3. Results and discussion

3.1. NOM fouled membranes

3.1.1. Membrane flux

The initial pure water flux of the membranes is shown in Table 3 whilst the flux decline trend during fouling is shown in Figure 1. All fouled membranes exhibited significant rapid flux decreases by up to 69%, 79% and 51% after only 2 minutes of operation for bare PVDF, CNTs-P/PVDF and CNTs-O/PVDF membranes, respectively. Following this rapid fouling period, the membrane fluxes slowly dropped until reaching constant values after approximately 2 hours of operation. The precipitous drop in permeate flux is the result of rapid interaction between NOM and the membrane surface to form a cake layer and possibly clogging of the internal pores of the membranes (Cho, Amy and Pellegrino, 1999).

Table 3: Pure water membrane fluxes (TMP of 3.85 bar, 1 L/min constant retentate flowrate)

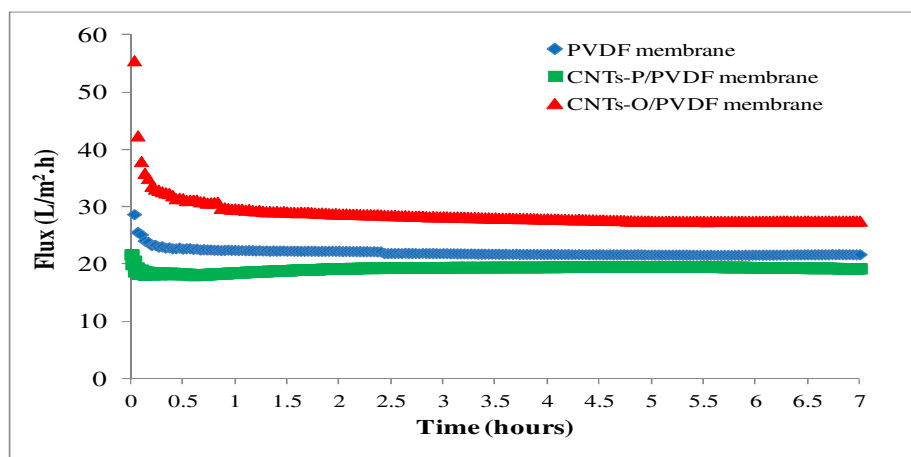| Membrane	Pure water flux (L/m^2.h)
Bare PVDF membrane	92.5
CNTs-P/PVDF membrane	101.8
CNTs-O/PVDF membrane	112.0

Figure 1: Membrane flux trends of 1 g/L NOM feed solutions filtered at a TMP of 3.85 bar, 1 L/min constant retentate flowrate, and pH 7.

Interestingly, Figure 1 shows that the CNTs–P/PVDF membrane exhibited a higher decreasing flux than the other membrane types. The addition of CNTs in PVDF membranes was projected to increase the membrane electronegativity and increase the membranes performance in repelling NOM which are negatively charged compounds at higher pHs. However, the high NOM hydrophobic fraction in Aldrich humic acid appears to result in higher hydrophobic interactions with the membrane. It is known that CNTs-P has high hydrophobic characteristics where their contact angle was approximately 105° (Werder et al., 2001). Thus, higher membrane hydrophobic character was obtained for the impregnated CNTs-P membrane than the bare PVDF membrane, which increases fouling.

Hydrophobic attraction is a natural tendency between membranes and solutes with a similar structure ("like attracts likes" interactions are generated from van der Waals force between molecules). The Van der Waals cohesive energy for a 12-C organic segment is approximately 30 kJ/mol which exceeds the electrostatic repulsion energy from dissociation of one charge group (Liu et al., 2001). Thus, hydrophobic adhesion will start to overcome the energy of electrostatic repulsion when the ratio of C-atoms to charged functional groups is greater than 12. This produces adhesion of solutes onto the membrane surface. These hydrophobic attractions were the main

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effects responsible for generating fouling of the membrane surface, and hence reducing the membrane electrostatic repulsion of CNT impregnated PVDF membranes.

3.1.2. Membrane rejection

According to Figure 2, CNT impregnated membranes show an improvement in the rejection of NOM as compared to the bare PVDF membrane following the order CNTs-O/PVDF > CNTs-P/PVDF > bare PVDF membrane. The rejections at 50 mL permeate were 78%, 82% and 88% for bare PVDF membrane, CNTs–P/PVDF membrane, and CNTs–O/PVDF membrane respectively (Figure 2). As permeation is extended, the rejections dropped slightly to reach at 200 mL permeate 70%, 74% and 84% for the same order of membranes used. The slight decrease of membrane rejection for longer operation could be explained by escaping fractions of the foulant which absorb UV254. On the other hand, the higher NOM rejection observed in CNTs/PVDF membranes may be caused by stronger membrane electronegativity imparted by the CNTs which improves the membrane ability to repel negatively charged NOM molecules. Moreover, the addition of carbon materials into the membrane matrix could improve the adsorption ability of the membrane for NOM and hence increase NOM rejection.
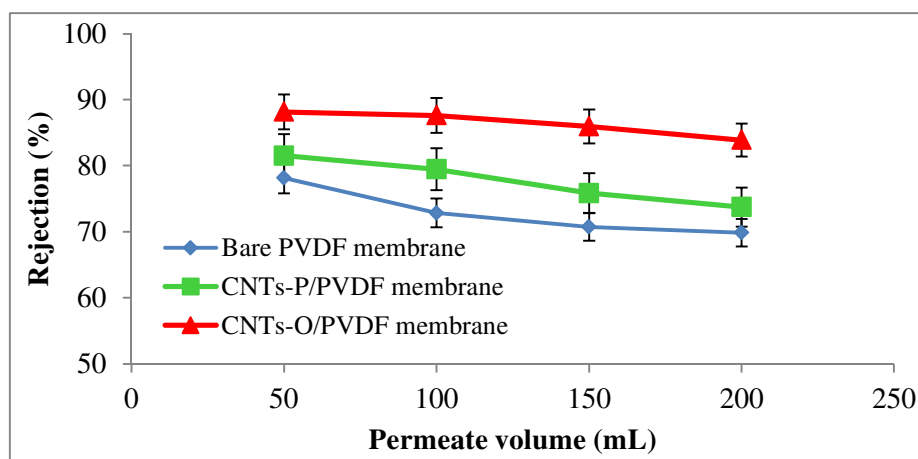

