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In-line coagulation to reduce high-pressure membrane fouling in an integrated membrane system: a case study

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ABSTRACT

Membrane fouling is a critical problem for many nanofiltration (NF) membrane plants. This study demonstrated that the poor spaces of the NF membrane were decreased for the deposition of natural organic matter (NOM) on the membrane surface. In-line coagulation was added prior to the low-pressure filtration step to remove more organic material by microfiltration (MF), thereby improving the quality of the feed-water entering the NF membranes. Three different types of coagulants, i.e. aluminum sulfate, ferric chloride, and polyaluminum chloride, with their different levels at different pH values were used for this study. The optimal dose of each coagulant was determined, and the impact on the NF membrane was assessed by batching and running 20 L of post-coagulation MF permeate through a bench-scale NF membrane for 200 h. Ferric chloride was found to perform the best of these three tested coagulants to reduce NF pressure fouling by reduction of NOM in the NF feed-water. High performance size exclusion chromatography study revealed that higher molecular weight fractions of NOM removed preferentially due to in-line coagulation processes. The scanning electron microscopy analysis of the fouled NF membrane trial revealed that the foulant layer consisted of a very large quantity of inorganic and organic matter, bacteria, which resulted in a very rough surface topography.

Keywords: Natural organic matter (NOM); Membrane fouling; Membrane processes; Coagulation; Nanofiltration

1. Introduction

In surface waters, natural organic matter (NOM) concentrations are typically high and increase seasonally especially in the spring and autumn as a result of heavy run-off and decomposition of organic matter [1,2]. Seasonal deviation results in high concentrations of terrestrial aromatics and other NOM fractions, which vary in molecular weight (MW), hydrophilicity, and fluorescence [2–5]. Reduction of NOM through feed-water pre-treatment is required for successful operation of high-pressure membranes [2,6]. Types of pre-treatment effective at mitigating NOM fouling include: filtration, coagulation, and advanced oxidation [7–9]. Coagulation has been favored for NOM

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removal due to its cost effectiveness and high removal capacity of humic matter [7,8,10]. Furthermore, membranes are capable of removing a wide range of organic and inorganic contaminants while maintaining a small footprint [11].

High-pressure membranes in integrated membrane systems (IMS) are attractive in drinking water treatment given their capacity to meet the increasingly stringent disinfection by-products standards [9,12]. Decreasing source water quality and invasion of saline waters into fresh water aquifers requires the implementation of membrane treatment to produce high-quality potable water [1,2]. The removal of NOM from water with pre-treatment results in more efficient and sustainable in membrane operation [6,11,13]. One of the disadvantages of using membrane in water purification systems is membrane fouling. Membrane fouling is characterized by increased transmembrane pressure (TMP) and decreased membrane performance [14]. Therefore, it consequences in increase the operational costs and decreased membrane life and permeate quality [15,16]. Membrane fouling and its effects are addressed using pre-treatment or operational parameters to improve the quality of the membrane feed-water [14,17].

Mitigation of nanofiltration (NF) membrane fouling would decrease operation costs and increase efficiency in water treatment facilities Therefore, this research project was directed to evaluate the addition of in-line coagulation prior to low-pressure filtration to mitigate high-pressure membrane fouling in an IMS for drinking water treatment. The specific objectives of this project were (1) evaluate the effect of low-dose in-line coagulation process prior to low-pressure membrane filtration in pre-water treatment for NF, (2) analyze the effectiveness of in-line coagulation with three coagulants, i.e. ferric chloride, aluminum sulfate, and polyaluminum chloride (PACL), followed by microfiltration (MF) as a pre-treatment.

2. Materials and methods

2.1. Collins park water treatment plant

The water treatment plant studied is a small system that supplies approximately 64 m^3/d in Nova Scotia [18]. The plant draws water from a lake in an unprotected watershed impacted by treated wastewater, storm water, and recreational activities. As such, it is susceptible to a wide range of contaminants, and its water quality is seasonally dependent, characterized by high concentrations of NOM in the autumn months. High levels of dissolved NOM (total organic carbon (TOC): 4.82 ± 1.2 mg-C/L and dissolved organic carbon (DOC): 4.57 ± 1.32 mg-C/L) occur in Lake Fletcher water (Table 1) due to decomposition of terrestrial humics.

Collins Park water treatment plant (CPWTP) operates an IMS with ultrafiltration (UF) and NF. The plant consists of two major stages: filtration and disinfection. The low-pressure, dead-end UF membranes (HYDRAcap, Hydranautics, Nitto Group Co., CA, USA) remove suspended matter to reduce the operation pressure of the NF modules (ESPA4, Hydranautics, Nitto Group Co., CA, USA). The UF modules operate in a dead-end filtration mode at a design flow rate of 3.18×10^{-3} m^3/s (191.2 L/min) per rack at a flux of 2.58×10^{-5} m^3/m^2 s (93 L/m^2 h) and recovery of 95.7%. The disinfection stage consists of primary disinfection with ultraviolet radiation for inactivation of microbiological contaminants and secondary disinfection with sodium hypochlorite to protect from biological growth within the distribution systems. A schematic diagram for the operating systems of CPWTP is shown in Fig. 1.

