Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20618

78 (2017) 117–126
June

Effects of ozone as a stand-alone and coagulation-aid treatment on the reduction of trihalomethanes precursors from water with high DOC and low calcium hardness

Mehrnaz Sadrnourmohammadi[a],*, Beata Gorczyca[b]

[a]*SNC-Lavalin Ltd., 148 Nature Park Way, Winnipeg, Manitoba, Canada R3P 0X7, email: mehrnaz.sad@gmail.com*
[b]*Department of Civil Engineering, University of Manitoba, 15 Gillson Street, EITC E1-386, Winnipeg, Manitoba, Canada R3T 5V6, email: beata.gorczyca@umanitoba.ca*

Received 19 July 2016; Accepted 18 February 2017

ABSTRACT

This study investigates the effect of calcium on the water's susceptibility to the coagulating effects of ozone. Natural water from the Rainy River, characterized by high dissolved organic carbon and low calcium concentration was used in this study. The results were compared with the authors' previous study conducted on high dissolved organic carbon (DOC) and high calcium concentration water of Assiniboine River. Results showed that pre-ozonation of water prior to coagulation did not result in higher DOC removal efficiencies at coagulant dose of 6 mg L^{-1} determined as the optimum dose. However, at the low coagulant dosages (0–2 mg L^{-1}), the DOC removal by pre-ozonation–coagulation surpasses that achieved by the coagulation alone. The adverse effect of ozone on DOC removal by subsequent coagulation was related to low concentration of calcium hardness in the source water (Rainy River). This was confirmed by the results of pre-ozonation–coagulation of synthetic water containing different level of calcium. For both high and low calcium content waters, application of ozone prior to coagulation was beneficial in terms of reduction of specific trihalomethane formation potential due to transformation of hydrophobic DOC fraction to hydrophilic fractions by ozone. However, the hydrophilic DOC fractions, can only be successfully removed when sufficient concentration of calcium is present.

Keywords: Ozone; Dissolved organic carbon; Calcium hardness; Trihalomethanes precursors; Coagulation aid

1. Introduction

Water treatment plants supplied by surface waters in Canada deal with high concentrations of chlorine disinfection by-products (DBPs) such as trihalomethanes (THMs). In the Province of Manitoba, about 70% of potable water treatment plants using surface water sources are reported not to be in compliance with THMs regulations set by the Province [1]. Water treatment facilities are aiming to improve or optimize the treatment steps for dissolved organic carbon) (DOC) removal from the raw water before chlorination in order to reduce total THMs to meet current provincial guidelines.

The DOC concentration for the Canadian Prairies and the Canadian Shield water sources can vary from 8 to 25 mg L^{-1}; the level of calcium hardness for these waters varies significantly from 60 to 350 mg L^{-1} $CaCO_3$ [2,3].

The Guidelines for Canadian Drinking Water Quality (GCDWQ) divide water hardness into the following categories: 0–60 (mg L^{-1} $CaCO_3$) classified as a soft water; 61–120 (mg L^{-1} $CaCO_3$) as moderately hard water; 121–180 (mg L^{-1} $CaCO_3$) as a hard water; and more than 180 (mg L^{-1} $CaCO_3$) as a very hard water [4]. The water of Rainy River used in this study can be classified as a soft water (low hardness) whereas the Assiniboine River used in authors' previous study is classified as high hardness water [2].

Currently, there is no federal guideline for DOC in potable drinking water in the GCDWQ. However, DOC

---

* Corresponding author.

concentrations greater than 5 mg L^{-1} have been reported to complicate water treatment and resulting in DBPs to be formed in amounts exceeding the standards [5]. Based on the above, both Assiniboine River and Rainy River water with DOC concentration of 16 mg L^{-1} certainly can be classified as extremely high DOC water [2].

Chemical coagulation has been applied widely for DOC removal in drinking water treatment. However, the effect of this process on the removal of DOC from water depends on several factors such as DOC concentration, DOC chemical composition, coagulant type, coagulant dosage, pH, and water alkalinity [6]. Also for waters with extremely high concentration of organic compounds, high coagulant dosage required for removal of DOC results in excessive sludge production. Moreover, maintaining alkalinity and pH required to optimize the removal of DOC by coagulation can be very costly for waters with such extremely high DOC concentration [3].

The application of ozone in drinking water treatment as disinfectant is widespread due to its high oxidation potential. Besides, other beneficial effects of ozone, such as aiding coagulation and filtration have also been observed. Some water treatment systems have taken advantage of the benefits of ozonation to improve coagulation (coagulation aid), and its ability to control DBPs formation. However, the reported effects of ozonation by different researchers are ambiguous and range from being beneficial to detrimental depending on the reported raw water quality [7,8]. Some studies pointed out the deteriorative effect of pre-ozonation on subsequent coagulation in terms of reduction of DOC and THMs [9]. Others have reported cases in which the application of ozone prior to coagulation offered potential benefits in terms of improved DOC removal and reduced coagulant dosages [2,10,11]. The coagulant type, coagulation pH, ozone dose, and water characteristics (DOC and calcium hardness concentration) have been reported as important variables that can determine the effect of ozone on coagulation [12,13]. Therefore, the effect of ozone as a coagulant aid on DOC removal from any source water and its DBPs formation potential needs to be evaluated for each specific water source.

1.1. Ozone dosage

According to the literature, the most commonly used ozone doses in drinking water pre-treatment are in the range of 0.2–1.0 mg ozone/mg DOC. It has been reported that this low dose of ozone results in partial oxidation of organic carbon, altering the nature of DOC, rather than completely oxidizing the DOC. Ozone dose of 8 mg ozone/mg DOC is reported to result in complete mineralization which is not needed nor economically feasible in water treatment [13].

Ozone converts hydrophobic DOC to hydrophilic, low molecular weight compounds (e.g., short-chained carboxylic acids). The hydrophilic DOC fractions are not removed effectively by coagulation. At higher ozone dosages, the DOC conversion to hydrophilic fractions is too severe. Therefore, applied ozone doses not higher than 1 mg ozone/mg DOC has been reported to be the most effective on the coagulation [14].

Moreover, application of low dosage of ozone results in desorption of some natural organic matter (NOM) from inorganic particles. This results in improved particle aggregation in the coagulation process [15,16]. Ozonation of natural water at low dosage also leads to the breakup of organometallic complexes, thereby releasing metal species that can interact with particles and soluble NOM, aiding the coagulation process.