Figure 2: Profile of NOM rejection for an operating TMP of 3.85 bar, 1 L/min constant retentate flowrate, and pH 7.

3.2. Membrane cleaning

The fouled membranes were cleaned by three different methods which were cleaning by water (method A), cleaning by water and followed by 3mg/L ozonated water (method B), and cleaning by only 3mg/L ozonated water (method C). Each cleaning method was conducted using a 1 L/min flowrate for 10 minutes in a single pass (i.e. the cleaning solution was not returned into the feed tank). The applied ozone concentration in the water for membrane cleaning was set at 3 mg/L.

3.2.1. Cleaned membrane flux profile

Once the membrane has been cleaned using either method A, B or C, pure water was passed through the membrane for 30 minutes. The changes of flux with time for fresh, fouled and cleaned membranes are shown in Figure 3 and the flux recovery ratios (RR) of cleaned membranes using the three different methods are shown in Table 4. The ozone cleaning (method C) gave the highest flux recovery as shown in both Table 4 and Figure 3. The flux of the bare PVDF membrane was increased from 22 $L/m^2.h$ for the fouled membrane to 59 $L/m^2.h$ after 10 minutes of cleaning using pure water (method A). Meanwhile, method B (5 minutes water cleaning followed by 5 minutes ozone cleaning) was able to increase membrane flux by 33% more than method A. Application of ozonation for 10 minutes was very effective and reinstated the flux to almost its initial value for the clean membrane. With 10 min ozonation (method C), the flux increased by 52% more than method A. Similar trends were also obtained for impregnated CNTs-P/PVDF membrane. Meanwhile, water cleaning performed for CNTs-O/PVDF membrane was able to improve the flux up to 82.2 $L/m^2.h$ and method C fully recovered the flux of this membrane to almost its initial value (Figure 3). Ozone is a strong oxidant that reacts with NOM to form molecules with lower molecular masses (e.g. organic acids, aldehydes and ketones) which can easily be detached and transported away from the pores upon permeation of water. This results in the opening of the blocked membrane pores more effectively and reestablishment of the initial clean membrane flux.
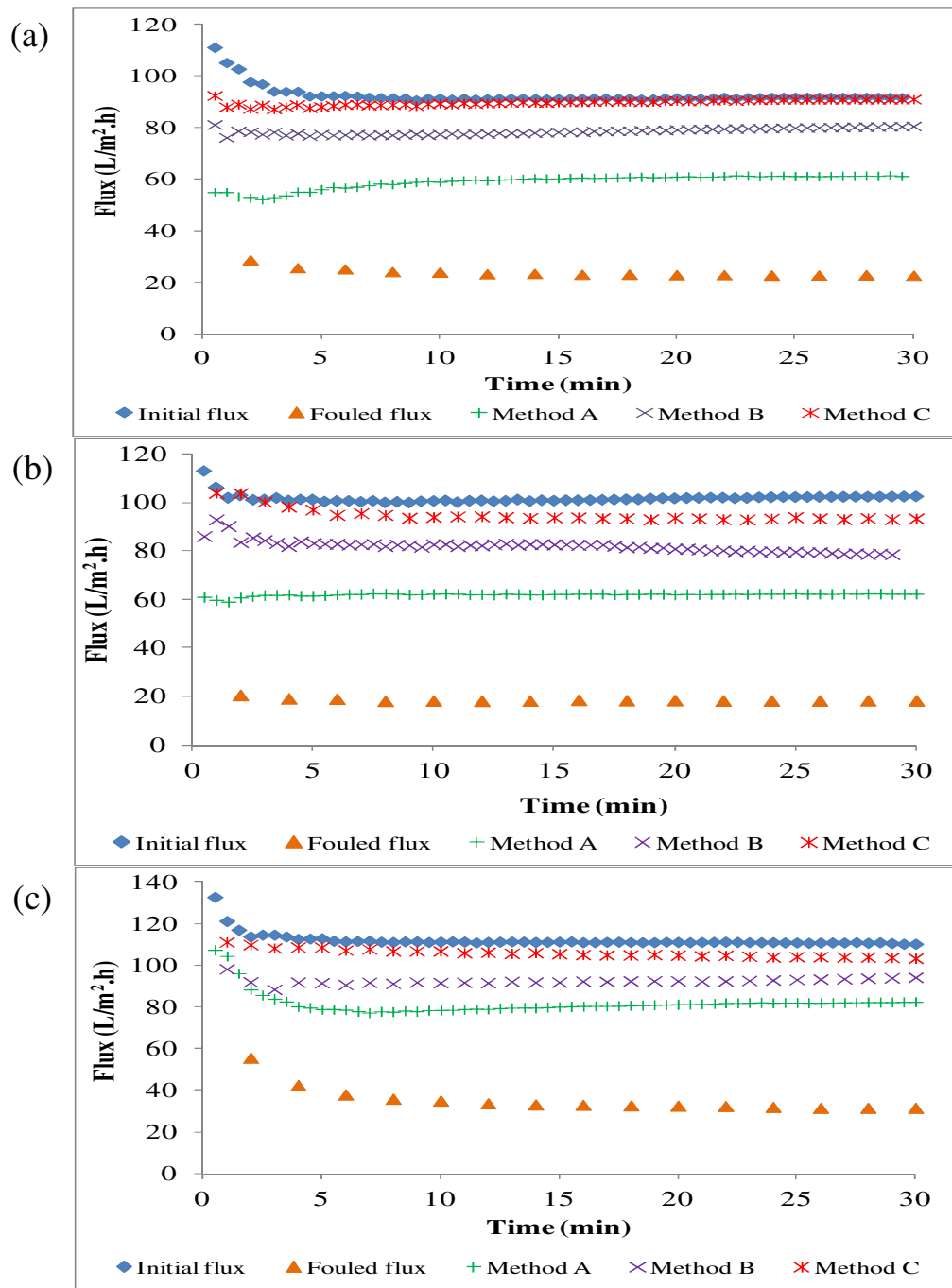
Figure 3: Profile of membrane fluxes before and after cleaning (a) PVDF membrane, (b) CNTs–P/PVDF membrane and (c) CNTs–O/PVDF membrane. Method A: 10 min water cleaning, Method B: 5 minute water cleaning followed by 5 minute ozonation cleaning, Method C: 10 minute ozonation cleaning. The cleaning methods used a 1 L/min retentate flowrate, 3.85 bar TMP, and 3 mg/L O₃ concentration, pH 7.

