Coagulation optimization for DOC removal: pilot-scale analysis of UF fouling and disinfection byproduct formation potential
Heather E. Wray, Robert C. Andrews and Pierre R. Bérubé

ABSTRACT
A pilot-scale study was performed to evaluate a coagulant dose which had been optimized for biopolymer (i.e., foulant) removal on subsequent ultrafiltration (UF) fouling, as well as disinfection by-product (DBP) precursor removal. Polyaluminum chloride (PACl) dosages were selected based on a point of diminishing returns for biopolymer removal (0.5 mg/L) and directly compared to that applied at full-scale (6 mg/L). Membrane fouling (reversible and irreversible) was measured as resistance increase over a 48 hour filtration period. DBP formation potential (total trihalomethanes (TTHMs), haloacetic acids (HAAs) and total adsorbable organic halides (AOX)) were measured in both raw and treated waters. Results of the study indicate that application of a PACl dose optimized for biopolymer reduction (0.5 mg/L) resulted in 65% less irreversible UF fouling when compared to 6 mg/L. The addition of PACl prior to the membrane resulted in up to a 14% reduction in DBP precursors relative to the UF membrane alone. A similar level of DBP precursor reduction was achieved for both 0.5 and 6 mg/L dosages. The results have implications for cost savings, which may be realized due to decreased chemical use, as well as increased membrane life associated with lower irreversible fouling rates.

Key words | coagulation, disinfection by-products, fouling, ultrafiltration (UF)

INTRODUCTION
The main drawback to ultrafiltration (UF) for drinking water treatment is membrane fouling by natural organic matter (NOM) (Huang et al. 2007; Neubrand et al. 2010), particularly the large molecular weight (>20 kDa) biopolymer fraction (Lee et al. 2004; Zheng et al. 2009). Coagulation is the most widely applied type of pre-treatment to UF (Huang et al. 2009), often to achieve fouling reduction via aggregation and removal of organic matter (Jarvis et al. 2004), with preferential impact on larger molecular weight organics such as biopolymers (Howe & Clark 2002; Haberkamp et al. 2007). As a result, coagulation prior to UF can be optimized to effectively aggregate the dissolved organic carbon (DOC) fraction responsible for much of the fouling observed in UF systems (Wray & Andrews 2014). UF membranes alone typically offer poor removal of other, smaller NOM fractions such as humic substances (<10% removal) (Howe & Clark 2002; Chen et al. 2007; Wray et al. 2014). The addition of coagulation prior to UF can improve the removal of low molecular weight NOM fractions (Jang et al. 2005). The fractions and character of NOM that remains in UF permeate is important as, upon disinfection, it can result in the formation of disinfection by-products (DBPs). Although biopolymers contribute to some formation of DBPs (Hua & Reckhow 2007), lower molecular weight (<1 kDa) NOM fractions (e.g., humic substances) are also DBP precursors (Singer 1999; Wassink et al. 2011). Therefore, optimization of coagulation pre-treatment to UF may also consider the removal of fractions of organic matter that form DBPs upon chlorination (USEPA 1999). The main DBPs of concern from the perspective of a drinking water treatment plant operator are trihalomethanes...
(THMs) and haloacetic acids (HAAs), as these are regulated at maximum contaminant levels (MCLs). Health Canada (2006) regulates total trihalomethanes (TTHMs) at a MCL of 100 μg/L. HAAs are not currently regulated in Canada but the guidelines for Canadian drinking water quality list a minimum acceptable concentration of 80 μg/L for HAAs (Health Canada 2008). USEPA regulations are 80 and 60 μg/L for TTHMs and HAAs, respectively. However, a recent study by Hrudey (2009) reported low health concerns for exposure to THMs and HAAs. As THMs and HAAs may account for <50% of the organic halides (commonly reported as total adsorbable organic halides, AOX) in chlorinated drinking water, it would also be useful to examine organic halide concentrations as a whole, to gain a better understanding of the overall concentration of DBPs in finished drinking water.

