Factors affecting coagulation as a pretreatment to ultrafiltration membranes

Marek J. Ratajczak, Kirsten N. Exall and Peter M. Huck

ABSTRACT

Low pressure membranes can be effective in treating various types of water, but are subject to fouling. In this work, chemical coagulation was studied as a pretreatment to ultrafiltration (UF), with the goal of mitigating fouling while maintaining high permeate water quality. Alum and ferric chloride were evaluated, as well as two polyaluminum chloride (PACl) products of different basicities and compositions. A bench-scale hollow fiber UF unit was developed to study the treatment of raw and pretreated water from two southern Ontario drinking water sources. The four coagulants were compared at optimal dosages, as well as at lower dosages. The roles of mixing and pH conditions were also evaluated. Membrane fouling was evaluated by observing changes in trans-membrane pressure (TMP) over 3-day experiments. Under optimal dose conditions, all four coagulants were able to reduce the rate at which the membrane fouled to varying degrees for each water source. Total organic carbon (TOC) removal by the membrane was also enhanced with coagulation pretreatment as would be expected. Experiments conducted with low coagulant dosages displayed under-dosing and a subsequent increase in membrane fouling. Experiments conducted with modified raw water pH improved both membrane performance and TOC removal, while experiments with modified mixing intensities proved ineffective.

Key words | coagulation pretreatment, enhanced coagulation, fouling, trans-membrane pressure, ultrafiltration

INTRODUCTION

Low pressure membrane systems have become widely accepted to augment conventional drinking water treatment. One of the primary limitations of membrane systems is fouling, which is primarily caused by inorganic particulates and dissolved or suspended organic materials that were adsorbed inside the pores and on the surface of the membrane (Howe & Clark 2002; Amy 2008). Particulate fouling can often be minimized with a backwash cycle, while organic fouling generally requires chlorine-based chemical cleaning of membranes for removal (Howe & Clark 2002).

Several pretreatment processes have been employed for reduction of particulate and organic fouling, which were recently reviewed by Huang et al. (2009) and Farahbakhsh et al. (2004) in detail. Coagulation has been identified as the most effective pretreatment method so far by Huang et al. (2009) and is most commonly conducted with the hydrolyzing metal salt (HMS) coagulants, alum or ferric chloride, or with prehydrolyzed HMS coagulants, such as polyaluminum chloride (PACl).

HMS COAGULANTS

When HMS coagulants are added to water, hydrolysis reactions produce a variety of mononuclear and polynuclear aluminum or iron species, as well as amorphous form metal hydroxide precipitates. Coagulation proceeds by two main mechanisms, depending on the coagulant dose and pH of the raw water. In a charge neutralization mechanism,
which occurs at lower pH values (5.5–6.5), small particles are destabilized by the charged metal species and aggregate together as flocs that can be more easily settled or filtered from suspension. At higher pH values (>6.5) and/or higher coagulant concentrations, the dominant process is sweep flocculation, in which particulates are removed as they are enmeshed in metal hydroxide flocs. The coagulation processes mainly target particulates, but some dissolved organics may also be effectively removed by complexation with coagulant species or binding to metal hydroxide flocs. In fact, the interactions between the coagulants and organics present in raw source water typically dominate the process and the effective coagulant dosage is often controlled by the natural organic matter (NOM) content in the raw water (Gregory & Duan 2001).

The effectiveness of coagulation as pretreatment for ultrafiltration (UF) can be improved by considered coagulant selection, as well as adjustment of dosage, mixing, and pH conditions. The use of HMS coagulants as pretreatment to UF membranes has been well documented in many studies that reported marked improvement in permeate quality and a possible reduction in fouling (e.g. Choi & Dempsey 2004; Farahbakhsh et al. 2004; Howe & Clark 2006). The interactions between source water constituents, coagulants and membrane materials are not well understood, and there remain organic foulants that are not amenable to removal by coagulation. It has been suggested by Amy (2008) that colloidal-size hydrophilic organics, particularly polysaccharide- and protein-like NOM components, produce the greatest difficulties in terms of fouling, but the exact structure and composition of many foulants have not been definitively identified, making accurate prediction of membrane fouling difficult (Huang et al. 2009).