Table 4: Effect of cleaning method on membrane fluxes

Membrane	Initial flux (L/m².h)	Fouled flux (L/m².h)	Flux after cleaning (L/m².h)			Flux recovery (%)		
			A	B	C	A	B	C
Bare PVDF membrane	92.5	22.0	59.0	78.6	89.8	63.9	85.0	97.1
CNTs–P/PVDF membrane	101.8	19.3	62.1	82.0	94.6	61.0	80.6	92.9
CNTs–O/PVDF membrane	112.0	28.7	82.2	92.3	105.7	73.4	82.4	94.4

Flux recovery obtained by method C was the highest for the all three types of membranes. However, flux recovery showed a different trend when comparing the bare PVDF membrane to the CNT impregnated membranes. Using method A, the flux recovery of the CNTs–O/PVDF membrane was the highest whilst the lowest flux recovery value was obtained for the CNTs–P/PVDF membrane (Table 4). However, as shown in Table 4, when ozone was used, the highest flux recoveries were obtained for the bare PVDF membrane but in terms of absolute permeate flux values, both of the CNT impregnated membranes gave higher fluxes than the bare PVDF membrane. For all cleaning methods, CNTs-P/PVDF membranes exhibited the lowest flux recovery as compared to the other membrane types.

Given that impregnated CNTs–P membranes exhibit higher hydrophobic properties, their hydrophobic attraction with NOM could also increase. Hence, this type of membrane will have a higher fouling tendency when compared to the other two membranes and will clearly require more rigorous action to be cleaned. On the other hand, higher flux recovery of CNTs–O/PVDF observed when only water was used to clean the membrane could be explained by increased hydrophilic properties of the membrane imparted by the oxidized functional groups in CNTs-O, which could also impose a greater electronegativity on the membrane thus increasing membrane repulsion of NOM. The electronegatively charged surface of the membrane also loosen the interaction with NOM making the cleaning process more easy to perform when only water was used.

3.2.2. Fouling characteristics

Total fouling ratios were obtained by comparing flux losses of fouled membranes to the initial water fluxes (Equation 3). As shown in Figure 4, the CNTs–P/PVDF membrane exhibited the highest fouling ratio (81%) which is likely due to stronger hydrophobic attraction between NOM and CNTs-P/PVDF membrane. Although the CNTs–O/PVDF membrane exhibits less hydrophobicity than the bare PVDF membrane, the two types of membranes have comparable total fouling ratios (76% for bare PVDF and 74% for CNTs–O/PVDF membranes – Figure 4).
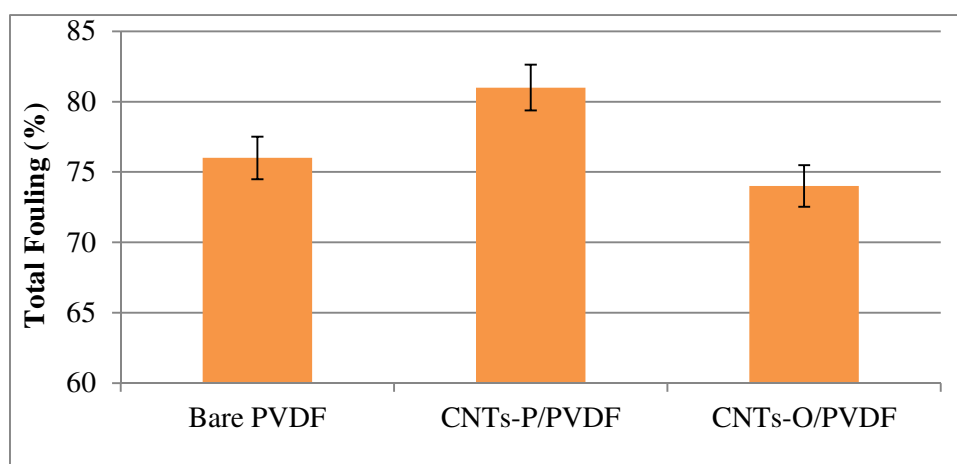

Figure 4: Total fouling ratio of the membrane after filtration at 1 L/min retentate flowrate, a TMP of 3.85 bar and pH 7 for 7 hours of operation.