Previous bench-scale studies have indicated that a low dose of coagulant (<1 mg/L), optimized with respect to diminishing returns for biopolymer removal, was effective at reducing UF fouling when considering a variety of surface waters (Wray & Andrews 2014). However, the dosage optimized for biopolymer removal was relatively low (0.5 mg/L) when compared to dosages commonly applied prior to UF membranes for surface waters in full-scale systems (up to 15 mg/L) and the impact of such low coagulant dosages on DBP precursor removal has not been extensively studied, especially at pilot-scale, or for conditions which are representative of full-scale drinking water treatment. The main objectives of this study were to compare pre-coagulation dosages (i.e., a dose optimized for biopolymer removal at bench-scale and the dose currently applied at full-scale) on membrane fouling at pilot-scale and to examine the impact on the formation potential of THMs, HAAs, and AOX.

**MATERIALS AND METHODS**

Studies were conducted at the Barrie South Surface Water Treatment Plant located in Barrie, Ontario, Canada. The full-scale treatment plant uses submerged hollow fiber UF membranes (ZW1000, GE Water & Process Technologies) to treat water from Lake Simcoe (Table 1). The membrane fibers were composed of polyvinylidene fluoride with a nominal pore size of 0.02 μm. The full-scale treatment process at the plant typically includes the addition of 6-8 mg/L of polyaluminum chloride (PACl) coagulant (PAX-XL1900, Kemira Water Solutions Canada, Inc.) added in-line prior to the membranes. This dosage was selected during design of the treatment process and was intended for fouling reduction and DBP precursor removal. Post-membrane filtration with granular activated carbon (GAC) (F500, Calgon Carbon) is also included, along with disinfection using chlorine prior to distribution.

All experiments were performed using a ZeeWeed®1000 pilot unit (GE Water & Process Technologies) with pre-coagulation. The pilot unit included a full ZW1000 membrane module (taken from the full-scale plant) and its operation was fully automated to mimic the full-scale coagulation and membrane treatment processes including in-line coagulation, backwashing, coarse bubble air sparging (during backwashing), membrane integrity testing and chemical cleaning. The pilot was a self-contained unit and consisted of online monitoring of transmembrane pressure as well as feed and permeate turbidity, pH and temperature. All data were recorded every 5 minutes.

Prior to commencing experiments, performance of the pilot apparatus was compared to full-scale (i.e., flux, water temperature, resistance, permeate turbidity, permeate DOC) for operating conditions typical of those at full-scale (i.e., coagulant dose of 6 mg/L) to ensure that the performance at pilot-scale was representative of full-scale. Experiments consisted of PACl addition prior to the pilot membrane module at dosages of 0.5 mg/L (optimized for biopolymer removal) (Wray & Andrews 2014) and 6 mg/L (the dose applied at

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Raw (feed) Lake Simcoe water characteristics (average ± standard deviation, six replicates)</th>
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<tbody>
<tr>
<td>Parameter</td>
<td>Concentration</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>4.71 (± 0.21)</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>4.12 (± 0.19)</td>
</tr>
<tr>
<td>Biopolymers (mg/L)</td>
<td>0.46 (± 0.01)</td>
</tr>
<tr>
<td>Humic substances (mg/L)</td>
<td>2.14 (± 0.14)</td>
</tr>
<tr>
<td>Building blocks (mg/L)</td>
<td>0.94 (± 0.12)</td>
</tr>
<tr>
<td>LMW neutrals (mg/L)</td>
<td>0.43 (± 0.08)</td>
</tr>
<tr>
<td>LMW acids (mg/L)</td>
<td>0.09 (± 0.02)</td>
</tr>
<tr>
<td>pH</td>
<td>8.29 (± 0.09)</td>
</tr>
<tr>
<td>SUVA (L/mg·m)</td>
<td>1.93 (± 0.09)</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.21 (± 0.04)</td>
</tr>
</tbody>
</table>