2.2. Bench-scale study

2.2.1. Pre-treatment: in-line coagulation

The bench-scale experiment was carried out with three different types of coagulants to determine the effect of inline coagulation/MF on the TMP and fouling of the membrane. Dead-end MF capsules were used at bench-scale to simulate full-scale UF operation. Aluminum sulfate, alum (assay: 99%, General Chemical, NJ, USA), ferric chloride, $FeCl_3$ (assay: 97%, Fischer Scientific, NJ, USA), and PACL (Kemira, FL, USA) were used as the coagulants to evaluate NOM removal from water. Each coagulant preceded 30 s of rapid mix, flocculation, and then MF. Twenty liters of batched feed-water were then run through the NF bench-scale experimental setup. The coagulants were adjusted to pH values ranging between 4.7 and 6.3 using 0.6 M HCl (assay: 37.4%, Fisher Scientific,

Table 1
Lake Fletcher water quality

Parameter	Units	Range	Average
pH	Unit	6.62–7.20	6.82
TOC	mg/L of C	3.97–5.67	4.49
DOC	mg/L of C	3.64–5.50	4.32
UV_{254}	cm^{-1}	0.145–0.211	0.173
SUVA	L/mg/cm	3.45–4.31	4.00
True color	Pt.Co	7.00–33.5	20.1
Turbidity	NTU	0.828–1.35	1.09

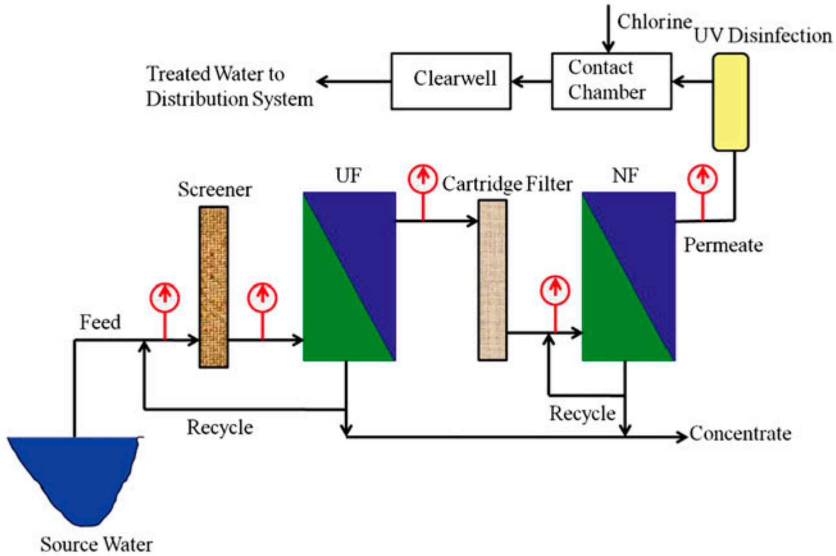

Fig. 1. CPWTP schematic (adapted from Lamsal [9]).

Canada), and 0.6 M NaOH (assay: 100%, Fisher Scientific, Canada), and doses ranged between 0.1 and 1.65 mg/L of the metals (Table 2).

2.2.2. *Jar tests*

Jar tests were used to determine the optimal coagulant dose and suitable pH using a 6 × 2 L PB-700™ Standard Jar Tester apparatus with rotating paddles (Phipps & Bird™, VA, USA). The variable flocculation speed was used to simulate in-line mixing of coagulants to control the velocity gradient. Turbulent in-line mixing was simulated at bench-scale with rapid mix at 300 rpm (revolutions/minute) for 30 s following the method described elsewhere [10]. Jar tests were performed at lab temperature (21 ± 1˚C), and pH was adjusted prior to coagulant addition. The optimal coagulant dose was determined using a modified point of diminishing returns for low-dose coagulation, when an increase in coagulant dose does not result in a significant improvement in NOM removal [17].

2.2.3. *Membrane filtration systems*

Bench-scale analysis of high-pressure membrane fouling was assessed using a bench-scale cross-flow filtration unit (Sepa CF II membrane cell, GE Osmonics, NY, USA). Feed and permeate spacers were used to improve hydrodynamic conditions, e.g. cross-flow velocity. Bench-scale flat sheet DK–NF thin film membranes (GE Osmonics, NY, USA) were used for this experimental analysis. The molecular weight cut-off (MWCO) was listed as 150–300 Daltons (Da). The membrane was operated in constant flux mode with variable pressures. Bench-scale NF flux was equivalent to the CPWTP (full-scale) flux at 20˚C: a bench-scale permeate flow rate of 6 mL/min. The total volume of NF permeate produced over the 200 h run time was 72 L, and this volume was used to calculate mass balances for each trial. The feed-water tank consisted of Lake Fletcher water that had undergone in-line coagulation followed by 0.45 μm filtration (Whatman POLYcapTM GW Capsule, Whatman Inc, NJ, USA). The feed-water was pumped (Hydracell Pump, Lincoln Motors, USA) from the feed tank through a cold water bath (Neslab RTE 17, Thermo Scientific, USA) to

Table 2
Coagulant factorial design

Coagulant	pH	Doses (mg/L of metal)
Aluminum sulfate	5.2, 5.5, 5.8	0.20, 0.40, 0.60, 0.70, 0.80, 0.90, 1.10, 1.30
Ferric chloride	4.7, 5.0, 5.3	0.10, 0.15, 0.25, 0.50, 0.75, 1.00
Polyaluminum chloride	5.7, 6.0, 6.3	0.15, 0.35, 0.55, 0.75, 0.95, 1.05, 1.15, 1.25, 1.45, 1.65

ensure a constant feed-tank temperature of 20 ± 1˚C. The NF membrane system was operated in recycle mode where the concentrate and permeate flows were returned to the feed tank. The feed, concentrate, and permeate were monitored throughout the 200 h experiment to ensure the water quality, flux, cross-flow velocity, and temperature remained constant. To maintain constant NOM and metals concentrations in the feed tank during the 200 h run time, a peristaltic pump circulated the feed tank to minimize settling.