PREHYDROLYZED COAGULANTS

The use of prehydrolyzed PACl coagulants for UF pretreatment has gained popularity in recent years. Prehydrolyzed coagulants are prepared by addition of a base during manufacturing, thereby promoting hydrolysis and the formation of polynuclear metal species. The basicity of a PACl coagulant, or the relative amount of base added, determines the extent of hydrolysis induced during the manufacturing of the coagulant. Many PACl products are available commercially, varying in terms of basicity, strength and presence of other species (such as sulfate or silicate). Specific benefits of the prehydrolyzed PACl coagulant products include improved performance, particularly in conventional treatment of low or high alkalinity waters and at low temperatures (Pernitsky & Edzwald 2006; Yan et al. 2008). Prehydrolyzed coagulants have also been found to be as effective as alum for UF fouling mitigation under such conditions as lower water temperatures (<10 ºC) (Gitis et al. 2005; Howe & Clark 2006).

COAGULATION CONDITIONS

Optimal doses of coagulants for coagulation-sedimentation processes have been shown to be very efficient at mitigating UF membrane fouling (Barbot et al. 2008; Huang et al. 2009). Although it is quite common practice to employ lower coagulant dosages in pretreatment for UF as the pinpoint flocs formed are still larger than the pores on the membrane surface, improper dosage conditions can exacerbate fouling (Choi & Dempsey 2004; Shon et al. 2005).

During coagulant addition, mixing is an important factor. Initial flash mixing allows thorough dispersal of the coagulant, while slow mixing during flocculation encourages particle collisions and formation of aggregates. If slow mixing is too vigorous or intense, shear forces may disrupt flocs, leading to poor settling and removal of contaminants. The optimal mixing conditions are a function of several parameters that vary for each water source depending on the NOM concentration, turbidity, temperature, alkalinity and coagulant dose itself (Barbot et al. 2008). The coagulation process is also strongly affected by the pH of the raw water, which can impact the charges on coagulant species, particulate contaminants and organic matter. Optimal pH levels for turbidity removal are in the range of 4.5–5.5 for iron-based coagulants, 5.5–6.5 for aluminum-based coagulants and 6.5–7 for PACl coagulants (Sharp et al. 2006). Optimum pH levels for removal of dissolved organics are usually somewhat lower, typically in the pH range of 5–6, because of the increased negative charge that is induced on the surface of the NOM (Gregory & Duan 2001).
THIS STUDY

The primary goal of this work was to investigate the impacts of various coagulation conditions on the effectiveness of four different coagulants (alum, ferric chloride, PACl Stern-Pac (SP) and PACl SternPac (SP) 70) as pretreatment to hollow fiber UF membranes. In this study, a bench-scale apparatus was designed to evaluate the fouling reduction that could be achieved with each coagulant for two very different water sources (Grand River and Lake Ontario), and to examine the effects of coagulant dosage, mixing intensity and pH.

METHODS

Raw water samples were collected between April and August 2006 from the intake at the Mannheim Water Treatment Plant in Kitchener, Ontario, for which the Grand River is the water source. Samples were collected between May and August 2006 from the Woodward Avenue Water Treatment Plant in Hamilton, Ontario, for which Lake Ontario is the water source. Data recorded by the Drinking Water Surveillance Program (DWSP, Table 1) show that Lake Ontario water typically has lower total organic carbon (TOC), alkalinity and turbidity levels than Grand River water, though similar pH levels.

Four coagulants were compared: alum, ferric chloride, and two prehydrolyzed products of different formulations, PACl SP (50% basicity, no sulfate) and PACl SP 70 (70% basicity, with sulfate). All four products were supplied by Eaglebrook International Group Ltd (now part of Kemira Water Solutions Inc., Matteson, Illinois). A summary of the coagulant properties is shown in Table 2.

Optimal coagulant dosing conditions for coagulation-sedimentation were determined by jar test trials conducted on a Phipps and Bird six-place stirrer. The jar test trials were designed following the methods proposed by Randtke (1988) and also based in AWWA (2005); these included a rapid mixing phase at 100 rpm (velocity gradient of 70 s⁻¹) for 2 min, a slow mixing phase at 20 rpm (10 s⁻¹) for 20 min and a settling period of 40 min without mixing. The coagulant dose that yielded the lowest TOC concentration in the settled water was chosen as the optimal dose and it was used in the subsequent membrane treatment experiments.

Coagulation-ultrafiltration bench-scale apparatus

A unique bench-scale coagulation and membrane apparatus was designed and constructed to perform all of the treatment tests. Figure 1 shows a flow diagram of the system.

