Practical Paper

Supplementing coagulation with powdered activated carbon as a control strategy for trihalomethanes: application to an existing utility

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ABSTRACT

To support a water treatment plant in meeting trihalomethanes (THM) legislation, different THM control strategies using existing treatment processes were investigated. The effectiveness of optimised coagulation and of powdered activated carbon (PAC) (0–25 mg/L) as a mean of supplementing natural organic matter (NOM) removal was assessed. Simultaneous full-scale and bench-scale trials were performed to document THM reductions. At the plant, source and treated water total organic carbon (TOC) was monitored online. At full scale, optimised acidified alum coagulation (3.2 mg/L Al) achieved the maximum NOM removal and the lowest THMFP concentration. Although PAC (11 mg/L) showed a small reduction in TOC (7%) and taste- and odour-causing compounds, results indicated no significant THM reductions. Coagulation and PAC adsorption trials showed a good agreement between bench-scale and plant results.

Key words | coagulation, full scale, jar test, PAC, THM

INTRODUCTION

Chlorine is the most commonly used disinfectant in the water industry due mainly to its proven efficacy against waterborne diseases. However, the reaction between chlorine and natural organic matter (NOM) generates chlorination by-products, including trihalomethanes (THM). Following increasing evidence of THM's carcinogenic potential and the controversy related to their adverse effects on pregnancy (Mills et al. 1998; Savitz et al. 2006; World Health Organisation 2006), many authorities have implemented a regulation limiting THM concentrations in drinking water. Inspired by the US disinfectant/disinfection by-product rule (USEPA 1998), Quebec's Ministry of Environment (MDDEP 2001) fixed the limit at 80 μg total THM/L. This limit is based on an annual running average of four samples collected quarterly at the extremity of the distribution system. Compliance to this rule might be a particular challenge for existing utilities relying on chlorine for disinfection.

The extent of THM formation is a function of source water quality and disinfection conditions (Singer 1999). THM formation generally increases with raw water NOM content, chlorine dosage, contact time, water temperature and water pH. Water utilities dealing with THM issues may therefore turn to different control strategies mainly based on the reduction of THM precursors or changes in disinfection conditions. For an existing facility seeking optimisation of its infrastructure, the first approach should target the removal of THM precursors. THM precursors are related to the NOM content of source water, mainly humic and fulvic substances, which are commonly characterised by total organic carbon (TOC) or ultraviolet absorbance at 254 nm (UV$_{254}$) measurements.

Enhanced coagulation is cited as one of the best available technologies to control THM in USEPA's Stage 2 Disinfectants and Disinfection By-products Rule (USEPA
The effectiveness of coagulation may vary with factors including concentration, nature and reactivity of organic matter, temperature, alkalinity of raw water, pH and flash mixing conditions. Among the properties of organic matter, molecular weight, solubility, charge density and functional group composition can influence the effectiveness of coagulation. Generally, higher molecular weight and hydrophobic fractions of NOM are more readily removed by coagulation than low molecular weight material, which has also demonstrated a high THM formation potential (Collins et al. 1986; Chang et al. 2001; Liang & Singer 2003). Because coagulation may only remove a finite fraction of NOM, activated carbon is often recommended as a means of supplementing coagulation to increase NOM removal and to control THM formation (Najm et al. 1998; USEPA 2006). PAC adsorption is commonly used to control taste- and odour- (T/O) causing compounds but it can also adsorb NOM fractions as well as other toxic substances. Some studies have reported a better NOM removal through the use of a combination of PAC and enhanced coagulation rather than enhanced coagulation alone (Najm et al. 1998; Uyak et al. 2007). In these studies, PAC removed the low molecular weight and uncharged NOM substances that were unaffected by coagulation. The organic matter of the source water studied by Najm et al. (1998) had a low humic content (SUVA < 1.7 L/mg m), which made it more difficult to remove by chemical coagulation. The coal-based carbon used was dosed up to 80 mg/L although their optimal treatment combination was 45 mg/L ferric chloride and 15 mg/L PAC to meet the THM guidelines. According to their study, most of the adsorption took place in the first 30 min of contact time. PAC application could account for 35–45% TOC reduction for the high dosage of 80 mg/L, depending on the coagulation scenario. The 10 mg/L PAC dosage gave additional TOC removals of less than 10%. Uyak et al. (2007) studied Turkish water with an average SUVA of 3.08 L/mg m and selected optimal dosages of 80 mg/L ferric chloride and 40 mg/L PAC. They chose the Kemisorb PAC for their tests on a NOM removal basis. The additional TOC removal attributed to PAC application was 31%.