It has been known that CNTs have shown an excellent performance in removing via adsorption both hydrophobic and hydrophilic organic matter in water (Lu and Su, 2007; Zhang et al., 2010; Zhang, Shao and Karanfil, 2011; Joseph et al., 2012). Hence, the adsorption of both hydrophilic and hydrophobic fractions of NOM could contribute to the overall fouling of the membranes. The fouling could cause either reversible or irreversible flux decline analogous to reversible or irreversible fouling. The reversible fouling is the fouling that can be removed by the applied cleaning method whilst the irreversible fouling is the fouling that remained in the membrane after the cleaning process is finished. Thus, irreversible fouling generates permanent flux loss.

Figures 5 and 6 show that method C produced the highest removal of reversible fouling and as a result the irreversible fouling was the lowest as compared to methods A and B. The use of ozone in membrane cleaning obviously reduced more of the organic foulant by converting the irreversible fouling into reversible fouling. Membrane cleaning using 3 mg/L of ozone concentration for 10 minutes significantly increased the reversible fouling up to 83% and decreased the irreversible fouling by up to 92% when compared to cleaning by water only.

Similarly, method B exhibited a significant increase in reversible fouling up to 53% and decreased the irreversible fouling by 58% when compared to method A. This two-step cleaning process has effectively removed the NOM foulant by firstly cleaning the concentration polarization in membrane surface and then reducing the foulant layer thickness through 5 minutes of water cleaning. Further cleaning using ozone has effectively converted irreversible fouling into reversible fouling since ozone can penetrate deeper into the membrane layer and opened the blocked pores. Although method B was quiet effective for reducing irreversible fouling, its performance was less superior than method C, which significantly reduced the irreversible fouling by 80% when compared to method B.

CNTs–O/PVDF membranes exhibited the highest reversible fouling removal via method A (47.8%), followed by the CNTs–P/PVDF membrane and the bare PVDF membrane (42% and 40%, respectively). On the other hand, ozone cleaning (methods B and C) has reversed this pattern where the CNTs–O/PVDF membrane showed the lowest reversible fouling removal (Figure 5).

The highest removal of fouling for the CNTs–O/PVDF membrane using the water cleaning method indicates that the fouling in this type of membrane was less bound than the other membranes. Stronger electronegativity and higher hydrophilic properties of this membrane are likely to be the main causes of this weakened interaction of NOM with the membrane surface. However for ozone cleaning, the fouling removal of the CNTs–O/PVDF membrane was slightly less than the bare PVDF and CNTs–P/PVDF membranes. Fouling removal was approximately 73% for the bare PVDF and the CNTs–P/PVDF membranes whilst for the CNTs–O/PVDF membrane was

approximately 69%. In addition to reacting with NOM, ozone may also react with CNTs-O (Hemraj-Benny, Bandosz and Wong, 2008; Morales-Lara et al., 2013), which could explain the reduced fouling removal in CNTs-O/PVDF membrane.
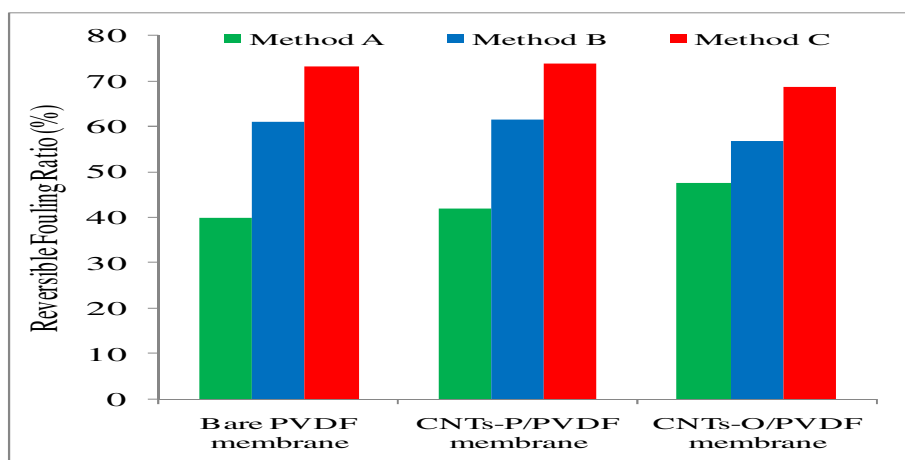