The raw water and coagulant streams were blended with an in-line mixer, and were then fed into the bottom of the flocculation tank, which had a 1.5 L capacity. All experiments were conducted in a flocculation tank with influent flow at the rate of 90 mL/min, yielding a hydraulic retention time of 16 min. A mechanical mixing blade, set to 30 rpm, was used for slow mixing. The flocculation tank also provided partial sedimentation, as many of the flocs generated settled to the bottom of the tank.

Table 1 | Water quality ranges for the two source waters (DWSP 2005)

<table>
<thead>
<tr>
<th>Water source</th>
<th>Alkalinity (mg CaCO₃/L)</th>
<th>TOC (mg/L)</th>
<th>Turbidity (NTU)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grand River</td>
<td>150–200</td>
<td>5.0–6.9</td>
<td>2.0–16</td>
<td>7.4–8.4</td>
</tr>
<tr>
<td>Lake Ontario</td>
<td>90–110</td>
<td>1.5–2.9</td>
<td>0.5–1.5</td>
<td>7.7–8.3</td>
</tr>
</tbody>
</table>

Table 2 | Coagulant properties

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Empirical formula</th>
<th>% Active metal as supplied</th>
<th>Basicity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum sulfate (Alum)</td>
<td>Al₂(SO₄)₃·14H₂O</td>
<td>4.3</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>FeCl₃</td>
<td>11</td>
<td>Not applicable</td>
</tr>
<tr>
<td>PACl SP</td>
<td>Al₂(OH)₃Cl·2H₂O</td>
<td>5.4</td>
<td>50</td>
</tr>
<tr>
<td>PACl SP 70</td>
<td>Al₁₃(OH)₂₇·2(SO₄)₂Cl₉·5</td>
<td>5.5</td>
<td>70</td>
</tr>
</tbody>
</table>
The flocculated water was fed by gravity into an acrylic membrane tank designed specifically for this application. The membrane tank was a cylinder, with an inner diameter of 0.076 m (3″), and a length of 0.356 m (14″). At each end, industrial strength PVC caps created a waterproof seal. The polyvinylidene fluoride (PVDF) hollow fiber membrane unit fit snugly in the acrylic tank, with no room to move laterally, which maximized the tank intensity of the system by minimizing the volume of feed water in the tank, while at all times keeping the module submerged. This was done to simulate a full-scale membrane treatment system, where fibers are packed compactly into cassettes. As seen in Figure 1, there were three points of automation that allowed the system to run in a continuous batch mode: (1) the air valve, (2) the permeate pump, and (3) the tank drain valve. The membrane system was designed to run for 3 days continuously without supervision, automated by a simple programmable logic controller (PLC; Rockwell Automation Inc., Milwaukee, WI). The PLC controlled the open/close operation of both the air and drain valves as well as the start/stop operation of the permeate pump. Trans-membrane pressure (TMP) was recorded with a pressure transmitter Model 68075 (Cole Parmer Inc., Vernon Hills, IL), installed at the bottom of the membrane tank as seen in Figure 1. All experiments were conducted with the following sequence of events:

1. Permeation at 45 mL/min for 35 min, equivalent to a gross flux of 30 L/m²h
2. Permeation stopped, backwash at 45 mL/min (30 L/m²h) with air pulse at 0.085 m³/min for 20 s measured using a rotometer
3. Tank drainage with air pulse at 0.085 m³/min for 20 s
4. Membrane tank re-fill (10 min), air and permeate off
5. Repeat.

Over a 24-h period, the overall net flux is calculated as 23 L/m²h, which takes into consideration the downtime attributed to the backwash, drain and fill cycles. When membrane modules were not in use, they were stored in a 100 mg/L solution of sodium hypochlorite to avoid microbiological growth and formation of biological foulants on the surface and inside the pores of the membrane fibers.

Membrane experiments design

All membrane experiments lasted for 3 days. The membrane experiments were designed to examine a number of parameters:

(A) raw water source (Grand River vs. Lake Ontario);
(B) coagulant dose (comparing optimal dose and half the optimal dose);
(C) mixing intensity in the flocculation tank; and
(D) modified pH.

Table 3 provides a concise summary of the experimental design, which includes the optimal coagulant doses as observed during the jar test trials. Hydrochloric acid was used to reduce the raw water pH to 5.0 for the ferric chloride experiments and 5.5 for both alum and PACI experiments, respectively.
A total of six ZeeWeed-1 hollow fiber membranes (GE Water and Process Technologies, ZENON Membrane Solutions, Oakville, ON) were used for this study. One membrane was designated for each of the four coagulants, and one for controls for each of the two raw water sources. The membranes were composed of PVDF, with a nominal pore size of 0.04 micron, a membrane surface area of 0.047 m² and flow rates of 1.4–3.3 L/h at operating pressures of 0–70 kPa.