Most studies describing the effect of enhanced coagulation and/or PAC on THM formation were performed at the bench scale without full-scale validation. TOC removal by PAC adsorption is also used in membrane systems, with the advantage that PAC is retained in the system long enough for adsorption to approach equilibrium (Adham et al. 1991).

The project described in this paper aimed at reducing THM formation through optimisation of the existing treatments in place (coagulation and PAC) at a water treatment plant (Pointe-Claire) located on the Island of Montreal (Canada). The objectives were twofold: (1) to evaluate the removal of THM precursors and the associated reduction of THM obtained by optimised coagulation and (2) to document the benefits of combining powdered activated carbon with coagulation in order to reduce THM formation. NOM removal and THM reductions were documented by performing and comparing bench-scale and full-scale trials carried out simultaneously.

**METHODOLOGY**

Effects of increasing coagulant dosages on NOM and THM reduction were assessed both at full scale (at the plant) and at bench scale (in jar tests). Two coagulants were tested: alum and acidified alum (5% by weight sulfuric acid). For activated carbon trials, coagulation was supplemented with PAC both in plant and jar tests. Impacts of increasing PAC dosages on NOM removal, THM reduction and taste and odour compounds were investigated.

**Full-scale trials**

**Water treatment plant description**

The drinking water treatment plant under investigation uses a conventional process including alum coagulation (with polyacrylamide polymer as a coagulant aid), sludge-blanket upflow clarifiers (Ultrapulsators), inter-chlorination, dual-layer sand-anthracite filtration and post-chlorination. The plant director estimates at 1 min the rapid mixing time and the time in the clarifiers at 2.5 h. Its source water is a mixture of the St. Lawrence and Ottawa Rivers. Location and mixing of the water bodies is influenced by many variables such as flow, wind, temperature, ice cover, spring runoff, etc. Since both sources have distinctive water characteristics, the plant experiences large variations (pH, conductivity, alkalinity,
TOC), on a daily and seasonal basis. This provides a fairly unique situation which emphasises the importance of coagulation for achieving optimal NOM removal.

**Plant sampling**

Raw water quality was measured through online TOC, turbidity, temperature, conductivity and pH measurements. Online TOC analyses of filtered water were also performed. Inter-chlorination was stopped over one filter for the duration of the trials in order to be able to use UVA measurements as a surrogate indicator of NOM removal without the interference of chlorine oxidation. A 12 h stabilisation period was provided after each change in coagulant/PAC dosage before treated water samples were collected for THMFP, UV$_{254}$ and alkalinity measurements. Samples were preserved at 4°C until analysis.

**Coagulants and powdered activated carbon**

The effects of two coagulants: (1) alum Al$_2$(SO$_4$)$_3$·14H$_2$O and (2) acidified alum (5% W/W sulfuric acid), were assessed in two trial series. Dosages were increased from 2.5–4.6 mg Al/L for alum and from 2.5–4.2 mg Al/L for acidified alum. Each coagulant dosage was applied for a 16 h period, which corresponds to the maximal time interval between filter runs (for the filter with stopped inter-chlorination).

PAC selection was not optimised for THM removal, but rather was based on performance comparison of two commonly used carbons for taste and odour control (Hydrodarco B by Norit and Calgon WPL). The majority of tests were performed using Calgon WPL (a coal-based powdered activated carbon). Dosages ranged from 4–8 mg/L (plant) and 0–25 mg/L (jar test). A dosage of 11 mg/L is the maximum applicable dosage at the plant using the existing PAC feeder.

**Jar tests**

**Jar-test procedure**

Jar tests were performed using a six square jars (2 L) apparatus (Phipps & Bird PB-900). Raw water was collected from the plant at the onset of full-scale trials. The 2 L samples were brought to a temperature of 22 ± 2°C, whilst water temperatures varied between 20.9 and 23.8°C at the plant. The jar-test procedure used was the one developed historically by the plant's operators in order to simulate the prevailing hydraulic conditions. It consisted of 15 s rapid-mix (133 rpm) after coagulant addition, two 120 s mixing periods at 53 and 95 rpm, respectively, followed by an 8 min period at 67 rpm. After a 20 min settling period, water was collected from the sampling port for turbidity, TOC, UV$_{254}$, alkalinity, pH and THMFP measurements.