2.3. Analytical methods

2.3.1. General water quality parameters

All methods, unless otherwise stated, followed the equipment manufacturer's procedures or the Standard Methods [19]. Total and dissolved organic carbon (TOC and DOC) were analyzed following the Standard Method 5310C [19] using a TOC-V_{CHP} TOC Analyzer (Shimadzu, Japan) with a Shimadzu ASI-V auto sampler (Shimadzu, Japan). True color and UV_{254} were measured using the DR/5000 UV Spectrophotometer (HACH Co., USA). Conductivity and zeta potential were measured with the Malvern zeta mater (ZetaSizer Nano ZS, Malvern Instruments Ltd., UK). pH and temperature measurements in all studied water samples were made using an Accumet electrode and Accumet Excel, XL50 (Dual channel pH/ion/conductivity) meter (Fisher Scientific, Singapore). The concentrations of aluminum, manganese, and iron in water samples were measured with inductively coupled plasma-mass spectrometry (Thermo Scientific X-Series2 ICPMS). High performance size exclusion chromatography (HPSEC) (Perkin Elmer, Series 200) with a UV/VIS detector was used to determine the MW distribution of DOM present in studied water samples. The surface images of the virgin and fouled membranes were analyzed using scanning electron microscopy (SEM) (Hitachi S-4700 FEG SEM, Japan). Statistical analysis was performed to determine if there was a statistically significant difference of means of the effect of pre-treatment type on NF feed-water and permeate quality. Tukey–Kramer significance test at a 95% significance level was applied to the data sets that varied in sample size and were non-parametric.

2.3.2. Silt density index

Silt density index (SDI-PU, Applied Membranes Inc., CA, USA) was used to analyze NF feed-water suitability of the optimal coagulant dose/pH conditions for NOM removal. SDI is usually used to measure the effect of particulate fouling on a high-pressure membrane. The manufacturer's procedure was followed and SDI was determined using the following equation (Eq. (1)):

$$\mathrm{SDI}_{\mathrm{T}} = \frac{\left[1 - \frac{t_{\mathrm{i}}}{t_{\mathrm{f}}}\right] \times 100}{T} \tag{1}$$

where T is length of time (15 min is most common, but 5 and 10 min may also be used), t_{i} is length of time (it takes to filter 500 mL from start) and t_{f} is length of time (it takes to filter 500 mL from time T).

3. Results and discussion

3.1. Pre-treatment under baseline conditions

The TMP, under base-line conditions, was increased from 70 to 95 psi (pounds per square inch) over the 200 h run time for the bench-scale NF membrane, and it was observed that the NF membrane had become fouled. Base-line conditions were experimentally substantiated by comparing SEM images for untreated membrane and treated membrane. Membrane fouling resulted in a smoother appearance of membrane surface by SEM analysis similar to the findings of Xu et al. [20].

On the other hand, HPSEC analysis indicated that MF removed higher MW fractions of NOM as identified by the 79.9 and 53.5% removal of organic compounds greater than 5,000 and 1,500–5,000 Da, respectively. This finding was consistent with the reported results in literature [2,21,22]. Kim et al. [1] found that fouling caused rapid TMP increase due to adsorption of NOM onto the NF membrane. The observed NOM removal (3.5%), increased TMP rate (0.111 psi/h) and SUVA value (3.04 L/mg/cm) indicated additional pre-treatment would be required for additional removal of organics from the NF feed-water. As described in the literature, the addition of coagulants prior to MF has been found to improve MF effectiveness of NOM removal [21,23,24].

3.2. Optimum coagulants' dose and pH values on baseline conditions

Lake water samples having TOC of 4.10 mg/L and DOC of 3.92 mg/L were used to determine the optimal coagulation conditions for three different types of coagulations, i.e. alum, $FeCl_3$, and PACl using a standard jar tester at different pH values, and different optimal coagulant doses (Table 2).

3.2.1. Aluminum sulfate on coagulation/MF pre-treatment

Aluminum sulfate (alum) conditions were assessed within a dose range of 0–1.3 mg/L of aluminum (Al) and at pH values of 5.2, 5.5, and 5.8, respectively. The results of the alum jar tests with TOC as a metric are shown in Fig. 2(a). Three optimal coagulant conditions for alum were designated, i.e. 0.6 mg/L of Al at pH 5.5, 0.7 mg/L of Al at pH 5.5, and 0.8 mg/L of Al at pH 5.2. These optimal coagulant conditions for alum were then assessed with SDI to ensure an improvement on baseline conditions. The SDI results for the three optimal coagulation conditions for alum were found to be 3.02, 2.49, and 1.75 % per min (%/min), respectively. However, based on SDI results, the optimal coagulation conditions for coagulation with alum were found to be 0.6 mg/L of Al, and a pH of 5.5. Our results were within the recommended feed-water quality guidelines for SDI value (3–5%/min), set by AWWA [25].

On the other hand, the optimal coagulation conditions are directed in good removal of humic matter as indicated by the SUVA value of 2.17 L/mg/cm (Table 3). The addition of alum at optimal coagulation conditions reduced the concentration of TOC from 4.10 to 2.72 mg/L (31.2%). The SDI value was decreased to 3.02%/min, and a large improvement from the baseline SDI of 4.40%/min was observed. In addition, the zeta potential of the NF feed-water was observed to increase at −1.55 mV, indicating near charge neutralization of NOM. The result on charge neutralization indicated the formation of stable floc, and the repulsion of less floc by the negatively charged of membrane surface.

3.2.2. Ferric chloride on coagulation/MF pre-treatment

Coagulation conditions of ferric chloride were assessed with a dose of 0–1.0 mg/L of iron at pH values of 4.7, 5.0, and 5.3. TOC removals with ferric chloride coagulation under the above conditions are shown in Fig. 2(b). The three optimal coagulation conditions for pre-treatment with $FeCl_3$ coagulation/MF were determined to be: 0.5 mg/L of Fe at pH 5.0, 0.75 mg/L of Fe at pH 5.0, and 0.75 mg/L of Fe at pH of 4.7, respectively. The three optimal ferric chloride coagulation/MF SDI analysis results were 3.39, 3.05, and 2.74%/min, respectively. From SDI analysis, a coagulation condition of 0.5 mg/L of Fe at a pH of 5.0 with a SDI value of 3.39%/min was selected as optimal as it produced a significant reduction on current operation conditions SDI by adding only 0.5 mg/L of Fe. Good removal of humic matter was attained with