Water quality analyses were performed with the water collected from the two water treatment facilities, as well as permeate samples collected daily during each of the experiments. Time-composite permeate samples were collected in a 1,000 mL graduated cylinder over a 20 min period half way through each of the 3-day experiments. Samples were collected at the same time for all membrane experiments to ensure any variation in water quality observed as a function of the run time was not a variable condition. The composite samples were then split for water quality analyses. TOC was measured by wet chemical oxidation (OI Analytical, College Station, TX). Turbidity was measured with a portable hand-held Hach 2100P turbidimeter (Hach Co., Loveland, CO). Alkalinity, TOC and turbidity were all measured according to Standard Methods (APHA, AWWA, WEF 2005).

### RESULTS AND DISCUSSION

#### Jar testing results

Table 4 summarizes the coagulant doses that yielded the highest TOC removals for both raw water sources, as well as the mean TOC removal achieved at that dosage. Results presented in Table 4 were taken as an average of two measured values of the same sample.

Comparing the optimal TOC removals for the two sets of raw water shows that for all the coagulants except ferric chloride, experiments conducted with Grand River water yielded higher percentage removals of TOC, taking into account the fact that the TOC levels were much higher in the Grand River; however, the differences in percentage removals between the four experiments for each water source were not large. On a molar basis, the lowest metal dosage was required for alum with both water sources, while the ferric chloride and both PACl products required...
roughly twice the metal dosage to bring about TOC removal. The ferric chloride proved to be least efficient at removing TOC in the Grand River water in that it required the second largest dose of coagulant (on a per mole basis) and resulted in the lowest percentage TOC removal.

Membrane treatment results

Raw water source

Figures 2 and 3 show the TMP plots for experiments conducted with the two raw water sources with no coagulation; each plot represents 13,000 data points collected over the duration of the 3-day membrane experiments. Data points were recorded every 20 s over the duration of the 3-day experiment by the PLC and automatically uploaded to a database. The TMP values are actually negative given that the system operates under vacuum, but are shown as absolute values for clarity of the figure. Each production cycle lasted 35 min, followed by 20 s of aeration at 0.085 m$^3$/min, then a 20 s tank drain, while maintaining aeration at 0.085 m$^3$/min. The pressure transducer recorded positive TMP values during the tank drain and fill which are not shown on this plot. Pressure data were recorded in units of psi, which is converted to kPa by multiplying by a factor of 6.89 (1 psi = 6.89 kPa).

As seen in both figures, the TMP was approximately 2.75 psi (6.9 kPa) at the beginning of the experiment. The rate at which the TMP rose (fouling rate) observed on the first day highlighted the difference in water quality in

| Table 4 | Jar test trials results summary |
| --- | --- | --- | --- | --- | --- |
| Coagulant | Grand River (6.8 mg/L average raw water TOC) Dosage (mg coagulant/L) | Dosage $(10^{-5}$ mol metal/L) | TOC removal (%) | Lake Ontario (2.2 mg/L average raw water TOC) Dosage (mg coagulant/L) | Dosage $(10^{-5}$ mol metal/L) | TOC removal (%) |
| Alum | 30 | 4.8 | 53 | 15 | 2.4 | 48 |
| FeCl$_3$ | 45 | 8.9 | 39 | 20 | 3.9 | 52 |
| PACl (SP) | 40 | 8.0 | 56 | 15 | 3.0 | 47 |
| PACl (SP 70) | 50 | 10.2 | 64 | 20 | 4.1 | 42 |

Figure 2 | Raw Grand River water 3-day membrane experiment.
these two water sources. For the Grand River experiment (Figure 2), the fouling rate was approximately 15.0 psi/day for the first 16 h, after which it levelled off to the much lower rate of 0.1–0.4 psi/day for the remainder of the 3-day experiment. For the Lake Ontario experiment (Figure 3), the fouling rate was moderate at 4.0 psi/day for the first 6 h, but it then levelled off to continue to rise at a rate of 0.5 psi/day for the duration of the 3-day experiment. The accelerated fouling rates observed at the beginning of the 3-day experiments are typical of a ‘break in’ process that is commonly observed with PVDF UF membranes (Mosqueda-Jimenez et al. 2008). During the first few production cycles, a fraction of pores are rapidly fouled; these are not readily recovered via backwashing and the TMP rises proportionally. The time required to break in a membrane is a function of the raw water quality, specifically organic and colloidal materials. After that period, the fouling rate stabilizes, making it easier to extrapolate a trend into the future production cycles (Mosqueda-Jimenez et al. 2008).