In order to duplicate plant trials, the coagulant dosages tested included the range applied at the plant (2.5–4.9 mg Al/L for both coagulants). For the activated carbon trials, PAC (4–25 mg/L) was first added as a 1% slurry to raw water and mixed for 30 s at 133 rpm before the onset of the above-described procedure. PAC was applied along with the identified optimal coagulant dosage. The flocculation period was extended from 8 to 60 min in order to maximise the adsorption contact time. As a reference point for performance comparisons, the conventional treatment (initial plant's conditions before full-scale trials) was 3.1 mg Al/L acidified alum.

**Analytical methods**

**UV$_{254}$ analysis**

UV$_{254}$ absorbance measurements were performed using a Cary 100 spectrophotometer (Varian) at a wavelength of 254 nm, with a 1 cm path length quartz cell. Samples were filtered through a prewashed 0.45 μm filter.

**TOC analysis**

Jar-test TOC analyses were performed according to the combustion-infrared 5310-C method from *Standard Methods* (1998), with a Sievers’ TOC analyser. At the plant, TOC concentrations for raw and treated water were monitored using two on-line TOC analysers (Sievers 900).

**THM analysis**

THM formation potential (THMFP) is a method promoting maximal THM formation and is commonly used to assess the performance of THM precursor's removal. Waters were first filtered on a 0.45 μm filter (raw water, filtered water...
and jar test). The pH of all water samples was adjusted to 8.0 with phosphate buffer in order to reproduce the distribution system’s pH. A 2:1 (W/W) chlorine to carbon oxidation level was selected. This approach provided a free chlorine residual of at least 2 mg Cl₂/L after a 7 d incubation period at room temperature (22°C ± 1°C). THMs were quantified with the liquid–liquid extraction method according to the Standard Methods 6232B modified by Koch et al. (1988) and Krasner et al. (1989). The sum of four trihalomethanes—chloroform, bromodichloromethane, dibromochloromethane and bromoform—was reported as the THMFP concentration. Analyses were performed with a gas chromatograph HP5890 Serie II-Plus with a micro-electron capture detector (GC-μECD).

**Taste and odour analysis**

Since MIB and geosmin are common compounds involved in T/O episodes (Zaitlin & Watson 2006), the impact of increasing PAC dosages on the removal of T/O-causing compounds was evaluated by using these metabolites as indicators. Raw water was doped with 50 ng/L MIB and geosmin. MIB and geosmin concentrations remaining after coagulation/PAC treatment were analysed by an external laboratory by a modified GC/MS method (Method 401GEO1 (Séguin 2007)).

**Additional water quality analysis**

Turbidity was characterised with an HACH 2100 AN turbidimeter. Temperature and pH were measured with an AB15 Accumet (Fisher Scientific) instrument. Alkalinity was evaluated using the titration method 2320B (Standard Methods 1998).

**RESULTS AND DISCUSSION**

**Effect of coagulation on the reduction of THM precursors**

**Jar tests**

THM precursors were evaluated through the analysis of TOC and UV254. Figure 1 shows TOC and UV254 removal obtained for increasing alum and acidified alum dosages. Clarified water pH values are also presented. Increasing dosages led to improved precursor’s reductions as indicated by both parameters. The optimal dosages were selected based on the measured TOC removals according to the enhanced coagulation specifications (USEPA 1999) (optimal dosage being the last dosage allowing a minimum reduction of 0.3 mg TOC/L for a 10 mg/L coagulant increase). For alum, a dosage of 3.9 mg Al/L was selected while 3.2 mg Al/L was chosen for acidified alum. These optimal alum and acidified alum dosages allowed, respectively, the removal of 42% and 54% source water TOC. The optimal acidified alum dosage was very close to the conventional treatment dosage (prevailing plant conditions at the beginning of the test: 3.1 mg Al/L acidified alum), no additional removals were calculated. The UV254 removals for the optimal dosages were 64% and 68% for alum and acidified alum, respectively. Since UV254 is an established indicator of NOM aromaticity (Reckhow et al. 1990), it was observed, as expected, that UV254 removals were higher than TOC removal in both jar-test series. This result is consistent with previous studies also showing that coagulation usually removes humic substances more effectively (Krasner & Amy 1995; Vrijenhoek et al. 1998).