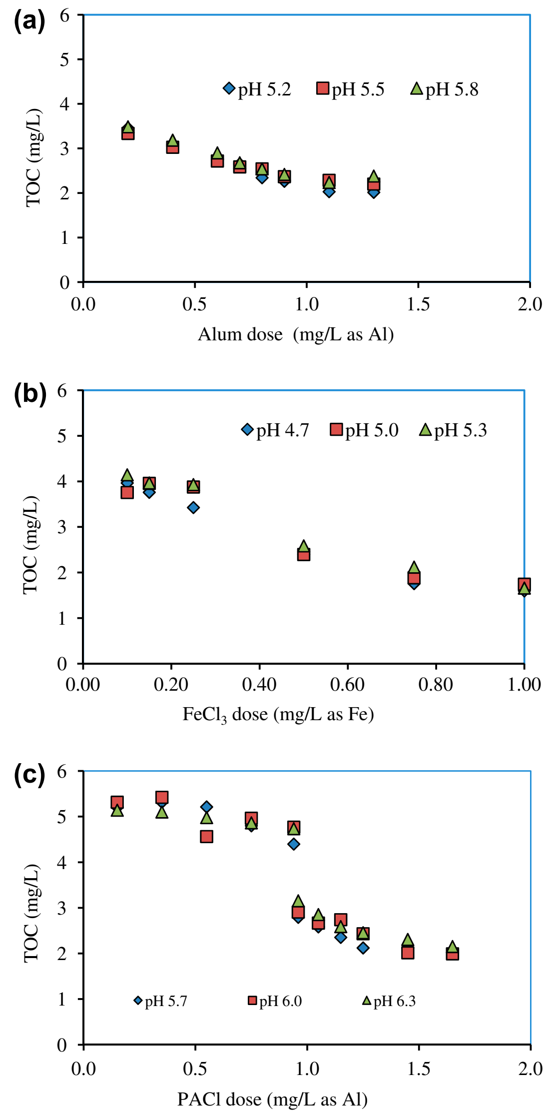

Fig. 2. Selection of optimal (a) aluminum sulfate dose/pH, (b) ferric chloride dose/pH, and (c) PACL dose/pH via TOC removal.

Table 3
NF feed-water quality 0.6 mg/L of alum/MF at pH 5.5

Parameter	Value
TOC (mg/L of C)	2.72
UV_{254} (cm^{-1})	0.059
SUVA (L/mg/cm)	2.17
SDI (%/min)	3.02
Zeta potential (mV)	−1.55
Conductivity (mS/cm)	0.195

the addition of $FeCl_3$ prior to MF as indicated by the SUVA value of 2.06 L/mg/cm (Table 4). Analysis of feed-water quality post $FeCl_3$/MF showed a great improvement on current operation feed-water quality. There was significant NOM removal as indicated by a significant reduction of TOC from 4.10 to 2.40 mg/L (39.3%). The zeta potential of the $FeCl_3$/MF pre-treatment was −4.6 mV indicating that charge neutralization did not occur and coagulation conditions were under-dosed.

3.2.3. PACL on coagulation/MF pre-treatment

PACL conditions were assessed with a dose of 0–1.65 mg/L of aluminum (Al) at pH values of 5.7, 6.0, and 6.3. The results of the alum jar tests with TOC as a metric are shown in Fig. 2(c). The PACl coagulation conditions were examined with Lake Fletcher water from two sampling dates with dissimilar NOM content. To account for unlike source water NOM concentrations, removal % of TOC was assessed to determine the optimal coagulation conditions for this study. The three optimal PACl coagulant conditions for this study were: 1.15 mg/L of Al at pH 5.7, 1.25 mg/L of Al at pH 5.7, and 1.25 mg/L of Al at pH 6. The SDI analysis of the three optimal coagulation conditions determined the suitability as NF membrane feed-water. The SDI results for the three optimal coagulation conditions were 3.46, 2.91, and 3.04%/min, respectively. The optimal coagulation condition of 1.15 mg/L of Al and pH of 5.7 were determined for in-line coagulation with PACl/MF for Lake Fletcher with a SDI value of 3.46%/min. At 1.15 mg/L of Al, the pre-treatment attained sufficient reduction of the 4.40%/min SDI at baseline conditions. Good removal of humic matter was attained with the addition of PACl prior to MF as indicated by the SUVA value of 2.02 L/mg/cm (Table 5). Pre-treatment with PACL addition prior to MF resulted in increased feed-water quality by reducing TOC from 4.10 to 2.35 mg/L (40.4%) and SDI by 0.94%/min. PACl/MF caused a significant zeta potential increase of the feed-water from −21.2 to −1.95 mV indicating charge neutralization occurred.

3.2.4. Comparison of coagulants on coagulation/MF pre-treatment

Addition of in-line coagulation prior to MF resulted in increased removal of NOM for NF feed-water. The optimal coagulation conditions for the three coagulants are presented in Table 6. This study revealed that ferric chloride coagulant was required the smallest dose (0.5 mg/L) to obtain improved removal of NOM, and SDI reduction from NF feed-water. Alum also required a low dose of 0.6 mg/L, while PACl required 1.15 mg/L for equivalent removal of NOM and particulate matter. This was consistent with the findings, where ferric chloride required a lower dose than aluminum-based coagulants for equivalent NOM removal [7,26]. Guigui et al. [7] and Tabatabai et al. [27] both found that $FeCl_3$ was effective at 0.5–1.0 mg/L at pH 5.0–5.5 for reduction of NOM and SDI. However, Tabatabai et al. [27] also found that at 0.5 mg/L and below, $FeCl_3$ formed small flocs that increased cake resistance. Similar coagulation conditions for PACl and alum were found to be reported in the literature [27–29].