1.2. Effects of calcium

Calcium concentration has been reported as a key factor in determining the effect of pre-ozonation on coagulation [17,18].

As already discussed, ozonation of water organic compounds can produce oxygen-rich compounds, such as carboxylic groups, where calcium presents leading to increased complexation of calcium with both aqueous NOM and particle-sorbed NOM [19–21]. Also, calcium can neutralize the particle anionic surface charge which can lead to a reduction in particle stability through surface charge reduction [18,22]. This mechanism is important when source water has a high level of calcium hardness [17].

The authors have already reported the effect of ozone stand-alone and as a coagulation aid on the reduction of DOC and trihalomethane formation potential (THMFP) from a typical Canadian Prairie River (Assiniboine River) characterized with a high level of DOC and calcium hardness [2]. For that particular water source, ozonation enhanced the reduction of DOC and THMFP by subsequent coagulation at ozone doses of 0.6 and 0.8 mg ozone/mg DOC. The enhanced removal of DOC was attributed to ozone-induced particle destabilization and DOC complexation by calcium, specifically: (a) transformation of hydrophobic DOC fraction to hydrophilic fractions with less particle adsorption affinity, and (b) an increase in calcium complexation with NOM constituents.

1.3. Objectives

This study presents the effect of ozone as a coagulation aid on a surface water source with a high level of DOC and low calcium hardness. The focus was to compare these results with the effects of ozone on the high calcium hardness water used in authors' previous study. The effect of calcium on the effect of ozone applied as a coagulation aid was also investigated. Additionally ozonation stand-alone and aluminum-base coagulation were also conducted to compare their efficiencies.

The specific objectives of this study are:

- To study the effect of ozonation stand-alone and as a coagulation-aid targeting for the reduction of DOC and total THMFP.
- To investigate the effect of calcium hardness on reduction of DOC and THMFP in ozone–coagulation process.

2. Materials and methods

2.1. Water sources

Two types of water have been used in this study: (1) a natural water collected from the Rainy River Water Treatment Plant intake, which is located on the Canadian Shield in the Town of Rainy River, Ontario (Canada). This water can be characterized by a high DOC and low calcium hardness

Table 1
General Rainy River raw water quality characteristics

Sample	Rainy River water
DOC (mg L^{-1})	16.1
UV_{254} (cm^{-1})	0.61
SUVA (m^{-1} mg^{-1} L)	3.23
pH	6.5
Alkalinity (mg L^{-1} $CaCO_3$)	26
Total hardness (mg L^{-1} $CaCO_3$)	65
Calcium (mg L^{-1} $CaCO_3$)	44

(Table 1). (2) A synthetic water prepared using Suwannee River humic acid (HA) standard with similar pH and DOC values to those of Rainy River water. Synthetic water containing different levels of calcium were tested to further investigate the effect of calcium specifically, and eliminate interfering effect of other compounds which present in real water in pre-ozonation–coagulation.

2.2. Coagulation experiments

The coagulation experiments were conducted using a conventional method in six paddle PB-700TM standard jar testers by Phipps & Bird (Richmond, USA) at room temperature. Three commercial aluminum-based coagulants obtained from ClearTech Industries Ltd., Canada, were used in this study: aluminum sulfate (alum) with basicity value of 0; polyaluminum chloride (ClearPAC 180, denoted as PACl) with basicity value of 43%; and aluminum chlorohydrate (CTI 4900, denoted as ACH) with basicity value of 83%. Basicity value or degree of neutralization, as defined below, is used to characterize polyaluminum coagulants [23].

$$B = \frac{\left[\mathrm{OH}^-\right]}{\left[\mathrm{Al_T}\right]}$$

$$\text{Basicity} = \left(\frac{B}{3}\right) \times 100\%$$

A range of zero to three for B value corresponding to a basicity of 0 to 100% is reported. For commercial polyaluminum coagulants basicity is reported to be in the range of 15%–85%.

For coagulation tests, 1 L of water was placed in each jar. A measured amount of coagulant was pipetted into the test water to give a desired coagulant concentration while stirring rapidly at 120 rpm for 1 min, followed by a slow mix at 40 rpm for 30 min. The samples were then allowed to settle for 30 min.

Coagulant doses applied were in the range of 1–10 mg L^{-1} Al based on the authors' previous experience with the similar water [3].

2.3. Ozonation experiments

Ozonation was conducted on a semi-batch basis by bubbling the desired amount of ozone through the 2 L water sample. Ozone was produced by a laboratory ozone generator (Model OZO 1VTTL, Ozomax Ind., Canada) employing the corona discharge method using dehumidified atmospheric air as the feed gas to generate ozone.

Ozone output from the generator and ozone concentration in the reactor off-gas were determined by the iodometric method [24], while the indigo method was used for the aqueous phase [25]. Nitrogen gas was bubbled into the water sample after each ozonation run for at least 10 min to purge the unreacted ozone gas.

To observe the effects of ozone on coagulation, the raw water was ozonated and subsequently coagulated with the three aluminum-based coagulants.

Throughout this article, ozone dose refers to the transferred ozone dose (difference of the mass of applied ozone and the mass of ozone in the off-gas), which in this study ranged from 0 to 0.8 mg ozone/mg DOC. As already described the applied ozone doses less than 1 mg ozone/mg DOC has been reported to be the most effective on the coagulation [14].

The schematic diagram of ozonation setup has been reported in author's previous study [2].

2.3.1. Analytical methods

DOC concentrations were determined using a total organic carbon analyzer (Phoenix 8000, Tekmar Dohrmann, USA) after filtering water samples through a 0.45-μm nitrocellulose filter paper. The UV absorbance at 254 nm of filtered samples (UV_{254}) was measured using a UV/visible spectrophotometer Ultraspec 2100 pro (GBC Scientific Equipment, Australia) with a 1 cm quartz cell. Specific UV absorbance (SUVA) was calculated as UV_{254} normalized for DOC.

The pH of the samples was measured using a Fisher Scientific Accumet 50 pH meter (Fisher Scientific, New Jersey, USA). Alkalinity was determined as mg L^{-1} $CaCO_3$ by titration of sample water with 0.02 N sulfuric acid titrated to pH 4.48 according to Standard Methods 2320B [24]. All measurements were repeated at least three times to assure the reproducibility of experimental results.