The Grand River contained a very high concentration of solids and TOC (8.1 NTU and 6.3 mg/L, respectively) compared to the very low turbidity Lake Ontario water (0.5 NTU), and as a result, the accumulation of the solids caused a great deal of fouling, reaching 12 psi before the end of the first day of the experiment. The lack of recovery of TMP observed after each tank drain and backwash suggests that fouling was not simply cake layer formation, but rather caused by small colloids and/or organic compounds adsorbed to the surface and inside the pores of the membrane fibers (e.g. Hallé et al. 2009). The trends observed during the Lake Ontario raw water experiment showed a reduced rate of fouling over the duration of the entire 3-day experiment, but the rate after the break in period was slightly higher than that seen with Grand River water.

The permeate water quality during and after the break in period was similar for both the Grand River and Lake Ontario experiments. The TOC concentrations and turbidity in the permeate varied by an average of only 10–15% throughout the experiments.

Coagulant type and dose

Figures 4 and 5 show summaries of the Grand River and Lake Ontario membrane experiments conducted with the optimal doses for all four coagulants determined during the jar test trials (Table 4). In both figures, each of the five plots represents a simplified trend line extracted from the
raw data points by taking an average value of 10 pre-backwash TMP readings and plotting the corresponding points. The pre-backwash TMP readings represent the most severe fouling trend, as this is the point where the most solids will have accumulated on the surface of the membrane. The ‘post tank drain’ TMP trend line shown for the raw water experiment represents the TMP readings recorded 15 s after a new production cycle begins. The difference in
TMP between the ‘post tank drain’ and pre-backwash trend line represents the extent to which the TMP rises during each production cycle.

During the experiments conducted with Grand River, alum proved most effective in reducing the membrane fouling, with a final TMP of 5.3 psi; this represents a 57% reduction compared to the raw water membrane experiment, which yielded a final TMP of 12.5 psi. The three other coagulants yielded TMP reductions of 44, 46 and 40% for ferric chloride, PACl SP and PACl SP 70, respectively, when compared to the 3-day experiment conducted with no pretreatment. It was surprising that alum outperformed both PACl coagulants in terms of fouling reduction, given that slightly better TOC removals were achieved during the jar test trials with PACl SP and PACl SP 70. This trend indicates that alum better targets the material that contributes most to fouling, rather than removing TOC as a whole.

Although the floc size was not directly measured for each coagulant and water combination, it was clear that the ferric chloride floc size was substantially larger than those formed using the three aluminum-based coagulants. The larger flocs settled well to form a noticeably thicker sludge blanket at the bottom of the flocculation tank, which likely contributed to the reduced fouling observed with ferric chloride. The floc sizes for the three aluminum-based coagulants were very similar, as was the extent to which the flocs were transferred to the membrane tank. Overall, the results presented in Figure 4 demonstrate that TOC removal in a jar test is not necessarily a good indicator of fouling mitigation.

During the experiments conducted with Lake Ontario water, the two prehydrolyzed coagulants were most effective at slowing the rate of fouling, reducing the final TMP by 20 and 22% for PACl SP and PACl SP 70, respectively. Alum and ferric chloride yielded TMP reductions of 12 and 15%, respectively.

Tables 5 and 6 present a summary of the TOC and turbidity removal data for both sets of membrane experiments. Samples were taken from the membrane system on a daily basis in duplicate. In both tables, TOC and turbidity results are presented for samples taken after coagulation and after

### Table 5 | TOC and turbidity removals during bench-scale membrane experiments with optimal coagulant doses using Grand River source water