Subsequently, Fig. 3 shows that the studied coagulants were effective in removal of NOM from the water samples. Coagulant addition resulted in about 30% NOM removal for all coagulant types. PACl and $FeCl_3$ were most effective in NOM removal with 37% TOC reduction. These results were consistent with the reported results in literature [28]. The reduction of feed-water NOM with pre-treatment contributed to a reduction of NF feed-water SDI. Pre-treatment with coagulation was capable of reducing the SDI by greater than 20%. Reduction of TOC did not have a correlation with SDI reduction as SDI is a measure of particulates and organic fouling mechanisms are not accounted for [30]. The SUVA values indicated that the humic fraction was reduced with the addition of all three coagulant types. However, alum was found to be the most effective in particulate removal as indicated by the 31% reduction in SDI.

Table 4
NF feed-water quality 0.5 mg/L of $FeCl_3$/MF at pH 5.0

Parameter	Value
TOC (mg/L of C)	2.40
UV_{254} (cm^{-1})	0.049
SUVA (L/mg/cm)	2.06
SDI (%/min)	3.39
Zeta potential (mV)	−4.60
Conductivity (mS/cm)	0.191

Table 5
NF feed-water quality 1.15 mg/L of PACl/MF at pH 5.7

Parameter	Value
TOC (mg/L of C)	2.35
UV_{254} (cm^{-1})	0.047
SUVA (L/mg/cm)	2.02
SDI (%/min)	3.46
Zeta potential (mV)	−1.95
Conductivity (mS/cm)	0.171

Table 6
Pre-treatment optimal coagulation conditions

Pre-treatment type	Coagulant dose	pH
Non-coagulated/MF	–	6.8
Aluminum sulfate/MF	0.6 mg/L of Al	5.5
Ferric chloride/MF	0.5 mg/L of Fe	5.0
Polyaluminum chloride/MF	1.15 mg/L of Al	5.7

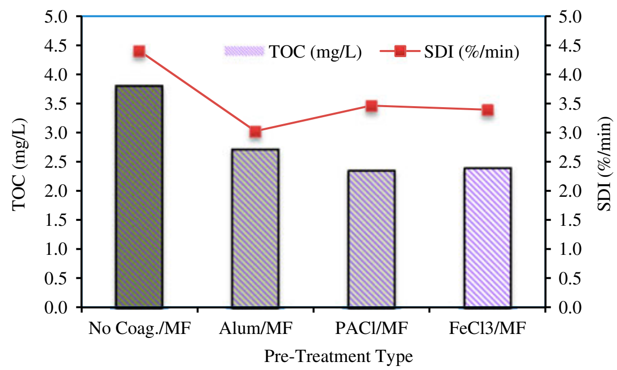

Fig. 3. Analysis of pre-treatment NOM and particulate removal.

3.3. Analysis of in-line coagulation/MF as NF pre-treatment

Bench-scale trials to simulate NF membrane fouling were performed to assess the impact of in-line coagulant addition prior to MF for three different types of coagulants. Each trial was performed with Lake Fletcher water from unique dates that varied in quality from each other and from Section 3.2. Analysis of in-line coagulation/MF as NF pre-treatment using three different types of coagulants is discussed below separately.

3.3.1. Aluminum sulfate

Alum was dosed at pre-determined optimal coagulation conditions of 0.6 mg/L at pH value of 5.5 (Table 6). The water was then microfiltered, batched, and applied as feed-water for bench-scale NF. The water quality of permeate and feed-water of the NF system from the alum/MF trial are presented in Table 7. The following parameters were held relatively constant throughout the 200 h bench-scale NF operation. The feed-water possessed relatively low concentrations of organics (Table 7).

This study revealed that the concentration of organics was significantly reduced by 46.3% within the pre-treatment stage. This NOM reduction via pre-treatment increased the quality of the feed-water resulting in retention of 149 mg (46.1%) of NOM within the NF membrane. Alum/MF pre-treatment was capable of reducing both low and high MW ranges (Fig. 4). NOM sizes of 5,000 Da and greater were completely removed with pre-treatment. A 67.7% reduction of the 1,500–5,000 Da range was also accomplished. Low removal of NOM less than 1,500 Da was obtained with alum/MF. The NF removal had high retention of NOM between 1,000 and 5,000 Da but not NOM less than 1,000 Da.

This study showed that the transmembrane flux (TMF) did not linearly increase over the 200 h run-time for pre-treatment with alum/MF (Fig. 5). The TMP rose drastically within the first 50 h of operation before leveling off and then spiking once again at the 150 h mark. The sharp increase in TMP may have been due to severe reduction of the cross-flow velocity. The cross-flow velocity was very difficult to maintain a steady flow throughout the alum/MF trial. The alum/MF pre-treatment trial was not successful in reduction of TMP, as the TMP increased by nearly 100% and had the same TMP at 200 h as the trial under baseline conditions. When the value of the cross-flow velocity approached is zero, the NF membrane operated in dead-end filtration mode and resulted in increased cake resistance and fouling rates. The TMP for the bench-scale NF trial with alum/MF pre-treatment increased at a rate of 0.17 psi/h, and averaged 69.7 psi over the 200 h NF operation.

3.3.2. Ferric chloride

Optimal coagulant conditions for $FeCl_3$/MF pre-treatment were determined to be 0.5 mg/L of Fe at pH of 5. This trial was performed in October 2012 when Lake Fletcher TOC levels were 5.30 mg/L. The NF permeates and feed-water quality is presented early in Table 7.