2.3.2. Trihalomethane formation potential

THMs formation potential measurements were conducted according to Standard Methods 5710B [24]. Details of this procedure have been described elsewhere [2,3,26]. 50 mg L^{-1} sodium hypochlorite was added to each filtered sample to ensure that there was a sufficient amount of chlorine available to react with the organics. All samples were buffered to pH = 7 by using a phosphate buffer. Sample vials were sealed with TFE caps and were kept in the dark at 4°C for 7 d. After 7 d all samples were found to have >1.0 mg L^{-1} (3–5 mg L^{-1}) free chlorine which shows that all THM formation reactions were driven to completion.

An alteration to the 5710B procedure was the chlorinated water incubation temperature. In this study, chlorinated water samples were incubated at 4°C to simulate the water temperature in distribution systems, representative for the Canadian cold region. THMs concentrations were determined with the liquid–liquid extraction method according to Standard Methods 6232B [24].

THMs concentration were determined using an Agilent 7890A GC System (Agilent Technologies, Santa Clara, California) equipped with a CombiPAL CTC Analytics auto sampler and used electron capture detection.

2.3.3. DOC fractionation

DOC fractions were characterized using solid phase extraction (SPE) method developed by Ratpukdi et al. [26]. This SPE method reduces the need for long resin preparation time and for specialized equipment, making this an attractive alternative to classic resin separation method [27]. Prior to fractionation, all samples were filtered through 0.45-μm nitrocellulose filter paper and were brought to room temperature. In this method, three Bond Elute ENV cartridges (Varian Inc., Lake Forest California), one Phenomenex Strata XC cartridge, and one Phenomenex Strata X-AW cartridge (Phenomenex, Torrance, California) were used to separate DOC into the six fractions isolated: hydrophilic acid (HPIA), hydrophilic base (HPIB), hydrophilic neutral (HPIN), hydrophobic acid (HPOA), hydrophobic base (HPOB), and hydrophobic neutral (HPON) [28]. The full fractionation procedure can be found in Ratpukdi et al. [26].

3. Results and discussion

3.1. General water quality

Table 1 shows the general water quality of the Rainy River water sample. Rainy River water source has a high level of DOC (16.1 mg L^{-1}) accompanied by low level of calcium hardness (44 mg L^{-1} $CaCO_3$). The SUVA value higher than 3 m^{-1} mg^{-1} L for Rainy River raw water is representative of a water source more hydrophobic in character [29]. The fractionation results of the Rainy River water are shown in Table 2. The results showed that more than 55% of DOC is hydrophobic fractions, and up to 49% of the organic matter is associated with the HPOA fraction. The HPOA fraction (the DOC fraction forming most THMs) in the Rainy River water is very similar to that reported for Assiniboine River in authors'earlier study [3].

Results also showed the lowest concentration of HPOB fraction in this source water, which is consistent with previous reports showing that many natural surface waters are low in this fraction [30].

The HPOA fraction is made up of HA and fulvic acid, 1- and 2-ring phenols, 1- and 2-ring aromatic carboxylic acids, and C5–C9 aliphatic carboxylic acids [30] while HPIN fraction is reported to be composed of polysaccharides and short chain alcohols, aliphatic amines ketones, aldehydes, and esters [27,30]. The general chemical groups and composition of each DOC fraction is reported by Leenheer [27].

Table 2
The DOC composition of the Rainy River water sample

Fraction	Concentration (mg L^{-1})	DOC %
Hydrophobic neutral (HPON)	0.43 ± 0.02	2.68
Hydrophobic base (HPOB)	0.57 ± 0.06	3.54
Hydrophobic acid (HPOA)	7.94 ± 0.15	49.3
Hydrophilic base (HPIB)	0.92 ± 0.04	5.73
Hydrophilic acid (HPIA)	0.12 ± 0.01	0.75
Hydrophilic neutral (HPIN)	6.12 ± 0.14	38
Total	16.11 ± 0.20	100

3.1.1. Chemical coagulation

3.1.1.1. DOC, UV_{254}, and pH The effects of coagulation conditions, including coagulant type and coagulant dosage, on Rainy River water UV_{254} and DOC were investigated and the results are shown in Fig. 1. Fig. 1(a) shows that the depression of solution pH, due to coagulant addition, follows the order of alum > PACl > ACH; this correlates with the basicity ratios of these coagulants. The difference in pH depression between PACl and ACH appears to be non-significant, as expected.

Fig. 1(b) shows the DOC removal by different coagulants. Considering the DOC removal effectiveness, the coagulants can be ranked in the following order: alum > ACH > PACl. These results are consistent with the authors' recent study [3] where the mechanisms of DOC removal by aluminum-based coagulants is shown to be related to aluminum species formed during the coagulation. In that study, alum at pH 6, showed the highest content of in situ formed coagulant polymeric species (Al_b). The removal of DOC has been found closely related to the content of Al_b [3,31,32]. For all coagulants the DOC removal increased with higher coagulant dosage. All three coagulants achieved the highest DOC removal at the dose of 10 mg L^{-1} Al. However, most of this removal was achieved with the coagulant doses of about 6 mg L^{-1} Al. The additional DOC removal at coagulant doses greater than 6 mg L^{-1} Al was found statistically insignificant at a significance level (α) of 0.05 [33]. At this coagulant dose (6 mg L^{-1} Al) alum showed the greatest reduction of DOC with the final DOC concentration in coagulated water of 5.5 mg L^{-1} (62% reduction), whereas PACl was only able to reduce the DOC to 8.5 mg L^{-1} (41% reduction). Literature has shown that the performance of each coagulant depends on water characteristics and applied test conditions [34]. Author's previous study conducted on the Assiniboine River (a typical Canadian Prairie water) showed the similar results where alum achieved the highest DOC reduction (71%) followed by ACH (68%) and PACl (54%) at pH 6 [3]. UV_{254} removal shows similar trend as DOC removal does, with alum showing the most efficient removal followed by ACH and PACl (Fig. 1(c)).

3.1.1.2. Removal of DOC fractions The DOC of water coagulated with 6 mg L^{-1} Al was fractionated to determine the removal of specific DOC fractionsby coagultion (Table 3). This dose of coagulant was selected to be optimal, due to statistically insignificant improvement in the DOC removals at doses higher than 6 mg L^{-1} Al.

All coagulants were found to achieve high removal of the HPOA fraction with the highest removal by alum (86%) followed by ACH (77%) and PACl (70%). These results are consistent with other research showing that alum is more effective in removal of HPOA fraction of DOC than the coagulants with preformed Al species [35,36].

Alternatively, the coagulants used were not able to remove HPIN fraction with 52%–55% of these fractions remained following coagulation (Fig. 2).