TOC — total organic carbon; DOC — dissolved organic carbon; LMW — low molecular weight; SUVA — specific UV absorbance.
full-scale during the experimental period). Experiments without the addition of coagulant were also conducted. No pH adjustment during coagulation was considered as part of the current study as it was not practiced at full scale. All experimental trials were conducted in duplicate and consisted of 48 ± 5 hours of continuous permeation and backwashing. Permeation cycles were extended from 30 minutes (typical operation) to 4 hours in order to accelerate fouling and observe measurable differences in resistance for the various coagulant dosages applied. The target permeate flux was 40 LMH (litres per m² per hour) which was consistent with full-scale conditions. Backwashing was initiated after each permeation cycle for a period of 10 minutes, with 1.24 scfm (standard cubic feet per minute or 2.12 cubic metres per hour) of continuous coarse bubble air sparging, to mimic full-scale conditions. The membrane tank was drained after each backwash. Between each experimental trial, the membrane module was cleaned with 500 mg/L NaOCl and 200 mg/L citric acid for a soak time of 12 hours which was effective at recovering 100% of the permeability. A membrane integrity test (pressure hold test) was also performed after every trial. No integrity breaches were found during the experimental period.

Fouling was quantified using a resistance-in-series approach (Cho et al. 2004; Busch et al. 2007) to separate out hydraulically reversible fouling (i.e., that which was removed during backwashing) and hydraulically irreversible fouling (i.e., that which was not removed during backwashing). Resistance values were normalized to the intrinsic membrane resistance at the beginning of the experimental trial. The temperature of the water fluctuated slightly over the course of each trial (10 ± 2 °C). Therefore, viscosity (μ) in the resistance calculation was adjusted for temperature according to Equation (1) (Zheng et al. 2010):

\[ \mu = \frac{0.497}{(T + 42.5)^{1.5}} \]

where \( T \) is the feed water temperature (°C).

Feed water samples were collected prior to each experiment and permeate samples were collected at the end of each 48 hour trial. Liquid chromatography-organic carbon detection (LC-OCD) was used to characterize dissolved organic matter in the feed and permeate waters on the basis of size and chemical properties into five fractions (biopolymers, humic substances, building blocks, low molecular weight organic acids and neutrals). LC-OCD analysis was conducted on filtered (0.45 μm) water samples at the University of Waterloo based on methods described by Huber et al. (2011). Permeate samples were also analyzed for dissolved aluminum on filtered samples (0.45 μm) following the Eriochrome Cyanine R Method using a Hach kit (DR1010, Hach Canada Ltd, Mississauga, ON).

DBP (TTHMs, HAA₉ and total AOX) formation potentials were assessed in raw (1.2 μm filtered) and treated water following chlorination under Uniform Formation Conditions (UFC) as described by Summers et al. (1996), i.e., a target residual of 1.0 ± 0.4 mg/L Cl₂ at a temperature of 20.0 ± 1.0 °C for 24 ± 1 hours at a pH of 8.0 ± 0.2. These conditions were chosen because they closely match the conditions for the full-scale treatment plant, i.e., ~1 mg/L chlorine residual after 24 hours in treated water. Chlorination was performed with the addition of a sodium hypochlorite stock solution (850 mg/L NaOCl). Chlorine concentrations were measured using the DPD colorimetric Standard Method 4500-C1 G (APHA et al. 2005) with a HACH kit (DR2O10, Hach Canada Ltd, Mississauga, ON). Following chlorination samples were quenched using 100 mg of L-ascorbic acid prior to DBP analysis.

AOX were analyzed using a Trace Elemental Instruments Xplorer Instrument (TE Instruments, Delft, The Netherlands). Powdered activated carbon (50 mg, Trace Elemental Instruments CON100400) (to adsorb organic halogens) was mixed with 100 mL of the water sample to be analyzed on an orbital shaker for 1 hour. Samples were then filtered through a quartz frit to recover the activated carbon. Combustion followed by coulometric titration of organic halogens released was used to determine AOX. All samples were analyzed in duplicate.

TTHM and HAA₉ analyses were conducted according to Standard Methods 6232B and 6251B, respectively (APHA et al. 2005), and analyzed via gas chromatography with electron capture detection (GC-ECD) on a Hewlett Packard 5890 Series II Plus Gas B, Chromatograph equipped with a DB 5.625 capillary column (Agilent Technologies Canada Inc., Mississauga, ON).