Table 7
NF bench-scale water quality post alum/MF, PACl/MF and $FeCl_3$/MF

Alum/MF	Permeate	Feed
TOC (mg/L of C)	0.284 ± 0.127	2.91 ± 0.283
UV_{254} (cm^{-1})	0.0022 ± 0.0007	0.080 ± 0.0080
$FeCl_3$/MF		
TOC (mg/L of C)	0.271 ± 0.126	2.32 ± 0.175
UV_{254} (cm^{-1})	0.0030 ± 0.0011	0.0477 ± 0.0026
PACl/MF		
TOC (mg/L of C)	0.252 ± 0.039	3.99 ± 0.218
UV_{254} (cm^{-1})	0.0019 ± 0.0008	0.130 ± 0.0091

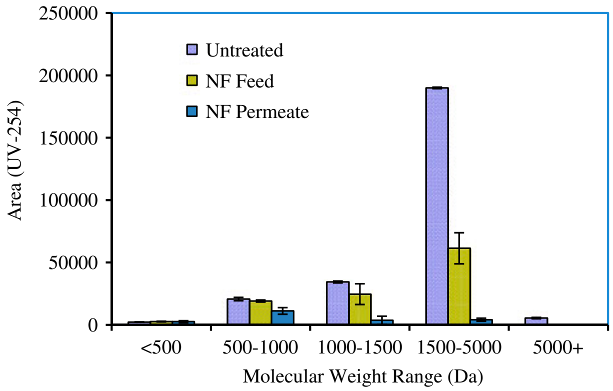

Fig. 4. HP-SEC of NF bench-scale organic fraction removal with alum/MF pre-treatment (error bars represent standard deviation).

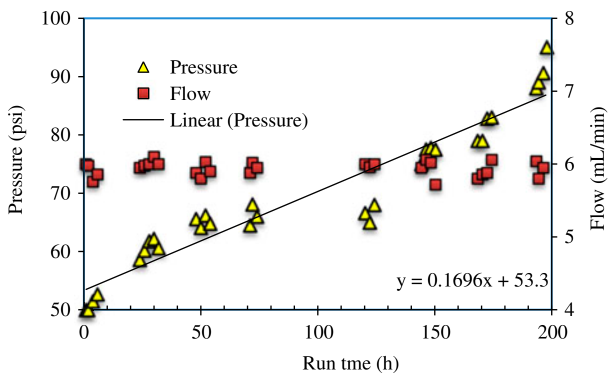

Fig. 5. TMP increase over 200 h operation with alum/MF pre-treatment.

Though $FeCl_3$/MF was very effective in removal of NOM, this study revealed that 199 mg (52.5%) of NOM was removed with pre-treatment, which greatly reduced the NOM retained by the NF membrane to only 163 mg (43.8%). $FeCl_3$/MF resulted in a larger amount of NOM removal within the MF membrane than the NF membrane. HP-SEC analysis found that near complete removal of high MW of NOM could be obtained with $FeCl_3$/MF as indicated by the 92.1 and 100% removal of MW ranged 1,500–5,000 Da and greater than 5,000 Da, respectively (Fig. 6). The range of MW of NOM foulant for the NF membrane was 1,000–1,500 Da with 82.1% retained by the NF membrane.

NF feed-water pre-treatment with $FeCl_3$/MF pre-treatment led to decreased TMP to increase over the 200 h run time of the bench-scale NF membrane compared to baseline conditions (Fig. 7). The initial TMP was 60 psi and remained relatively constant over the 200 h run-time. The divergence from the linear increase in TMP is consistent with variation of the feed-tank water temperature that occurred between 120 and 170 h. The TMP for the NF bench-scale setup with $FeCl_3$/MF feed-water increased at a rate of 0.0422 psi/h and averaged 63 psi.

3.3.3. *Polyaluminum chloride*

PACl/MF was assessed for NF feed-water pre-treatment under coagulation conditions of 1.15 mg/L of Al at pH 5.7. The PACl/MF trial was performed with Lake Fletcher water sampled in November 2012, when Lake Fletcher NOM concentrations were most elevated. Permeate and feed-water quality for the 200 h bench-scale NF trial is shown in Table 7. The concentrations of NOM were held relatively constant throughout the trial during the 200 h run time.

Pre-treatment with PACl/MF effectively reduced the concentrations of influent NOM to the bench-scale NF system. Following PACl coagulation the MF membrane retained 121 mg (29.7%) of NOM that resulted in the NF membrane retention of 269 mg (65.9%) of NOM. The NF bench-scale system attained very good NOM removal with a permeate TOC concentration of 0.25 mg/L, below the equipment RDL of 0.3 mg/L. HP-SEC analysis indicated that higher MW fractions of NOM were effectively removed by pre-treatment (Fig. 8). The removal of NOM with PACl/MF pre-treatment was 42.7 and 94.8% for MW ranges 1,500–5,000 Da and greater than 5,000 Da, respectively. The NF membrane retained NOM with MW greater than 1,000 Da and achieved 63.2% removal of NOM between 500 and 1,000 Da.

The reduction of NOM with PACl/MF pre-treatment did not result in as great of a TMP increase as baseline conditions over the 200 h run time of the

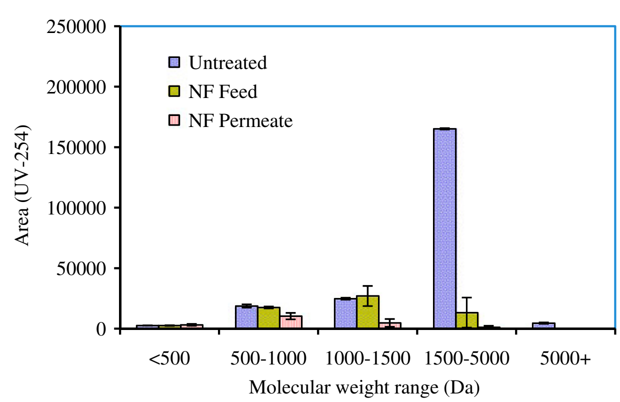

Fig. 6. HP-SEC of NF bench-scale organic fraction removal with $FeCl_3$/MF pre-treatment (error bars represent standard deviation).

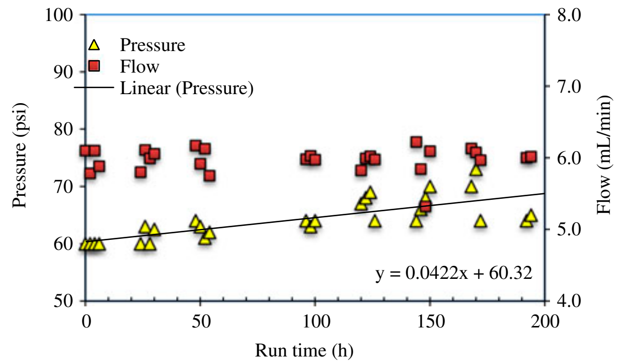

Fig. 7. TMP increase over 200 h operation with $FeCl_3$/MF pre-treatment.