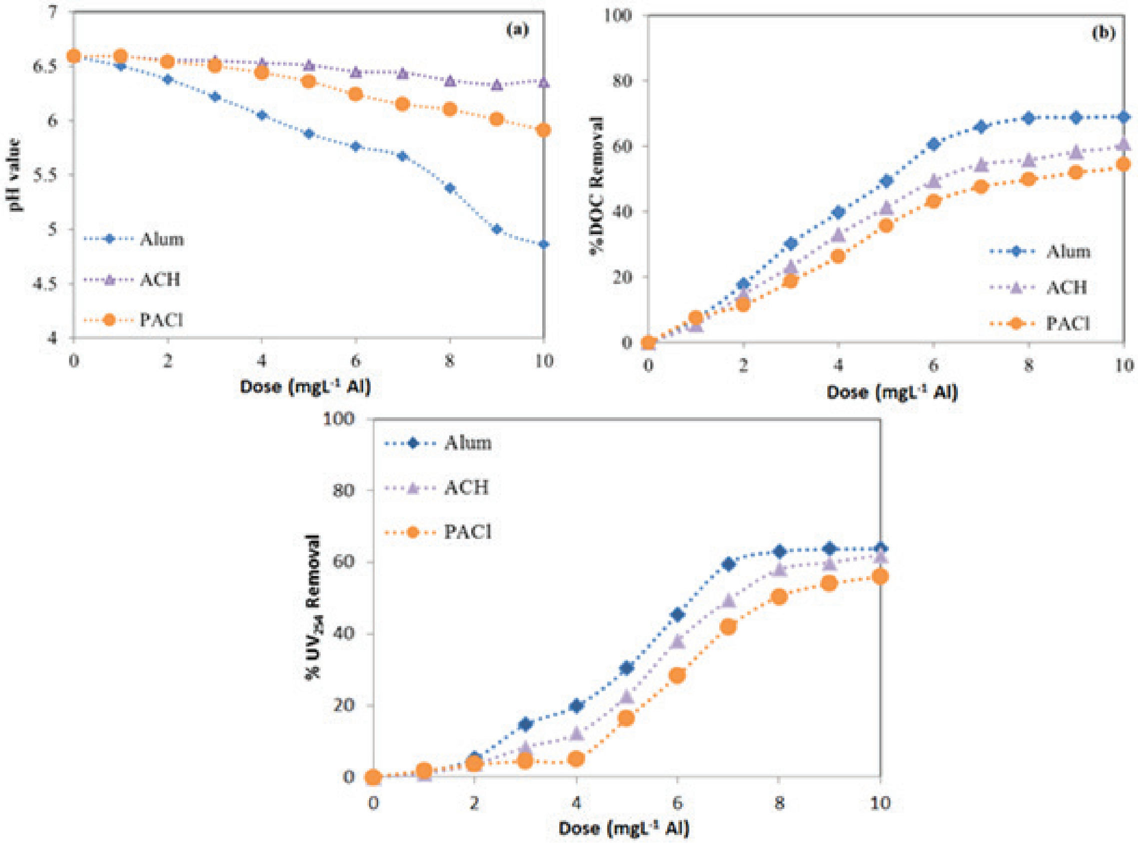

Fig. 1. Effect of coagulant type and dosage on pH (a), DOC (b) and UV254 (c) (Rainy River raw water pH 6.5).

Table 3
DOC fractions (shown as % DOC remaining), following coagulation at coagulant dose of 6 mg L^{-1} Al

Sample	% DOC					
	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
Raw	2.68	3.54	49.3	5.73	0.75	38.0
Alum	1.84	2.93	20.5	9.53	10.1	55.1
ACH	2.01	3.29	25.3	7.20	8.10	54.1
PACl	2.08	3.41	27.5	4.51	10.2	52.3

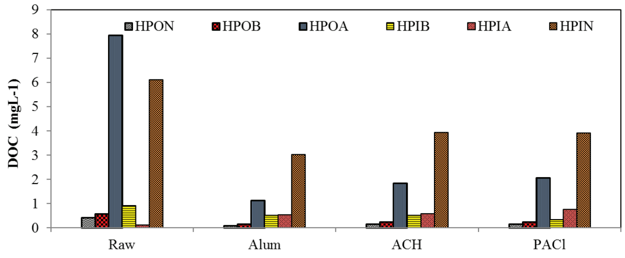

Fig. 2. DOC fractions remaining in solution following coagulation at coagulant dose of 6 mg L^{-1} Al.

This study supports the previous literature showing that hydrophobic (HPO) fractions specifically HPOA one, are more amenable to be removed by coagulation while hydrophilic (HPI) ones are less treatable by this treatment process [37]. The HPOA fraction has been reported to be most reactive in formation of THMs.

Some increase of HPIA fraction can be observed in all coagulated waters. With aluminum-based coagulants, the metal ion is hydrolyzed to form aluminum hydroxide floc as well as hydrogen ions. The hydrogen ions will decrease the pH of the water that might be responsible for water characteristics change such as increased level of acidic DOC fraction, i.e., HPIA.

3.1.1.3. THMFP Table 4 shows the THMFP values for the raw water and coagulated water with 6 mg L^{-1} Al. The raw Rainy River water had a THMFP of 308.4 μg L^{-1} (Table 4). All three coagulants reduced the THMFP with alum and PACl showing the highest and the least reduction of THMFP to 113.1 and 137 μg L^{-1}, respectively.

Alum outperformed ACH and PACl in terms of THMFP reduction which is related to effective removal of HPOA fraction by alum reported to have the greatest potential to form THMs [3].

3.1.2. Ozonation

3.1.2.1. DOC and UV_{254} removal The effect of ozone on the Rainy River raw water was investigated (results not shown here). Data showed increased DOC removal and UV_{254} reduction at increased ozone doses. Ozone dose of 0.8 mg ozone/mg DOC

Table 4
THMFP for Rainy River raw and coagulated water samples (at coagulant dose of 6 mg L^{-1} Al)

Sample	DOC (mg L^{-1})	$CHCl_3$ (μg L^{-1})	$CHBr_3$ (μg L^{-1})	$CHClBr_2$ (μg L^{-1})	$CHCl_2Br$ (μg L^{-1})	THMFP (μg L^{-1})
Raw	16.1 ± 0.2	304.9 ± 2.05	ND	ND	3.5 ± 0.2	308.4 ± 2.7
Alum	5.5 ± 0.12	110.6 ± 1.31	ND	ND	2.5 ± 0.3	113.1 ± 1.11
PACl	8.5 ± 0.17	134.2 ± 3.12	ND	ND	2.8 ± 0.07	137.0 ± 2.01
ACH	7.3 ± 0.07	130.3 ± 1.01	ND	ND	2.4 ± 0.11	132.7 ± 2.31

achieved the highest reduction of DOC (31%) and UV_{254} (90%), respectively.