Fouled membrane fibers were collected from the module and examined using Field Emission Scanning Electron Microscopy (FESEM) in order to provide a visual of...
fouling morphology. FESEM analysis was conducted at GE Water and Processing Technologies (Oakville, ON) on a Supra™ 40 instrument (Carl Zeiss Ltd, Toronto, ON) at a variety of magnifications. Prior to analysis, fiber samples were dried in a dust-free cabinet for 24 hours.

RESULTS AND DISCUSSION

Pre-coagulation and membrane fouling

The application of 6 mg/L PACl prior to the membrane resulted in significantly higher fouling when compared to the 0.5 and 0 mg/L dosages (Figure 1). There was no significant difference in fouling rates when comparing the 0 and 0.5 mg/L coagulant dosages (P > 0.05) although, in general, measured rates of fouling (total, reversible and irreversible) were slightly higher for the 0.5 mg/L dosage when compared to conditions where no coagulant was applied (Figure 2).

Most (>50%) of the total resistance measured for all experimental conditions was hydraulically reversible in nature. For conditions where no coagulant or a low dose (0.5 mg/L) was applied prior to the membrane, no significant increase in reversible fouling occurred over the 48 hour experimental period (Figure 2(b)). However, the irreversible resistance for a given filtration cycle increased over time with the application of the 6 mg/L coagulant dose (>50% increase in resistance after 36 hours compared to the start of the experiment) (Figure 2(b)). The irreversible resistance for the 6 mg/L dose also increased over time (Figure 2(c)).

Irreversible fouling occurred and increased over time for all three coagulant dosages; however the increase in irreversible fouling was highest for a coagulant dosage of 6 mg/L PACl. The addition of 0.5 or 0 mg/L PACl reduced the irreversible fouling rates by 52 and 66%, respectively, relative to the 6 mg/L dose. When considering the total fouling resistance, the 0.5 and 0 mg/L PACl dosages resulted in 78 and 87% lower total fouling, respectively, relative to the 6 mg/L dose.

The results indicated that the addition of coagulant at a dosage typical for the full-scale UF system contributed to high reversible and irreversible fouling of the membrane over time. Examination of the fouled membrane fibers...
with FESEM showed precipitation of PACl onto the membrane surface when applied at a dosage of 6 mg/L (Figure 3), which is consistent with other studies reporting fouling resulting from coagulant addition (Jang et al. 2005). When comparing the fouled membrane fibers following addition of the 0 and the 0.5 mg/L coagulant dose, an apparently more prominent fouling cake layer was observed for the 0 dose than the 0.5 mg/L dose, even though fouling rates were slightly (though not significantly) more elevated following the addition of 0.5 mg/L coagulant. It is possible that the formation of small flocs at a low dose of coagulant resulted in pore blocking or narrowing (Citulski et al. 2008), although this cannot be concluded based on the FESEM images.

Permeate turbidity remained constant (<0.012 NTU), irrespective of the coagulant dose applied or the fouling observed. In addition, dissolved aluminum concentrations were <0.01 mg/L in permeate waters following pre-coagulation at all applied dosages.

**Pre-coagulation and DBP formation**

The fraction of non-identified DBPs was quantified as the difference between the total AOX concentration and the sum of TTHMs and HAA₉, measured as equivalent μg/L Cl⁻. TTHM and HAA₉ concentrations contributed to 47–55% of total AOX observed in feed and permeate samples, i.e., 45–53% of DBPs formed were non-identified. This is consistent with a recent study conducted by Zheng et al. (2015), which reported a range of 34–60% of unknown DBPs for Ontario surface waters, including Lake Simcoe.