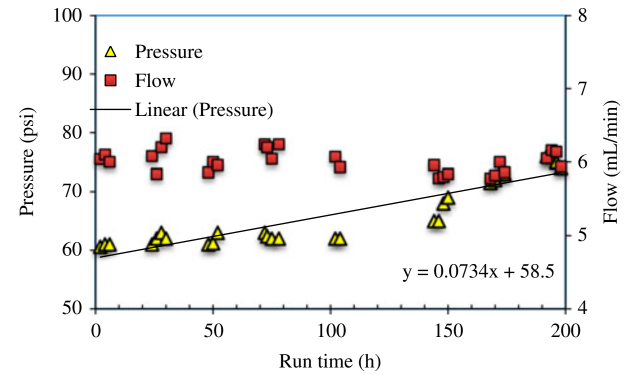

Fig. 9. TMP increase over 200 h operation with PACl/MF pre-treatment.

bench-scale NF membrane (Fig. 9). The initial TMP of 60psi was maintained for nearly 150 h of operation, indicating minimal fouling occurred until this point. The sudden increase in TMP at 150 h may be concurrent with partial or full blockage of membrane pores. The TMP for the NF bench-scale setup with PACl/MF feed-water decreased slightly at a rate of 0.0734 psi/h and averaged 66 psi.

3.4. Changes of membrane properties

Membrane analysis was performed with SEM to obtain surface morphology images of the NF membrane foulant surface. SEM imaging identified three likely types of dominant fouling: NOM, inorganics and bacteria. The semi-uniform cake layer, rod-shaped matter and irregularly shaped particulates were presumed to be NOM, bacteria and inorganics respectively. Cracks within the cake-layer were assumed to be a result of membrane drying and not membrane tears.

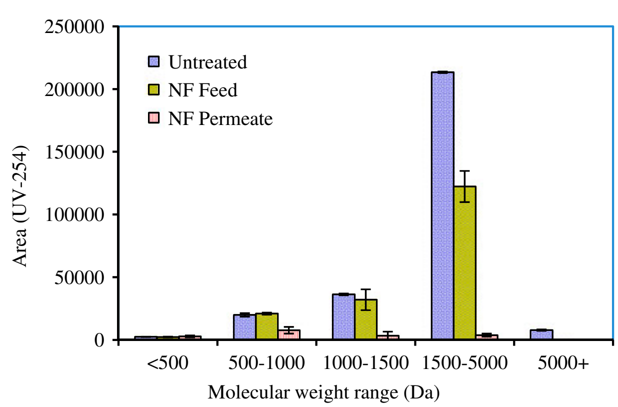

Fig. 8. HP-SEC of NF bench-scale organic fraction removal with PACl/MF pre-treatment (error bars represent standard deviation).

SEM analysis of the fouled NF membrane for the Alum/MF trial is shown in Fig. 10(a). The increase in TMP from 50 to 95 psi indicated that severe fouling occurred during the alum/MF trial. The SEM image indicates that the majority of the fouling that occurred was NOM fouling due to the retention of organic matter within the feed-water. Evidence of bacteria within the cake layer was obvious. The deep cracks from membrane drying were indicative of a thick foulant layer that corresponds to a large TMP increase. The surface topography appears to be relatively smooth and uniform with evidence of inorganics deposition.

SEM imaging of the fouled NF membrane for the $FeCl_3$/MF trial is shown in Fig. 10(b). Relatively few bacteria are present and the major foulant constituent appears to be NOM. The small, shallow cracks due to drying indicate that the foulant layer is relatively thin; this is also consistent with the low increase of TMP throughout the 200 h bench-scale run time. Membrane analysis indicated that the $FeCl_3$/MF trial had a thin foulant layer with little bacterial content, especially compared to the PACl/MF trial.

The PACl trial had the most bacteria collected within the foulant layer that did not appear to have a direct effect on the TMP. Alum had the highest TMP increase which likely corresponded to the thick NOM cake layer. Tabatabai et al. [27,29] found that the addition of low-dose coagulants substantially decreased the TMP during NF operation. The SEM analysis of the fouled NF membrane for the PACl/MF trial revealed that the foulant layer consisted of a very large quantity of bacteria, which resulted in a very rough surface topography (Fig. 10(c)). A rough surface topography may correspond to the TMP increase in the final hours of bench-scale NF operation as

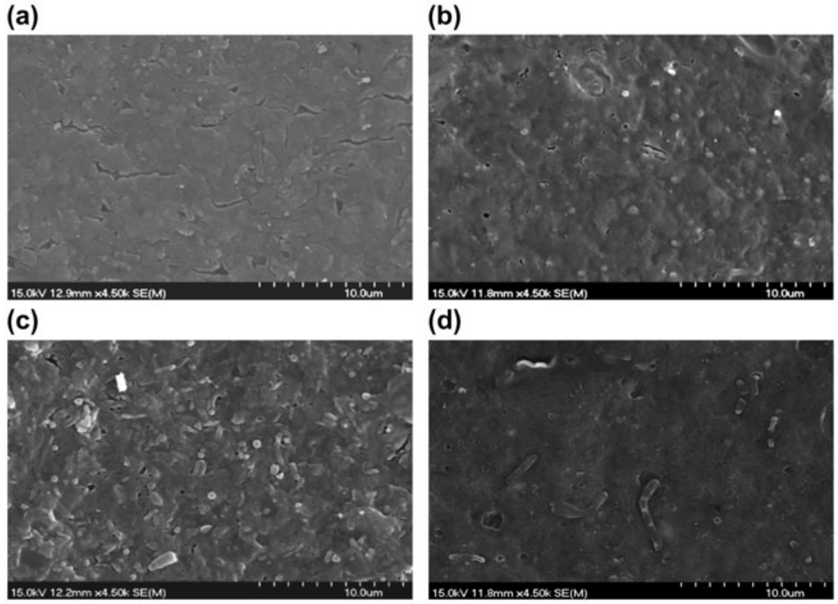

Fig. 10. SEM imaging of fouled NF membrane post (a) alum/MF, (b) PACl/MF, (c) $FeCl_3$/MF pre-treatment, and (d) MF pre-treatment only.

contaminants are collected within the foulant layer valleys. The deposition of bacteria likely did not result in TMP increase as the relatively large size of bacteria would result in a porous substructure that water can pass through. Retention of NOM by the NF membrane was also evident with a cake layer covering the membrane pores and fibers. The thickness of the foulant layer appears to vary with location and relative thickness is difficult to determine due to the large amount of bacteria.