These results are very similar to those reported for high DOC and high calcium hardness water of Assiniboine River (DOC reduction of 27% and UV_{254} reduction of 86%, respectively) [2], and are within the range of the published data [38]. Furthermore the low pH value of 6.5 of the Rainy River water in this study can also contribute to higher DOC removal [39]. Low pH results in less OH^- concentration, which hinders the decomposition of ozone to $OH^\bullet$ and consequently increase the direct reaction between the ozone and the dissolved compounds. Higher ozone dosage provides more available ozone molecules and hydroxyl radical, which results in improved reduction of organic carbon [39]. Generally UV_{254} indicates the relative amount of unsaturated and/or aromatic carbon of DOC. For all ozone doses, a decrease of UV_{254} was observed, indicating the oxidation of unsaturated and/or aromatic carbon molecules, which is in accordance with previously reported results [30]. Higher UV_{254} reduction compared with DOC removal suggests incomplete mineralization of organic molecules degraded from unsaturated and/or aromatic organics [39].

3.1.2.2. THMFP THMFP of ozonated water samples at four applied ozone doses was determined. Generally, as the dose of ozone increased, the value of THMFP decreased. The raw water of Rainy River had a THMFP of 308.4 μg L^{-1} and a specific THMFP of 19.1 μg THM/mg DOC. These results are within the range of those reported for high DOC and high calcium hardness water of another Canadian river from the same geographical area – Assiniboine River (THMFP of 202.0 μg L^{-1} and specific THMFP of 14.6 μg THM/mg DOC, respectively). Ozonation at ozone dose of 0.8 mg ozone/mg DOC resulted in a significant decrease of THMFP to 135.8 μg L^{-1} and specific THMFP of 12.23 μg THM/mg DOC.

DOC fractionation of ozonated samples was not conducted on Rainy River water; however, the authors performed DOC fractionation of ozonated samples on Assiniboine River, which is also located in central Canada and have similarly high water DOC concentrations and characteristic as Rainy River. The results for Assiniboine River demonstrated that ozone transforms hydrophobic DOC into hydrophilic fractions less amenable to react with chlorine and produce THMs compared with HPO fractions [2].

3.1.3. Ozonation prior to chemical coagulation

3.1.3.1. DOC removal Fig. 3 shows the effect of pre-ozonation on the removal of the Rainy River water DOC by subsequent coagulation process. Three ozone doses (0.2, 0.6, and 0.8 mg ozone/mg DOC) were applied followed by three aluminum-based coagulation. Results show that ozonation alone, results in removal of DOC, which is due to DOC partial mineralization and oxidation. Increased ozone dose results in higher DOC removal, with maximum 31% removal at ozone dose of 0.8 mg ozone/mg DOC. DOC removal by ozonation depends on the water characteristics such as DOC concentration and composition; therefore, often cannot be compared for different water sources. However, the values obtained in this study can be compared well with other published works, showing DOC reduction from 5% to 25% under typical ozone dose of 0.4–1 mg ozone/mg DOC [38].

As results show, pre-ozonation did not enhance DOC removal by coagulation at coagulant dose of 6 mg L^{-1} determined as optimum in a standard jar test without ozone pre-oxidation. This optimum dose was selected based on the fact that for coagulant dosages higher than 6 mg L^{-1} the improvement of DOC removal was statistically insignificant (Fig. 1). However, at lower coagulant dosages (0–2 mg L^{-1}) pre-ozonation–coagulation shows higher DOC removal compared with coagulation alone.

Coagulation with alum at the dose of 6 mg L^{-1} Al achieved 61% of DOC removal when no ozone was applied. When 0.8 mg ozone/mg DOC ozone was applied before coagulation, the DOC removal dropped to 54%. This adverse effect of ozone on DOC removal by subsequent coagulation could be related to insufficient concentration of calcium hardness in this specific water source [2,21]. Calcium has been reported as a key parameter in ozone-enhanced coagulation. It has been reported that ozonation, prior to coagulation, benefits waters with moderate to high levels of calcium hardness. Chandrakanth [40] reported ozone-enhanced coagulation cases only when the raw waters had calcium hardness concentration higher than 100 mg L^{-1} $CaCO_3$.

Calcium can enhance the coagulation by forming the NOM-coagulant species bridging which results in improved DOC removal [41]. This topic is discussed further in section 3.1.4.

This negative effect of the pre-ozonation on coagulation was not observed at low coagulant dosages (0–2 mg L^{-1} Al). At the low coagulant dosages, the DOC removal by ozonation alone (due to partial mineralization and oxidation of DOC) surpasses that achieved by the coagulation alone.

3.1.3.2. THMFP The effect of pre-ozonation–coagulation on the reduction of THMFP for the Rainy River water samples is shown in Table 5. THMFP of pre-ozonated and coagulated water at 6 mg L^{-1} Al was determined (Table 5). The results show that pre-ozonation prior to coagulation can reduce THMFP at all ozone doses. An increase in ozone dose resulted in an increase in THMFP reduction with ACH showing the highest reduction of specific THMFP. As shown in Table 4, Rainy River raw water sample had a THMFP of