Figure 5: Reversible fouling ratio (removed) of the tested membranes; cleaned by 10 minutes water (method A), 5 minutes water followed by 5 minutes ozonated water (method B) and 10 minutes ozonated water (method C) at 3.85 bar TMP, 1 L/min retentate flowrate, and 3 mg/L of ozone concentration in water.
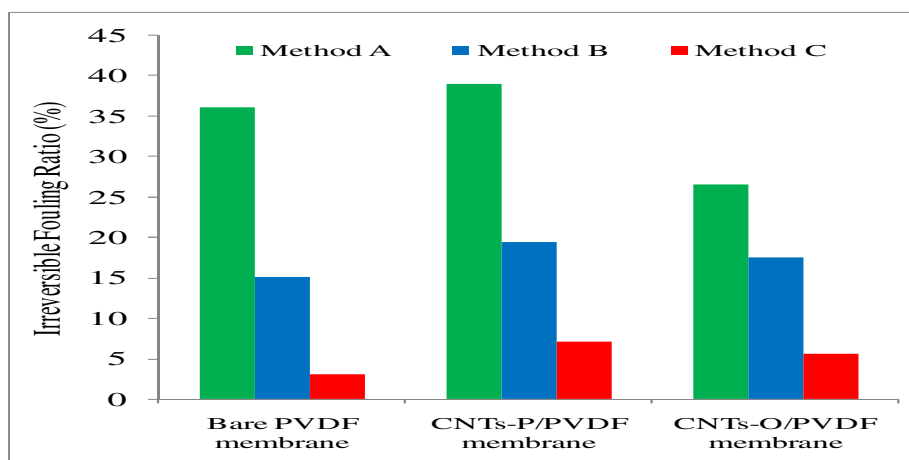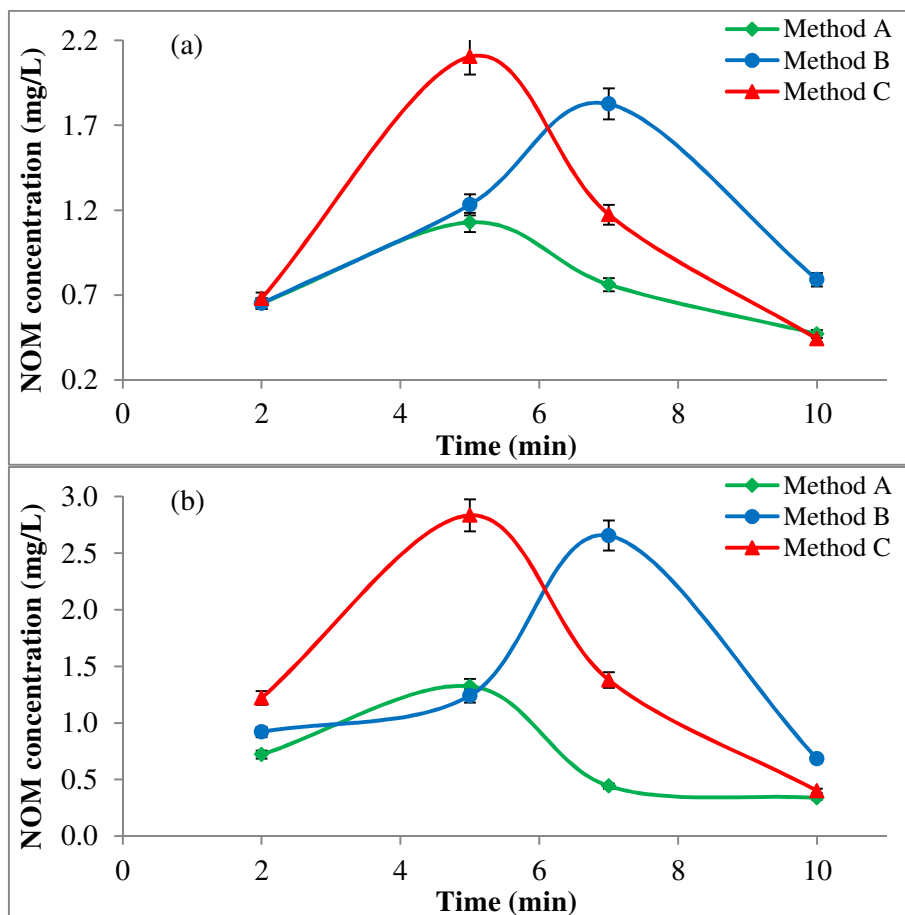

Figure 6: Irreversible fouling ratio (remained) of the tested membranes; cleaned by 10 minutes water (method A), 5 minutes water followed by 5 minutes ozonated water (method B) and 10 minutes ozonated water (method C) at 3.85 bar TMP, 1 L/min retentate flowrate, and 3 mg/L of ozone concentration in water.

3.2.3. Ozone and NOM exposure in permeate during cleaning

NOM deposition on membrane surface and within the pores might come out as permeate product during cleaning, especially when ozone is used since oxidation of NOM leads to easily detachable

smaller fractions of the NOM compounds. Hydrodynamic pressure may also affect the mobility of NOM and eventually leads to NOM exiting in the permeate.