When no coagulant was added prior to UF, formation of AOX and HAAs in the permeate water was greater (average of 12 and 22%, respectively) than the formation potential of the raw feed water. This may be attributed to lower bulk consumption of chlorine by organics in the membrane permeate, leaving more to react to form DBPs. The 24 hour chlorine demand for raw water ranged from 2–3 mg/L whereas for UF permeate without pre-coagulation the chlorine demand was approximately 2 mg/L. Pre-coagulation with PACl resulted in decreased DBP formation potentials relative to raw feed water (Figure 4). TTHM reduction was similar for both coagulant dosages (i.e., 11 and 10% reduction for 0.5 and 6 mg/L PACl). The mean reduction of HAA formation was greater (8% reduction) following a pre-coagulant dose of 6 mg/L compared to the 0.5 mg/L dose (1% reduction). It is likely that a higher dose of PACl was able to remove more HAA precursors.
from the water. Although pH adjustment was not considered as part of this study, pH suppression and/or the use of other coagulants may result in enhanced optimization of DBP precursor removal; this would require further study.

**LC-OCD results**

Biopolymers were the main DOC fraction removed during UF, regardless of the coagulant dose. Retention of biopolymers by the membrane was 59, 58, and 66% for pre-coagulation conditions of 0, 0.5, and 6 mg/L PACI, respectively (Figure 5). Humic substances were not removed by the UF membrane when no coagulant was applied prior to the membrane, or for the condition of 0.5 mg/L PACI pre-coagulation. When 6 mg/L coagulant was applied prior to UF, permeate water showed a reduction of 11% in humic substances (Figure 5).

The reduction in humic substances may be due to the higher fouling observed under these conditions altering the selectivity of the membrane to allow for removal of smaller NOM fractions, including humic substances. A higher removal of humic substances following pre-coagulation at 6 mg/L may also indicate that humics are precursors for HAA formation, which was slightly lower at a PACI dose of 6 mg/L; however further study would be required to determine this. Previous research has reported that coagulation may preferentially remove HAA precursors, as opposed to THM precursors, due to a suggested higher aromatic content of HAA precursors (Liang & Singer 2003).

**Analysis of full-scale treatment processes**

Based on the results of pilot experiments, LC-OCD and DBP formation was assessed for raw water, post-coagulation, and post-UF treated water, in order to further identify DBP precursor and UF organic foulant removals. Analysis of full-scale treatment processes indicated that biopolymers (i.e., organic foulants) were reduced to some extent (19%) by the addition of 6 mg/L coagulant, and a further 42% by the UF membranes. Coagulation at full-scale reduced humic substances by 1%, whereas the membranes removed a subsequent 16% (Figure 6). Therefore, the removal of humic substances by the membrane was likely due to membrane fouling altering the selectivity of the membranes to remove smaller organic components.
With respect to DBP precursor reduction, analysis of the full-scale treatment processes indicated that similar removals of AOX and TTHMs were achieved by coagulation and the UF treatment steps (9–12% reduction). At full-scale, neither coagulation nor the UF membranes were observed to remove HAA precursors (Figure 7). This suggests that HAA precursors in the source water were due to low molecular weight acid fractions of NOM (not HAAs as potentially possible based on pilot-scale studies), which did not exhibit any reductions by coagulation or UF processes.

Results of this study indicated that the coagulant dose applied at full scale (6 mg/L) could be reduced to decrease membrane irreversible fouling while still maintaining similar reductions in DBP precursors as those achievable at the existing dose. Reducing the coagulant dose would be expected to generate cost savings for the treatment plant, both with respect to decreasing chemical (PACl) demand, as well as decreasing membrane replacement costs associated with decreased irreversible fouling extending membrane life.

CONCLUSIONS
This study highlighted the importance of pilot-scale testing for coagulation optimization prior to UF and the value of pilot-scale studies in general when optimizing full-scale treatment processes. In addition, this research suggests that the application of a low coagulant dose, optimized for biopolymer removal, may be preferential with respect to reducing membrane fouling, than the application of higher dosages frequently applied at full scale drinking water treatment plants. For waters with relatively low concentrations of organic matter, the application of too much coagulant prior to UF membranes may result in the coagulant itself being the primary membrane foulant. In addition, this study highlighted the modest reductions of DBP formation (<14%) with the addition of coagulant at both 0.5 and 6 mg/L dosages, relative to conditions where no coagulant is applied.

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