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>TOC&lt;sup&gt;a&lt;/sup&gt; (Raw water concentration, mg/L)</th>
<th>% Removal after coagulation</th>
<th>% Removal after coagulation-UF</th>
<th>Turbidity&lt;sup&gt;b&lt;/sup&gt; (Raw water turbidity, NTU)</th>
<th>% Removal after coagulation</th>
<th>% Removal after coagulation-UF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum</td>
<td>6.6</td>
<td>53 (1.1)</td>
<td>60 (0.5)</td>
<td>10.1</td>
<td>73 (0.6)</td>
<td>&gt;99 (0.1)</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>6.7</td>
<td>60 (2.4)</td>
<td>67 (0.8)</td>
<td>9.2</td>
<td>65 (4.3)</td>
<td>&gt;99 (0.3)</td>
</tr>
<tr>
<td>PACl (SP)</td>
<td>6.2</td>
<td>48 (2.0)</td>
<td>55 (1.3)</td>
<td>5.2</td>
<td>78 (5.3)</td>
<td>&gt;99 (0.4)</td>
</tr>
<tr>
<td>PACl (SP 70)</td>
<td>6.4</td>
<td>53 (1.4)</td>
<td>60 (1.0)</td>
<td>8.1</td>
<td>73 (5.7)</td>
<td>&gt;99 (0.3)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Note: Average measured initial values for Grand River water: TOC = 6.8 mg/L, turbidity = 5.6 NTU.
<sup>b</sup>Standard deviation values calculated using daily sample results shown in brackets.

### Table 6 | TOC and turbidity removals during bench-scale membrane experiments with optimal coagulant doses using Lake Ontario source water

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>TOC&lt;sup&gt;a&lt;/sup&gt; (Raw water concentration, mg/L)</th>
<th>% Removal after coagulation</th>
<th>% Removal after coagulation-UF</th>
<th>Turbidity&lt;sup&gt;b&lt;/sup&gt; (Raw water turbidity, NTU)</th>
<th>% Removal after coagulation</th>
<th>% Removal after coagulation-UF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum</td>
<td>2.8</td>
<td>33 (4.2)</td>
<td>45 (2.0)</td>
<td>0.52</td>
<td>35 (12.0)</td>
<td>95 (4.0)</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>2.6</td>
<td>28 (2.1)</td>
<td>35 (2.5)</td>
<td>0.66</td>
<td>8 (7.50)</td>
<td>95 (2.3)</td>
</tr>
<tr>
<td>PACl (SP)</td>
<td>2.7</td>
<td>23 (2.4)</td>
<td>31 (0.8)</td>
<td>0.38</td>
<td>55 (10.5)</td>
<td>95 (3.0)</td>
</tr>
<tr>
<td>PACl (SP 70)</td>
<td>2.5</td>
<td>18 (3.0)</td>
<td>25 (3.0)</td>
<td>0.62</td>
<td>35 (22.0)</td>
<td>95 (2.5)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Note: Average measured initial values for Lake Ontario water: TOC = 2.2 mg/L, turbidity = 0.5 NTU.
<sup>b</sup>Standard deviation values calculated with daily sample results shown in brackets.
UF treatment. There was no statistically significant difference based on the analysis completed in duplicate for the TOC results for samples taken at the beginning, middle or end of the 3-day experiment.

As previously mentioned, alum performed best at reducing the membrane fouling during the experiments conducted with Grand River, but did not yield the highest TOC removal results. Experiments conducted with ferric chloride yielded slightly higher TOC removal results, at least 7% higher than seen with the other coagulants. Considered along with the patterns in TMP reduction, these results show that although alum was not the most effective in terms of overall TOC reduction, it was in fact the most efficient at removing the constituents that were primarily responsible for fouling of the UF membrane. An additional 20–35% turbidity removal was observed after UF filtration across all experiments when compared to the turbidity following coagulation, demonstrating that regardless of which of the four coagulants are selected, there will be a fraction of coagulated solids that are carried through to the UF tank under the operating conditions used in this pretreatment process. The solids that were rejected by the membrane were drained from the tank during each tank drain cycle.

Comparing the results provided in Table 6 for the Lake Ontario experiments, the PACI coagulants provided the worst TOC removal results, but were the most effective in controlling membrane fouling. When designing a coagulation pretreatment process, a utility should therefore carefully consider the goals of pretreatment and may need to compromise between bulk TOC removal and fouling reduction. Note that the jar tests (Table 4) underestimated TOC removal by FeCl₃ in Grand River water and overestimated TOC removal in Lake Ontario water for FeCl₃ and the PACI products. This further emphasizes the influence of operating conditions on the effectiveness of organic matter removal by coagulation processes and highlights the utility of alternative bench-scale testing procedures for combined coagulation-UF processes.