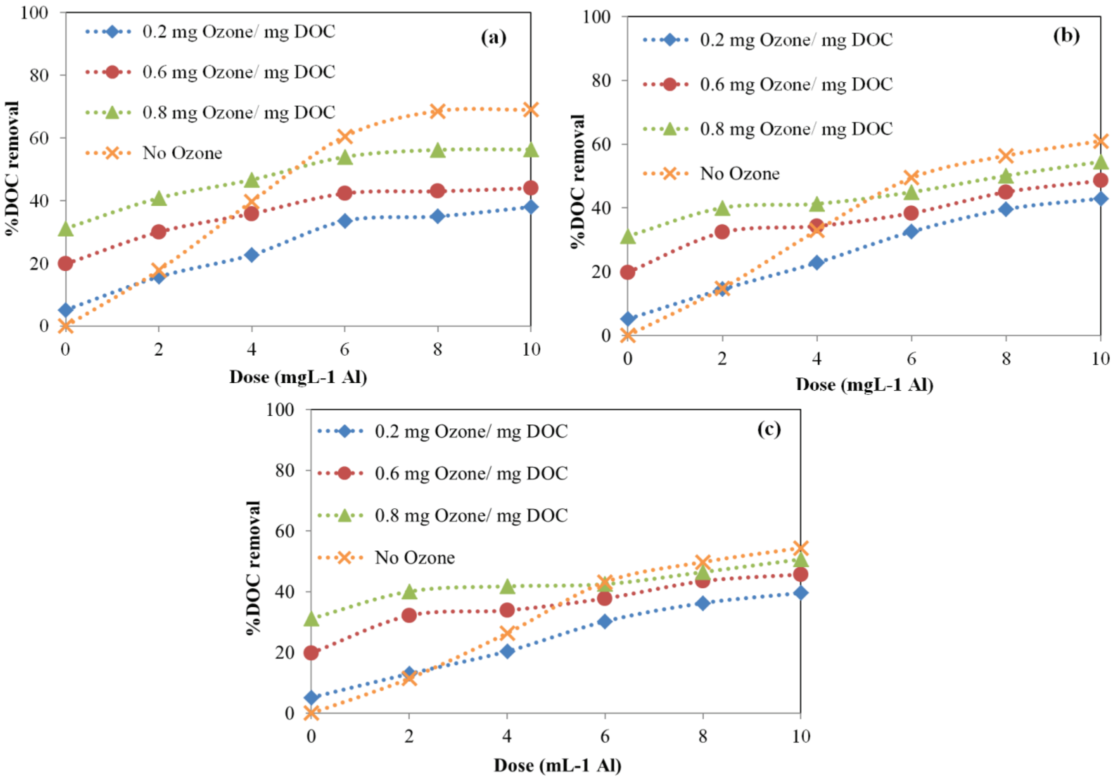

Fig. 3. Removal of Rainy River DOC at varying ozone and coagulant doses: (a) alum, (b) ACH and (c) PACl.

308.4 µg L^{-1} and a specific THMFP of 19.1 µg THM/mg DOC. Comparing these results with Table 5, it can be concluded that pre-ozonation–coagulation at ozone dose of 0.6 and 0.8 mg ozone/mg DOC, results in higher THMFP reduction rather than ozonation alone. When ozone is applied at 0.6 and 0.8 mg ozone/mg DOC dose prior to coagulation, the highest reduction in specific THMFP is achieved by ACH (46% and 70%) followed by PACl (42% and 66%) and alum (41% and 60%), respectively (Table 5).

Based on the literature and our previous work the improved THMFP reduction after pre-ozonation–coagulation can be explained as follows:

- HPO fractions of DOC are known to contain most THMs precursors. Ozone transforms hydrophobic DOC fraction to hydrophilic fraction which results in lower specific THMFP.
- The remaining HPO fractions and some part of HPI fractions still present in the pre-ozonated water are further removed by subsequent coagulation [14]. Consequently, coagulation of ozonated water results in further decrease of THMFP level.

3.1.4. Effect of calcium in ozone-enhanced coagulation

To further confirm the effect of calcium in pre-ozonation–coagulation, experiments using synthetic water containing different levels of calcium, but the same level of DOC as Rainy River were conducted. Synthetic water containing HA with a concentration of 16 mg L^{-1} and different Ca concentration (0, 40, 140, and 240 mg L^{-1} $CaCO_3$) were pre-ozonated and further coagulated by alum (Fig. 4). Results showed the beneficial effect of calcium in coagulation of pre-ozonated water samples. Non-ozonated HA sample without Ca achieved 60% of DOC removal whereas the DOC removal decreased by applying pre-ozonation. This trend changes for water samples containing Ca with concentration of 140 and 240 mg L^{-1} $CaCO_3$ where pre-ozonation increased the DOC removal by further alum coagulation (Fig. 4). Results also show that for non-ozonated samples increased concentration of Ca improved the DOC removal by coagulation alone. Calcium can enhance the HA coagulation by forming the HA-coagulant species bridging which results in improved DOC removal [40].

The transformation of hydrophobic DOC fraction to hydrophilic fractions upon ozonation results in reduction of THMFP regardless of level of calcium hardness in source water [28]. However, the hydrophilic DOC fractions, released in ozonation, can be complexed and incorporated into a coagulation floc resulting in overall DOC reduction only when sufficient concentration of calcium is present. This was the case in authors' earlier study, where ozone application on water with high level of DOC and calcium hardness showed improved reduction of both DOC and THMFP by subsequent coagulation [2]. The enhanced removal of DOC in that study was understood to be attributed to complexation of calcium with both aqueous NOM and particle-sorbed NOM upon ozonation [19,21]. On the contrary, the Canadian Shield water (Rainy River water) used in this study has a low level of calcium

Table 5
Effects of pre-ozonation–coagulation on THMFP removal; coagulants dose = 6 mg L^{-1} Al

Sample	DOC (mg L^{-1})	$CHCl_3$ (μg L^{-1})	$CHBr_3$ (μg L^{-1})	$CHClBr_2$ (μg L^{-1})	$CHCl_2Br$ (μg L^{-1})	THMFP (μg L^{-1})	Specific THMFP (μg THM/mg DOC)
Alum							
0.2 mg ozone/mg DOC	10.7 ± 0.3	187.4 ± 2	ND	ND	7.4 ± 0.12	194.8 ± 3.2	18.2 ± 1.4
0.6 mg ozone/mg DOC	9.2 ± 0.4	102.5 ± 4	ND	ND	2.4 ± 0.09	104.9 ± 4.4	11.3 ± 1.1
0.8 mg ozone/mg DOC	7.4 ± 0.11	54.9 ± 2.1	ND	ND	2.2 ± 0.06	57.1 ± 2.11	7.7 ± 0.09
ACH							
0.2 mg ozone/mg DOC	10.8 ± 0.3	155.2 ± 5.2	ND	ND	2.8 ± 0.1	158.0 ± 2.09	14.5 ± 1.03
0.6 mg ozone/mg DOC	9.9 ± 0.2	100 ± 1.1	ND	ND	2.5 ± 0.1	102.5 ± 1.11	10.3 ± 0.82
0.8 mg ozone/mg DOC	8.8 ± 0.2	48.2 ± 2.01	ND	ND	1.95 ± 0.09	50.15 ± 2.07	5.6 ± 1.01
PACl							
0.2 mg ozone/mg DOC	11.2 ± 0.09	206.1 ± 4.3	ND	ND	3.2 ± 0.08	209.3 ± 4.3	18.6 ± 2.1
0.6 mg ozone/mg DOC	10.0 ± 0.11	108.6 ± 2.1	ND	ND	2.6 ± 0.1	111.2 ± 2.2	11.1 ± 1.04
0.8 mg ozone/mg DOC	9.1 ± 0.1	57.5 ± 3.6	ND	ND	2.1 ± 0.2	59.6 ± 4	6.5 ± 1.13