Overall, acidified alum achieved a better NOM removal at a slightly lower dosage. Many studies report pH as being a determinant factor governing NOM removal by coagulation (Gregor et al. 1997; Bell-Ajy et al. 2000). Lower pH increases protonation of NOM, making it more
hydrophobic and prone to adsorption on metal hydroxides (Edwards 1997). The pH values obtained at the optimal dosages are suspicious (\(pH_{\text{ac,alum}}: 6.87\), \(pH_{\text{alum}}: 6.74\)) and could not account for the better NOM removal observed. According to theory, the two optimal dosages (3.9 mg Al/L alum and 3.2 mg Al/L acidified alum) should present equivalent pH values for this water, which also does not explain the better performance of acidified alum.

**Full-scale plant trials**

The same alum and acidified alum dosages were applied at the plant, with online recordings of source and treated water TOC values. Figure 2 illustrates the results for the acidified alum assay. The highly variable nature of source water organic matter content is clearly visible. During the one week study period, TOC levels fluctuated between 3.94 and 7.24 mg C/L. Conductivity (90–230 \(\mu\)S) and pH (7.9–8.9) also greatly varied. As expected, increasing coagulant dosage lowered the treated water TOC content. However, raw water variability made TOC removal calculations difficult to interpret, increased raw water TOC being associated with increased TOC removal. Since the optimal dosage could not be based on TOC removal, it was based on the filtered water TOC. The lowest dosage giving a stable (<0.1 mg/L variation) filtered water TOC was selected. The optimal dosage identified was 3.9 mg Al/L for alum and 3.2 mg Al/L for acidified alum (Table 1), the same dosages as for the jar tests.

**Impact of coagulation on THM formation potential**

THMFP measurements obtained for all coagulation trials are presented in Figure 3 as a function of TOC concentration. Lower THM values are clearly associated with lower TOC concentrations. Figure 4 shows more explicitly results for TOC and THMFP as a function of increasing acidified alum dosages. According to plant results, optimised coagulation conditions (3.2 mg Al/L acidified alum) allowed for nearly maximum reduction of THMFP. However, jar-test results tend to indicate higher possible removals for higher coagulant dosages. The alum results (not shown) also indicated that greater removals could be obtained with dosages higher than the optimal one (based on TOC). Providing that higher coagulant dosages could be applied at the plant without deteriorating water quality (aluminium concentration, filtered water turbidity), this strategy could be explored by the plant to limit THM formation during critical periods.

**Table 1** Summary of optimal dosage and associated results for coagulation trials carried out concurrently in jar test and at the plant

<table>
<thead>
<tr>
<th></th>
<th>Alum</th>
<th>Plant</th>
<th>Acidified alum 5%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Jar test</td>
<td>3.90–6.68</td>
<td>5.06</td>
</tr>
<tr>
<td>TOC raw water</td>
<td>4.11</td>
<td>3.9</td>
<td>3.2</td>
</tr>
<tr>
<td>Optimal dosage (mg Al/L)</td>
<td>3.9</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>6.74</td>
<td>n.a</td>
<td>6.87</td>
</tr>
<tr>
<td>Alkalinity (mg CaCO₃/L)</td>
<td>87.2</td>
<td>n.a</td>
<td>60.8</td>
</tr>
<tr>
<td>(\text{UV}_{254}) (cm⁻¹)</td>
<td>0.033</td>
<td>0.039</td>
<td>0.043</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>2.37</td>
<td>2.15</td>
<td>2.85</td>
</tr>
<tr>
<td>THMFP (µg/L)</td>
<td>(\approx 149^*)</td>
<td>141</td>
<td>143</td>
</tr>
</tbody>
</table>

*Estimated value from regression curve.
Although full-scale results showed lower THMFP values than jar tests (Figure 4), the latter predicted accurately the trend obtained at full scale. The higher performance under full-scale conditions was not unexpected, especially when considering that settling is performed using a sludge blanket clarifier. Since jar-test water was filtered before performing THM, the difference cannot be attributed to the better solids separation normally observed at full scale (lower settled water turbidity). The longer solids retention time in the sludge blanket increases the adsorption capacity and therefore removes TOC and THM precursors more efficiently. TOC results confirm this hypothesis.

Impact of PAC on NOM removal

The additional impact of PAC application during optimised coagulation is shown in Figure 5. Measurements of UV$_{254}$ decreased modestly with increasing PAC dosage in both jar and plant tests. As compared to optimised coagulation alone, the plant’s maximum applicable PAC dosage (11 mg/L) provided an additional 7.7% UV$_{254}$ reduction and a 6.7% TOC reduction. Increasing PAC dosage to 25 mg/L as tested in the jar test would not be justified by the gain in UV$_{254}$ (12.3%) or TOC (11.9%) reductions. The measured impact of PAC application on NOM removal is thus limited for the conditions investigated (<25 mg/L of Calgon WPL PAC).