Similar to the results presented for the Grand River experiments, Table 6 also provides a summary of the ability of the UF membrane to remove particulate TOC that is not removed by coagulation alone. An additional 7–10% TOC removal was observed after UF filtration across all experiments.

In comparing the results for the two water sources, it can be seen that the PACI products were very effective for the lower alkalinity, lower TOC Lake Ontario water, while alum was far more effective in the higher alkalinity, higher TOC Grand River water. Compared to alum, a higher molar dosage of FeCl₃ was required in both water sources, but better TOC removals were also observed with FeCl₃, suggesting a difference in the interactions between the organic matter and the iron hydrolysis products formed under these conditions, compared to those formed with alum. Further investigation of the hydrolysis reaction products formed with each coagulant type would be needed to better understand such interactions.

Walsh et al. (2009) found that lower coagulant dosages were adequate for UF pretreatment than might be required for conventional treatment. To determine if there was a benefit of operating a coagulation process for UF pretreatment with doses that were lower than the optimal doses determined by jar test, alum and SP were applied to Grand River water at 15 and 20 mg/L, respectively, corresponding to half the optimal dose for both coagulants. The results of the two sets of dose experiments (optimal dose and half optimal dose) are compared in Figure 6.

Dosing at half of the optimal coagulant concentration yielded TMP reductions of 22 and 17% for alum and SP, respectively. These results compare poorly with the 57 and 46% TMP reductions observed for optimal doses of alum and SP, respectively. Although some evidence has suggested that lower doses of coagulant may be preferred during pretreatment for membrane filtration (e.g. see Walsh et al. 2009), other results have shown that underdosing may exacerbate the rate at which fouling occurs, and ultimately accelerate the time during which the membrane reaches a terminal TMP level, where backwashing and/or chemical cleaning is required (Farahbakhsh et al. 2004). The results in Figure 6 indicate that the low doses used here simply did not provide a sufficient amount of coagulant to accommodate the high concentration of solids and organics in the raw Grand River water. Visually, it was clear that floc formation was not as effective during these sets of experiments; the water flowing into the membrane tank maintained a brownish, turbid appearance, with an average turbidity of 5.2 and 5.7 NTU for alum and SP respectively, as compared to the experiments conducted with optimal doses.
which had values of 2.2 and 2.8 NTU. The TOC removals for the half optimal dose experiments were 42 and 31\% for alum and SP, respectively, as compared to 53 and 56\% for the same coagulants at optimal doses. These results were attributed entirely to the under-dosing of both coagulants. Other studies have demonstrated that dosing alum at doses considered suboptimal for conventional water treatment (i.e. less than 10 mg/L) prior to UF treatment resulted in TOC removal ranging from 30 to 50\%, but improved incrementally with a further increase in coagulant dose up to 30 mg/L, where a removal of 76\% was achieved (Walsh et al. 2009).

**Mixing intensity in the flocculation tank**

The optimal mixing conditions for pretreatment processes preceding UF membranes are typically determined experimentally during pilot tests. Grand River membrane experiments were conducted using the optimal doses of all four coagulants, with mixing intensities in the flocculation tank elevated from 30 to 45 rpm. The bench-scale apparatus developed for this research provided a great deal of flexibility to be able to modify the operational parameters such as the mixing intensity, coagulant dose, raw water pH using smaller volumes of water than in a pilot test and without having to make any mechanical modifications.

During operation at 30 rpm, a particle concentration gradient developed in the flocculation tank and the accumulation of flocs on the bottom of the tank could be observed. At the top of the tank, where the effluent spout was located, there were relatively few flocs. The system thus behaved essentially as a conventional filtration unit (i.e. with sedimentation), rather than a direct filtration pretreatment system. In contrast, during the experiments conducted with the elevated mixing intensities (45 rpm), the solids gradient and the accumulation of particles on the bottom of the tank was not clearly observed, as a larger proportion of particles remained suspended and were thereby transferred to the membrane tank. The results of the modified mixing intensity experiments (45 rpm) are shown in Figure 7.

Increased shear stresses at higher mixing intensity have also been shown to reduce the size of the flocs produced (Droppo et al. 2008), which could lead to greater carry-over into the membrane tank. Across all four experiments, the floc size was observed as being noticeably smaller and were approximately half the size of the flocs observed with the experiments conducted with optimal doses and a mixing intensity of 30 rpm. Because of the increased transfer
of smaller flocs from the flocculation tank into the membrane tank, the overall fouling rate increased across all for experiments, resulting in a final TMP that was 20–40% higher as compared to the experiments performed with a 50 rpm mixing intensity. The increased fraction of flocs transferring over to the membrane tank expanded the TMP range that was observed during each production cycle, but the system recovered after each backwash and drain cycle similarly to the optimal dose experiments, demonstrating that a substantial portion of the fouling is attributed to a solid cake formation which is readily removed during the backwash and aeration cycle.