In this study, high TMP was used to ensure that both the fouled membrane surface and the membrane internal pores are all cleaned. Figure 7 shows the NOM concentrations in permeate obtained during membrane cleaning by each method. According to the figure, all cleaning methods resulted in NOM exiting the membrane which indicates that NOM was indeed detached and displaced to the permeate. The high concentration of NOM used during the fouling step had severely fouled the membranes not only on their surface but also into the deeper parts of the membrane body. These adsorbed foulants were then brought out by the cleaning agent and were detected in the permeate product.
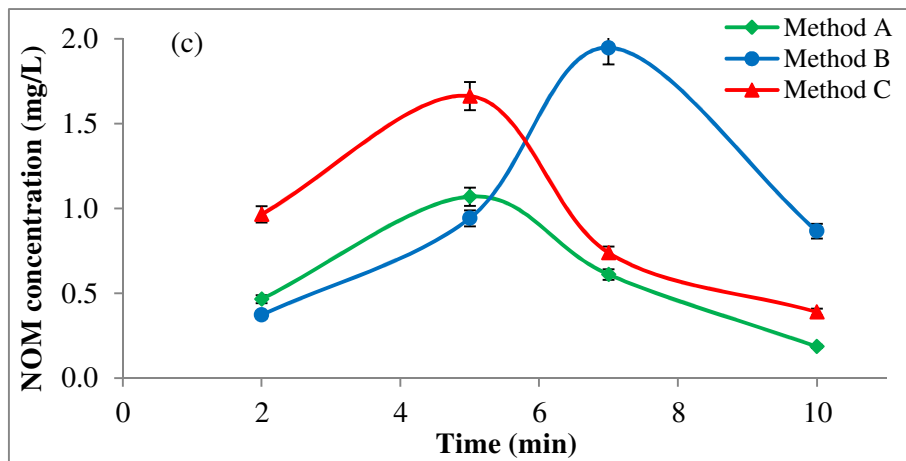
Figure 7: NOM profile in permeate product during cleaning (a) bare PVDF membrane (b) CNTs–P/PVDF membrane (c) CNTs–O/PVDF membrane cleaned by 10 minutes water (method A), 5 minutes water followed by 5 minutes ozonated water (method B) and 10 minutes ozonated water (method C) at 3.85 bar TMP, 1 L/min retentate flowrate, and 3 mg/L of ozone concentration in water.

Figure 7 also shows that a maximum NOM concentration in the permeate was obtained after 5 minutes for methods A and C whilst for method B it was obtained at 7 minutes. Further membrane cleaning after these times resulted in decreasing NOM content in the permeate product. The NOM concentrations after 5 minutes cleaning with method A and B are similar (Figure 7) because both methods used pure water during this period. However, as ozone was introduced in method B for the next five minutes of cleaning, the NOM concentration was increased further to reach a maximum at 7 minutes. This clearly shows that ozone was effective to remove any difficult NOM fouling attached to the membrane. For both methods B and C, membrane cleaning by ozonated water produced more NOM as measured by increased UV254 in the permeate (Figure 7). It seems that the longer chain NOM aromatic groups were degraded into smaller chains which give them a higher ability to penetrate the membrane pores and leave the membrane in the permeate. This is because ozone removes unsaturated bonds in the NOM molecule creating smaller organic molecules and producing more carbonyl, carboxyl, hydroxyl, alkoxyl and amino groups which have more hydrophilic properties as compared to the parent molecules (Van Geluwe et al., 2011).

The ratio of ozone concentration in the permeate to the feed cleaning solution concentration is shown in Figure 8. The figure shows that ozone concentration ratio increased as the cleaning time

increased. The lower ozone concentration in the permeate than the cleaning feed ozone concentration during the early part of the cleaning step (t < ~7 min) indicates effective ozone consumption by the NOM retained on the membrane. As NOM is oxidized and removed away from the membrane in the permeate, ozone concentration increases to reach the feed solution concentration after about 10 minutes operation (i.e. ozone concentration ratio ≈ 1). This indicates that ozone consumption becomes insignificant once the NOM has been removed.
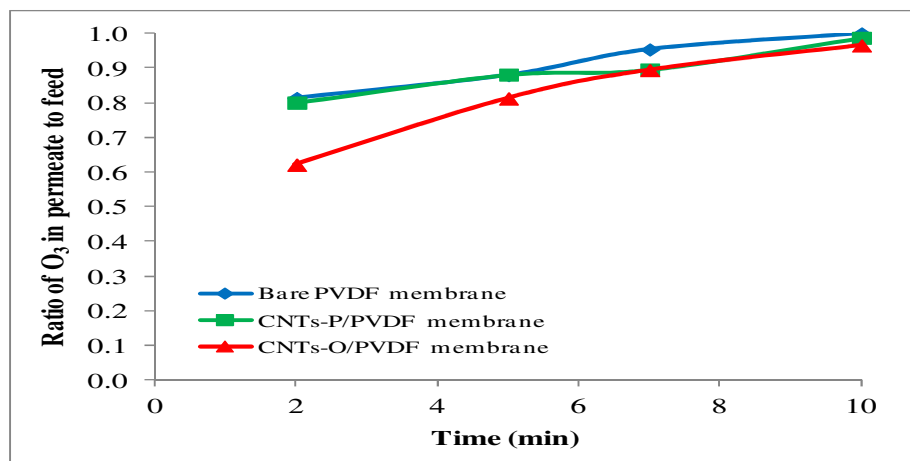

Figure 8: Ratio of ozone concentration in permeate to ozone concentration in feed during cleaning by 3 mg/L ozonated water.

3.2.4. Fouled membrane autopsy by contact angle

Figure 9 shows that all the membranes exhibited an increasing contact angle due to NOM fouling. The contact angles of the membranes were increased from 73°, 75°, and 72° to 81°, 83° and 78° for the bare PVDF, CNTs–P/PVDF and CNTs–O/PVDF membranes respectively. The increasing contact angle was due to the deposition of NOM on the membrane surface. This is because the used Aldrich humic acid contained a high hydrophobic fraction which is approximately 86% of the fractionated parts (Lin, Lin and Hao, 2000). Increasing of the contact angle due to NOM fouling is also in accordance with other studies (Cho et al., 1998; Al-Amoudi et al., 2008).