Impact of PAC application on THM formation potential

THM formation potential tests were used to assess whether the observed limited NOM removals (Figure 5) were associated with equivalent THM reductions. Total THMFP formed as a function of PAC dosages are shown in Figure 6. Both jar-test and plant results indicate negligible THM reduction from PAC application. As demonstrated earlier in Figure 4, plant treatment achieved lower THMFP. This is most likely associated with the better NOM removals obtained in the sludge blanket clarifiers as compared to the jar tests.

These results are similar to previous results obtained during the spring (test 2) and with a different PAC (PAC-2: Hydrodarco B). Although a maximum THM reduction reaching 9% was measured in one trial, most results showed a negligible impact of PAC application on THM formation potential (Figure 6). The lower settled water pH observed during the spring test (6.74 vs. 7.91) might be
responsible for the higher THM reduction observed with the Calgon carbon.

According to these results, activated carbon is not an effective means of supplementing coagulation for the reduction of THM formation for the given source water characteristics, even though PAC accumulates in the sludge blanket, therefore increasing the carbon concentration in contact with water. Although PAC could slightly reduce NOM (Figure 5) (approx. 7%), this removal was not associated with THM reduction, indicating that the fraction of NOM removed did not have a high THM formation potential. As stated earlier, high molecular weight NOM compounds are more effectively removed by coagulation than PAC which is more effective for the removal of non-humic or low molecular weight NOM fraction (Amy et al. 1992; Uyak et al. 2007). Besides, some studies have reported direct competition between MIB and small, low molecular weight NOM compounds for adsorption sites (Newcombe & Cook 2002; Hepplewhite et al. 2004).

Impact of PAC application on taste and odour

The effect of activated carbon on taste- and odour-causing compounds was also evaluated using MIB and geosmin as indicators. Figure 7 presents the impact of PAC dosage on MIB and geosmin removals. The application of 11 mg/L PAC could reduce MIB and geosmin concentrations by 12% and 39%, respectively. The use of PAC can therefore provide a taste- and odour-causing compounds’ reduction, although this reduction appears limited. At the usual dosages (2–6 mg/L) applied at this site, reductions of less than 20% can be expected. These results are fairly low in comparison to results obtained with the same PAC at a different plant drawing from the Ottawa River, where MIB reduction reached 40% for a 5 mg/L PAC dosage and a 60 min contact time (data not shown). At equilibrium, reduction of up to 60% MIB can be expected with 5 mg/L of Calgon WPH carbon in natural water according to Gillogly et al. (1999). However, contact time plays a major role in adsorption and reducing it to 60 min could reduce by half (50%) the possible adsorption of MIB (Crittenden et al. 2005). The relative effectiveness of PAC application for T/O control at the plant could be attributed to low concentrations of MIB and geosmin metabolites in the source water (low removals required), the presence of other compounds more readily removable by PAC or longer contact time (60 min in jar test vs. 75–150 min at the plant).

CONCLUSIONS

This study investigated the impact of optimised coagulation and PAC adsorption on the removal of organic matter as strategies for THM control. Total organic carbon, UV$_{254}$ absorbance and THMFP were used to evaluate treatment performance. Trials carried out at full scale and bench scale (jar tests) showed the following:
• Overall, acidified alum (5% sulfuric acid) coagulation achieved better THM precursors’ removal than alum, for lower dosages. The optimal dosage identified (3.2 mg Al/L) provided a significant THMFP removal but higher removals could be obtained by increasing the coagulant dosage. This plant would have to go beyond traditional optimised coagulation to lower their THM levels to a maximum using coagulation.

• In all trials, UV254 reductions were superior to TOC reductions, indicating a preferential removal of the aromatic fraction of NOM by coagulation.

• Although powdered activated carbon application (11 mg/L) showed a slight removal of NOM (7% TOC), it was found ineffective at reducing THMFP. This result was consistent with previous results obtained on the same source water.

• Even though it was expected that PAC accumulating in the sludge blanket clarifier could improve TOC removal, this hypothesis was not confirmed during full-scale trials.

• For the given source water characteristics, supplementing optimised coagulation with PAC adsorption was not justified from a THM control standpoint.

• Source water TOC variations constitute a major challenge for THM control at this specific plant. Even with the large variations measured during trials, jar tests proved to be an appropriate tool for predicting trends in NOM and THMFP removal.

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