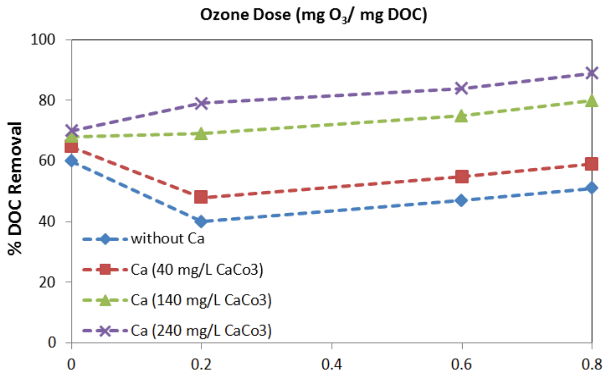

Fig. 4. Effect of calcium on pre-ozonation–coagulation, initial condition (HA concentration: 16 mg L^{-1}, coagulation: alum, coagulant dose: 6 mg L^{-1} Al, coagulation pH: 6.5).

hardness (44 mg L^{-1} $CaCO_3$); therefore, the beneficial effect of calcium hardness is negligible compared with the water from the Canadian Prairie studied earlier [2]. These results confirm that calcium hardness is a key factor involved in pre-ozonation–coagulation process.

4. Conclusion

This research investigated the effect of pre-ozonation as a coagulation aid for reduction of THMs formation in a water with low alkalinity and high DOC concentrations. These types of waters are quite common in the Canadian Prairie and the Shield. Therefore, the result of this research will benefit many Canadian communities with similar surface water quality and similar treatment technologies.

The results of this study along with authors' previous work [2], confirm that the effect of pre-ozonation on the efficiency of coagulation process aimed at reducing DOC strongly depends on the characteristics of the raw water and it needs to be evaluated for each specific water source. In this study, authors specifically focused on the role of calcium in this process.

The following conclusions can be made from this study:

- When coagulation was applied alone alum (6 mg L^{-1} Al) removed 66% of DOC and 83% of UV_{254}.
- All three aluminum-based coagulants used in this study removed hydrophobic DOC fractions better than hydrophilic ones. Fractionation results showed that alum has the highest removal (85%) of HPOA fraction of DOC.
- Coagulation with alum achieved the highest reduction in THMFP from 308.4 to 113.1 μg L^{-1} followed by ACH and PACl. The superior reduction of THMFP by alum is related to its effectiveness in reduction of HPOA.
- Application of ozone prior to coagulation did not enhance DOC removal at high coagulant dose of 6 mg L^{-1}. The pre-ozonation improved DOC removal at lower coagulant dosages (0–2 mg L^{-1}).
- This negative effect of the pre-ozonation on coagulation was not observed at low coagulant dosages (0–2 mg L^{-1} Al). At the low coagulant dosages, the DOC removal by ozonation alone (due to partial mineralization and oxidation of DOC) surpasses that achieved by the coagulant.
- The adverse effect of ozone on DOC removal by subsequent coagulation at coagulation dose of 6 mg L^{-1} was related to the low concentration of calcium hardness in this water source. Sufficient calcium concentration is required to complex with both aqueous NOM and particle-sorbed NOM released upon ozonation for enhanced DOC removal.
- Ozonation resulted in reduction of specific THMFP for both low and high calcium hardness waters studied by the authors.

It can be concluded that for this specific high DOC and low calcium water, application of ozone prior to coagulation is beneficial in terms of reduction of specific THMFP but not always in terms of reduction of DOC. While our previous study on water with high levels of DOC and calcium hardness showed the opposite effect [2]. This difference can be attributed to a significant role of calcium concentration in the removal of DOC by coagulation.

High coagulant dosages used for treatment of organic rich waters results in excessive sludge production. Ozone application prior to coagulation can achieve the same DOC removal at lower coagulant dosage, which in turn reduces the coagulation sludge production. This can imply significant reductions in energy demand and CO_2 emissions during sludge processing and transport.

References

[1] Manitoba Water Stewardship, Manitoba Water Quality Standards, Objectives, and Guidelines, Water Science and Management Branch, Manitoba, Canada, 2011. Available at: http://www.gov.mb.ca/waterstewardship/odw/public-info/general-info/water_system_data.html (Accessed December 2016).

[2] M. Sadrnourmohamadi, B. Gorczyca, Effects of ozone as a stand-alone and coagulation-aid treatment on the reduction of trihalomethanes precursors from high DOC and hardness water, Water Res., 73 (2015) 171–180.

[3] M. Sadrnourmohamadi, B. Gorczyca, Removal of dissolved organic carbon (DOC) from high DOC and hardness water by chemical coagulation – relative importance of monomeric, polymeric and colloidal aluminum species. Sep. Sci. Technol., 50 (2015) 2075–2085.

[4] Guidelines for Canadian Drinking Water Quality: Guideline Technical Document – Hardness. Available at: http://healthycanadians.gc.ca/publications/healthy-living-vie-saine/water-hardness-durete-eau/alt/water-hardness-durete-eau-eng.pdf (Accessed 5 November 2016).

[5] Saskatchewan Ministry of Health. Available at: http://www.saskh2o.ca/PDFWaterCommittee/DissolvedOrganicCarbon.pdf

[6] A. Matilainen, M. Sillanpää, Removal of natural organic matter from drinking water by advanced oxidation processes, Chemosphere, 80 (2010) 351–365.

[7] P.C. Chiang, E.E. Chang, C.H. Liang, NOM characteristics and treatabilities of ozonation processes, Chemosphere, 46 (2002) 929–936.

[8] P.C. Singer, C. Arlotta, N. Sinder-Sajdak, R. Miltner, Effectiveness of pre- and intermediate ozonation on the enhanced coagulation of disinfection by-product precursors in drinking water, Ozone Sci. Eng., 25 (2003) 453–371.

[9] W.C. Becker, C.R. O'Melia, Ozone, oxalic acid and organic matter molecular weight-effects on coagulation, Ozone Sci. Eng., 18 (1996) 311–324.