Table 7 provides a summary of the effects on TMP of applying optimal doses of the coagulants to Grand River water at the two mixing intensities.

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Mixing intensity (%)</th>
<th>Reduction in TMP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alum</td>
<td>30 rpm</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>45 rpm</td>
<td>33</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>30 rpm</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>45 rpm</td>
<td>32</td>
</tr>
<tr>
<td>PACI (SP)</td>
<td>30 rpm</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>45 rpm</td>
<td>28</td>
</tr>
<tr>
<td>PACI (SP 70)</td>
<td>30 rpm</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>45 rpm</td>
<td>23</td>
</tr>
</tbody>
</table>

*Relative to conditions observed without coagulant.

Although fouling was still reduced using all four coagulants at the higher mixing rate, it did not compare to the reductions observed at the lower mixing intensity. In spite of the reduction in fouling control, water quality results showed that the TOC concentration decreased by 6–17% for all four coagulants at the elevated mixing intensity.

**Modified pH**

The Grand River membrane experiments conducted with a reduced raw water pH are shown in Figure 8. The pH levels utilized represented those considered to produce optimal coagulation for TOC removal (Gregory & Duan 2004), a pH of 5.0 for the ferric chloride experiments and a pH of 5.5 for alum and the two PACI coagulants.

As with the experiments conducted with optimal coagulant doses without pH adjustment (Figure 4), alum was most effective at reducing the membrane fouling with Grand River water, with a final TMP of 4.8 psi. This was a slight improvement in TMP at the end of the 3-day experiment compared to the optimal dose experiments without pH adjustment (final TMP of 5.3 psi). The three other coagulants yielded final TMPs of 6.3, 6.0 and 6.7 psi, representing a slight improvement in all cases as compared to the experiments without...
pH adjustment. Under conditions of reduced pH, the charge neutralization mechanism dominates, which Lee et al. (2000) suggested was most efficient for fouling reduction for a submerged MF membrane due to improved organics removal and differences in cake resistance compared to sweep flocculation. In this study, a comparison of the TOC removal results showed that there was only a nominal improvement of 1–5% over the experiments conducted without pH adjustment for the four coagulants. While it was expected that reducing the pH would improve TOC removal during the coagulation step (Lee et al. 2000), this effect was not apparent in these experiments.

CONCLUSIONS

The following conclusions can be drawn from this bench-scale study of coagulation as a pretreatment to UF membranes, using two different water types:

- For Grand River water, alum performed best at reducing the membrane fouling, with a 57% reduction in overall TMP. The three other coagulants were slightly less effective in reducing TMP. During the Lake Ontario experiments, the two prehydrolyzed coagulants performed the best at reducing the membrane fouling, yielding approximately 20% reduction in final TMP.
- Water quality results complemented the TMP trends observed during the membrane experiments. The optimal Grand River experiments yielded TOC removals of 47–65%. Comparatively, the membrane experiments conducted with Lake Ontario water yielded TOC removals of 24–36%.
- The study showed that the highest TOC removals do not necessarily correspond to the lowest membrane fouling rate. Experiments conducted with alum yielded the best membrane performance using Grand River water, but ferric chloride was able to remove the highest fraction of TOC.
- The two membrane experiments conducted with half the optimal dose for alum and SP displayed characteristics of underdosing. Although removal of TOC and reduction of fouling were observed, the rate of TMP increase was higher than at optimal dosages.
- Increasing mixing intensity by 50% resulted in more rapid fouling as a larger portion of the flocs were transferred from the flocculation tank to the membrane tank. This contributed to a faster forming membrane fouling layer on the surface of the membrane.
• Membrane experiments conducted with modified raw water pH coupled with optimal coagulant doses yielded only a slight reduction in TMP for all four coagulants when compared with experiments conducted with no pH adjustment.
• The bench-scale apparatus developed for this study enabled the evaluation of factors influencing the effectiveness of coagulation-UF processes, in a way that is relevant to full-scale treatment systems, but without the time and volumes required in pilot tests.

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