The SEM analysis of the fouled NF membrane following pre-treatment with MF (Fig. 10(d)) shows that deposits of matter and bacteria covered the membrane pores and fibers, resulting in clogging or blockage of the membrane pores and increased TMP. EDS analysis indicated the composition of the foulant layer was primarily NOM with elemental analysis showing high levels of carbon, oxygen, and nitrogen.

4. Discussion

The average TOC concentration of the PACl/MF permeate was found to be 3.99 mg/L, and was not a significant ($\alpha = 0.05$) improvement on Non-Coag./MF feed-water compared with average concentration of 3.81 mg/L. Conversely, pre-treatment with $FeCl_3$/MF and alum/MF significantly improved TOC reduction with TOC concentrations of 2.24 and 2.92 mg/L, respectively. PACl/MF had a decreased percent of NOM removal from the preliminary trials which may indicate that an increased coagulant dose was required at decreased water qualities compared to $FeCl_3$ and alum [17].

NOM removal effectiveness within the MF/NF system did not appear to be dependent on NF feed-water quality. PACl/MF significantly had the lowest TOC concentrations in the NF permeate with 0.252 mg/L. This may be due varying charge densities. Yoon et al. [31] found that charge density was the most important factor in flux decline and NOM retention. The Alum/MF NF permeate (TOC = 0.284 mg/L) was a significant improvement on baseline conditions (TOC = 0.379 mg/L), but did not differ statistically from the TOC concentrations of $FeCl_3$/MF NF permeate (TOC = 0.341 mg/L). The TOC concentrations of $FeCl_3$/MF NF permeate did not statistically differ from baseline conditions.

The removal of certain fractions of NOM from the source water to the NF feed and permeate is shown in

Table 8
Percent removal of NOM MW fractions with pre-treatment

MW range (Da)	MF	Alum/MF	PACl/MF	$FeCl_3$/MF
<500	19.7	−18.6	5.65	1.08
500–1,000	26.6	7.69	−5.16	6.69
1,000–1,500	22.9	28.4	11.7	−8.93
1,500–5,000	53.4	67.7	42.7	91.9
5,000+	84	100	94.9	100

Table 9
Percent removal of NOM MW fractions with NF

MW range (Da)	MF	Alum/MF	PACl/MF	$FeCl_3$/MF
<500	−2.28	−17.2	−14.8	−22.5
500–1,000	70.1	46.0	61.3	44.5
1,000–1,500	96.0	89.1	90.6	80.4
1,500–5,000	99.1	97.8	98.2	99.2
5,000+	100	100	100	100

Tables 8 and 9, respectively. The negative values that are present in some of the smaller MW ranges are representative of NOM breakdown due to turbulence within either the MF or NF systems. This study revealed that pre-treatment NOM removal occurred mostly in the larger MW ranges: 1,500 Da or greater, which is consistent with the reported result in literature [32]. $FeCl_3$/MF and Alum/MF obtained 100% removal of NOM greater than 5,000 Da and had superior removal of NOM within 1,500 and 5,000 Da. The PACl/MF had higher removal of NOM with MW greater than that of 5,000 Da, but had lower removal of NOM with MW less than 5,000 Da than baseline conditions. $FeCl_3$/MF had superior removal of NOM greater than 1,500 Da for all pre-treatment types; this is consistent with findings in literature [17]. On the other hand, NF had poor removal of NOM within the MW range of 500–1,000 Da with removal percentage ranging from 44.5 to 70.1%. The membrane manufacturer, membrane specifications indicate a MWCO of 300 Da and the results in the present study were not in agreement.

5. Conclusions

This study investigated NF membrane fouling using Lake Fletcher water samples. The effectiveness of low-dose in-line coagulation addition prior to low-pressure membrane filtration for NF feed-water pre-treatment was assessed for reduction of NF membrane fouling. Analysis of bench-scale NF operation at baseline conditions indicated that there was significant NF membrane fouling and that pre-treatment for removal of NOM was required for improved NF membrane performance and decreased NF membrane fouling. In-line coagulation was effective in reduction of NF membrane fouling due to NOM. Coagulation addition resulted in the removal of humic matter within the NF feed-water. The addition of coagulant reduced the NF influent NOM and particulate matter, and increased the concentration of dissolved metals that resulted in decreased NF membrane fouling. The reduction of NF membrane fouling was found to differ with pre-treatment. $FeCl_3$/MF was determined to be the most effective NF pre-treatment. $FeCl_3$/MF effectively improved NF feed-water quality at a low-dose and did not result in severe membrane fouling, indicated by increased TMP. $FeCl_3$ differentiated from the other coagulants as $FeCl_3$ is an iron-based coagulant, and the mechanism of coagulation was under-dose. This study found that $FeCl_3$/MF was an effective pre-treatment for Lake Fletcher for one sample of source water.

Multiple trials for each pre-treatment type with varying water quality should be performed to determine the effect of each coagulant under various conditions. Improved methods for coagulation condition optimization should be investigated in subsequent trials. Identification of NOM foulant fractions for both low- and high-pressure membranes would be beneficial.

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