[10] R.P. Galapate, A.U. Baes, M. Okada, Transformation of dissolved organic matter during ozonation: effects on trihalomethane formation potential, Water Res., 35 (2001) 2201–2206.

[11] Y. Ma, Reaction mechanisms for DBPS reduction in humic acid ozonation, Ozone Sci. Eng., 26 (2004) 153–164.

[12] P. Bose, D.A. Reckhow, The effect of ozonation on natural organic matter removal by alum coagulation, Water Res., 41 (2007) 1516–1524.

[13] M. Yan, D. Wang, B. Shi, M. Wang, Y. Yan, Effect of pre-ozonation on optimized coagulation of a typical North China source water, Chemosphere, 69 (2007) 1695–1702.

[14] G.L. Amy, L. Tan, M.K. Davis, The effects of ozonation and activated carbon absorption on trihalomethane speciation, Water Res., 25 (1991) 191–202.

[15] S.D. Chang, P.C. Singer, The impact of ozonation on particle stability and the removal of TOC and THM precursors, J. Am. Water Works Assoc., 83 (1991) 71–79.

[16] F.J. Rodríguez, L.A. Marcos, L.A. Núñez, Influence of preozonation on the formation of chlorination disinfection by-products – a case study: the Úzquiza Reservoir Water, Ozone Sci. Eng., 34 (2012) 213–224.

[17] W.B. Dowbiggin, P.C. Singer, Effects of natural organic matter and calcium on ozone-induced particle destabilization, J. Am. Water Works Assoc., 81 (1989) 77–85.

[18] M.S. Chandrakanth, G.L. Amy, Effects of ozone on colloidal stability and aggregation of particles coated with natural organic matter, Environ. Sci. Technol., 30 (1996) 431–443.

[19] M. Edwards, M.M. Benjamin, Transformation of NOM by ozone and its effect on iron and aluminum solubility, J. Am. Water Works Assoc., 84 (1992) 56–66.

[20] M.S. Chandrakanth, G.L. Amy, Effect of NOM source variations and calcium complexation capacity on ozone-induces particle destabilization, Water Res., 32 (1998) 115–1241.

[21] F. Rodríguez, L.A. Marcos, L.A. Núñez, M. Garcia, Effect of ozonation on molecular weight distribution of humic substances and coagulation process—a case study: the Uzquiza Reservoir Water, Ozone Sci. Eng., 34 (2012) 342–353.

[22] M. Edwards, M.M. Benjamin, Effect of preozonation on coagulant-NOM interaction, J. Am. Water Works Assoc., 84 (1992) 63–72.

[23] D.J. Pernitsky, J.K. Edzwald, Selection of alum and polyaluminum coagulants: principles and applications, J. Water Supply Res. Technol., 55 (2006) 121.

[24] Standard Methods for the Examination of Water and Waste Water, American Public Health Association, American Water Works Association, and Water Environment Federation, Washington, D.C., USA, 2012.

[25] H. Bader, J. Hoigne, Determination of ozone in water by the Indigo method, Water Res., 15 (1981) 449–456.

[26] T. Ratpukdi, J.A. Rice, G. Chilom, A. Bezbaruah, E. Kahn, Rapid fractionation of natural organic matter in water using a novel solid phase extraction technique, Water Environ. Res., 81 (2009) 2299–2308.

[27] J.A. Leenheer, Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters, Environ. Sci. Technol., 15 (1981) 587–587.

[28] M. Sadrnourmohamadi, C.D. Goss, B. Gorczyca, Removal of DOC and its fractions from the high DOC and hardness surface waters of the Canadian Prairie, Water Sci. Technol. Water Supply, 13 (2013) 864–870.

[29] J.K. Edzwald, J.E. Tobiason, Enhanced coagulation: US requirements and a broader view, Water Sci. Technol., 40 (1999) 63–70.

[30] J. Swietlik, A. Dabrowska, U. Raczyk-Stanislawiak, J. Nawrocki, Reactivity of natural organic matter fractions with chlorine dioxide and ozone, Water Res., 38 (2004) 547–558.

[31] Z.L. Yang, B.Y. Gao, Q.Y. Yue, Coagulation performance and residual aluminum speciation of $Al_2(SO_4)_3$ and polyaluminum chloride (PAC) in Yellow River water treatment, Chem. Eng. J., 165 (2010) 122–132.

[32] B.G.Z. Yang, B. Cao, W. Xu, Q. Yue, Effect of OH^-/Al^{3+} ratio on the coagulation behavior and residual aluminum speciation of polyaluminum chloride (PAC) in surface water treatment, Sep. Purif. Methods, 80 (2011) 59–66.

[33] D.C. Montgomery, Design and Analysis of Experiments, John Wiley & Sons, Inc., New York, 2001.

[34] V. Uyak, I. Toroz, Disinfection by-product precursors reduction by various coagulation techniques in Istanbul water supplies, J. Hazard. Mater., 141 (2007) 320–328.

[35] B.Y. Shi, Q.S. Wei, D.S. Wang, Z. Zhu, H.X. Tang, Coagulation of humic acid: the performance of preformed and non-preformed Al species, Colloids Surf., A, 296 (2007) 141.

[36] C.R. O'Melia, W.C. Becker, K.K. Au, Removal of humic substances by coagulation, Water Sci. Technol., 40 (1999) 47.

[37] P.C. Singer, Humic substances as precursors for potentially harmful disinfection by-products, Water Sci. Technol., 40 (1999) 25–30.

[38] J. Molnar, J. Agbaba, B. Dalmacija, M. Klasnja, M. Watson, M. Kragul, Effects of ozonation and catalytic ozonation on the removal of natural organic matter from groundwater, J. Environ. Eng., 138 (2012) 804–808.

[39] T. Ratpukdi, S. Siripattanakul, E. Kahn, Mineralization and biodegradability enhancement of natural organic matter

by ozone–VUV in comparison with ozone, VUV, ozone UV, and UV: effects of pH and ozone dose, Water Res., 44 (2010) 3531–3543.

[40] M.S. Chandrakanth, Effects of Ozone on the Colloidal Stability of Particles Coated with Natural Organic Matter, Ph.D. Thesis, University of Colorado Boulder, CO, USA, 1994.

[41] J. Duan, X. Cao, C. Chen, D. Shi, G. Li, D. Mulcahy, Effects of $Ca(OH)_2$ assisted aluminum sulfate coagulation on the removal of humic acid and the formation potentials of tri-halomethanes and haloacetic acids in chlorination, J. Environ. Sci., 24 (2012) 1609–1615.