The membrane contact angle values decreased with respect to the cleaning method used where cleaning by method C gave the lowest contact angle followed by method B and method A. This

adds further support that the application of ozone in the cleaning of NOM-fouled membranes was very effective for NOM removal from membrane surfaces. The presence of ozone in water not only creates effective elimination of concentration polarization but it also oxidizes NOM into relatively smaller organic molecules that easily detach from the membrane surface. Therefore, the removal of NOM resulted in less fouled membranes as indicated by the contact angle values which decreased to almost their original values of each un-fouled membrane (Figure 9).
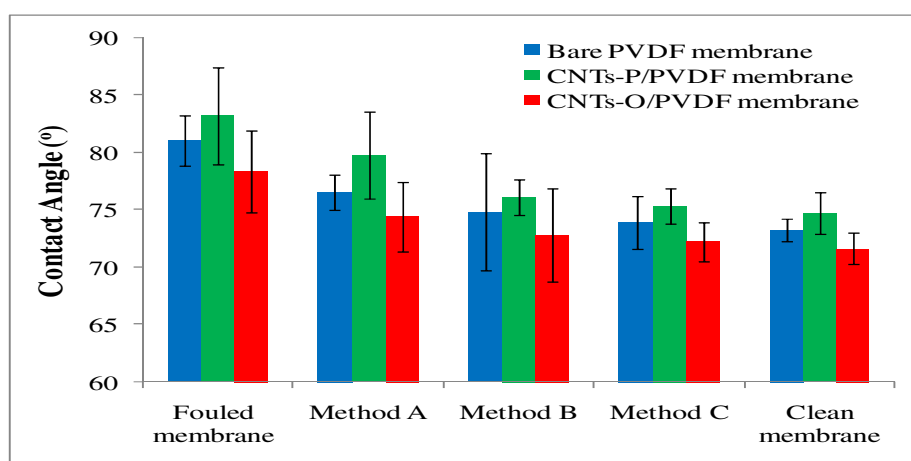

Figure 9: Average contact angles of the unfouled, fouled and cleaned membranes (measurement was made at 12s after the water droplet contacted the membrane surface).

3.2.5. IR spectra of fouled membranes

The infrared spectra of both clean and fouled membranes are shown in Figure 10. In general, all spectra show high peak bands at $1500 - 1800$ cm^{-1} and $2800 - 3100$ cm^{-1}. Absorbance at wavelengths $1600 - 1700$ cm^{-1} is due to C=O groups either in carbonyl or carboxyl groups (Bottino et al., 2006) whilst absorption at $1517 - 1590$ cm^{-1} represents the deformation of COO$^-$ functional groups (Zularisam, Ismail and Salim, 2006). Peak bands at 2850 and 2920 cm^{-1} are representative of the asymmetric and symmetric C–H stretching in methylene groups whilst symmetric C–H stretching in methyl groups and aromatic groups show peaks at 2980 cm^{-1} and $3000 - 3100$ cm^{-1} respectively (Stuart, 2005). All membranes show peaks at 1545 and 1660 cm^{-1} indicating the presence of C=O functional groups. These peaks become deeper as the membrane is fouled by NOM. Moreover, the broad peak at 3200-3550 cm^{-1}, which is due to the –OH group of phenolic and

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carboxylic moieties found in large numbers in humic acids, became stronger as the membrane was fouled is indicative of the deposition of NOM on the membrane surface (Stevenson, 1994).

Application of cleaning methods A, B and C on the fouled membranes lead to reduction of the FTIR bands that resulted from NOM deposition and the spectra of cleaned membranes, particularly by methods C and B, evolved to almost matching the spectra of the membranes before fouling. This indicates that the ozone-based cleaning methods have cleaned the membrane surfaces well and the addition of ozone was effective to fully remove the NOM deposited on the membrane. Importantly, ozone does not only attack the fouling on the surface as evidenced by FTIR results but also it degrades any deposited NOM molecules further deeper in the internal pores of the membrane and hence removes significantly the fouling as shown in Figures 5 and 6. The FTIR results are also in agreement with the flux results which showed that after cleaning with method C, the flux recovered to almost its initial value of un-fouled membrane (Figure 3).
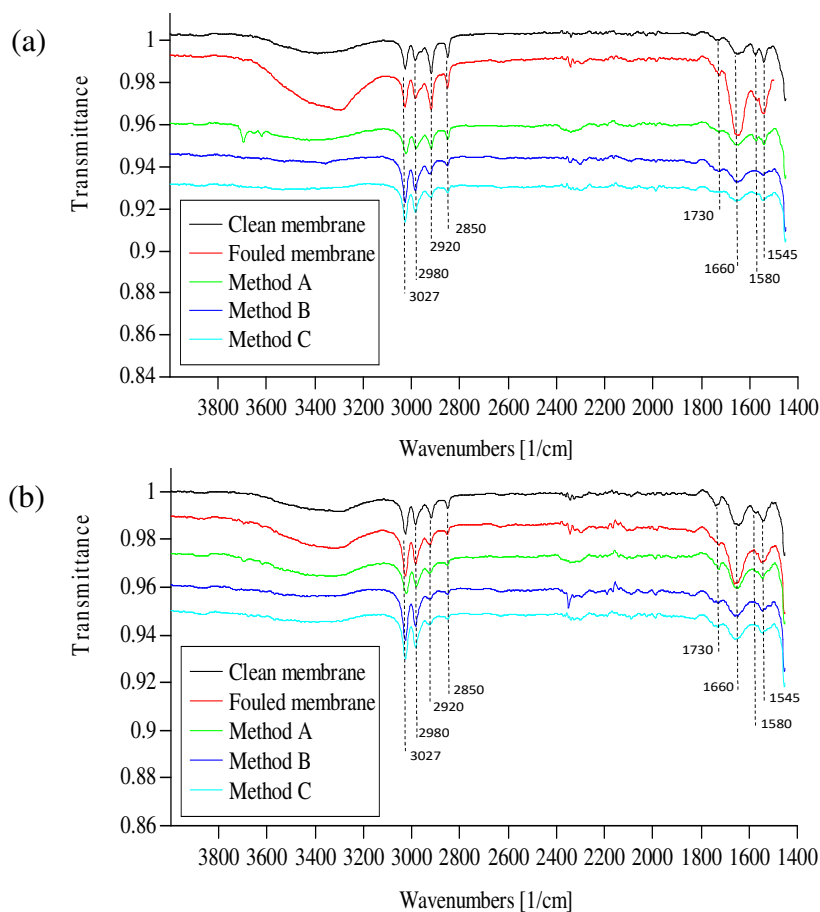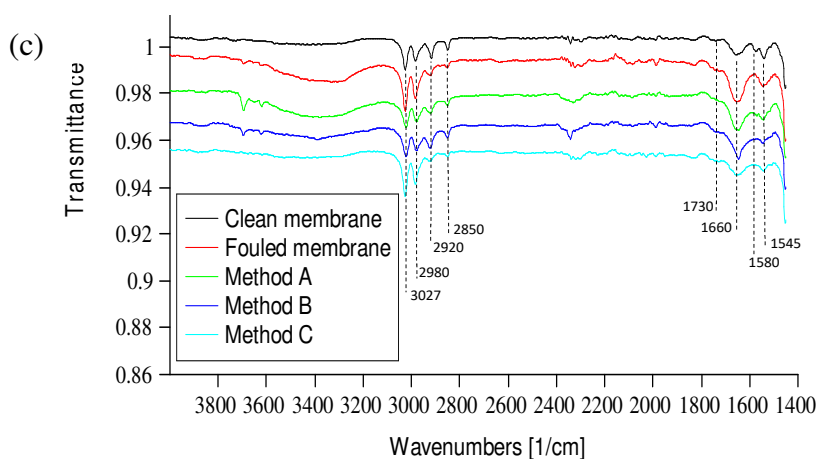
Figure 10: Infrared spectra of membranes; (a) PVDF membrane, (b) CNTs-P/PVDF membrane and (c) CNTs-O/PVDF membrane. Method A: 10min water cleaning, Method B: 5min water cleaning followed by 5min ozonation cleaning, Method C: 10min ozonation cleaning.

Conclusions

Three types of membranes (bare PVDF, CNTs-P/PVDF and CNTs-O/PVDF membranes) were fouled with NOM and then cleaned using three different methods including 10 minutes water cleaning (method A), 5 minute water cleaning followed by 5 minute ozonation cleaning (method B), and 10 minutes ozonation cleaning (method C). All membranes exhibited a significant flux decrease when high NOM concentrations were filtered through them by up to 69%, 79% and 51% after just 2 minutes of filtration for bare PVDF, CNTs-P/PVDF and CNTs-O/PVDF membranes, respectively. On the other hand, membrane rejections were also dropped to 78%, 82% and 88% when 50 mL of permeate was collected for the bare PVDF membrane, CNTs–P/PVDF membrane, and CNTs–O/PVDF membrane respectively.

Among the three methods used, flux recovery obtained by method C was the highest. This was due to ozone attacking NOM and degrading it into relatively smaller molecules that easily detach from the membrane surface, thus opening the blocked pores and improving membrane flux. When comparing the three types of membranes, flux recovery of the CNTs–O/PVDF membrane was the highest whilst the lowest flux recovery was obtained for the CNTs–P/PVDF membrane using method A for cleaning. The opposite result was observed when ozone was used in methods B and

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C as the highest flux recoveries were obtained for the bare PVDF membrane instead of CNTs impregnated membranes. This might be caused by a consumption of a portion of ozone by CNTs which lower the effectiveness of ozone in removing NOM from the membranes.

The CNTs–P/PVDF membrane exhibited the highest fouling with the total fouling ratio reaching 81%, whilst for the bare PVDF and CNTs–O/PVDF membranes the ratio reached 76% and 74%, respectively. Stronger hydrophobic attraction of CNTs–P/PVDF membrane is believed to be the main cause for the observed high fouling in this type of membrane. Meanwhile, CNTs–O/PVDF membranes exhibited the highest reversible fouling removal and the lowest remained irreversible fouling. Stronger electronegativity and higher hydrophilic properties of this membrane are likely the main causes of this weakened interaction between NOM and the membrane surface thus making the foulants more easily cleaned from the membrane surface.

The contact angle analysis showed that the fouled membranes exhibited higher contact angles when compared to the un-fouled membranes and cleaning, particularly method C, reinstated the contact angles to almost their original values. No significant further ozone consumption was observed after NOM was fully removed from the membrane. This study hence demonstrates that ozone is an effective technique for the removal of NOM fouling on PVDF polymeric membranes.

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