

## Preliminary investigation into the claims of the IBROM system

Zahra Vojdani and Beata Gorczyca

### ABSTRACT

Membrane filtration is commonly applied to reduce dissolved organic carbon (DOC) to control the formation of trihalomethanes (THMs); however, high levels of DOC can cause severe fouling of reverse osmosis membranes. The integrated biological and reverse osmosis membrane (IBROM) process is a combination of biological filters and reverse osmosis membranes. The IBROM process claims to remove biodegradable dissolved organic carbon (BDOC), which apparently should result in reduced membrane fouling. The goal of this research was to conduct a preliminary investigation into the claims of the IBROM system, using water collected from the Herbert water treatment plant (Saskatchewan). The plant is utilizing the IBROM for the treatment of a dugout and groundwater blend (DOC of 17.5–22.7 mg/L). The results demonstrated that BDOC concentrations did not change significantly throughout the plant. Optimized laboratory-scale coagulation with polyaluminium chlorohydrate achieved 58% removal of BDOC. Oxidation with permanganate increased the concentration of BDOC (from 5.7 to 8.8 mg/L). Overall, BDOC was effectively removed by optimized coagulation rather than the IBROM system. Moreover, the results show an inverse relationship between BDOC and THMs formation potential (THMFP) in both coagulated and oxidized water. For all concentrations, more biodegradable DOC had less tendency to form THMs based on the lower THMFP.

**Key words** | biodegradable dissolved organic carbon (BDOC), Integrated Biological and Reverse Osmosis Membrane (IBROM), membrane pre-treatment, natural organic matter (NOM), trihalomethanes (THMs)

**Zahra Vojdani** (corresponding author)  
**Beata Gorczyca**  
Department of Civil Engineering,  
University of Manitoba,  
Winnipeg, Manitoba R3T 2N2,  
Canada  
E-mail: z.vojdan94@gmail.com

### INTRODUCTION

Many potable water sources in the Canadian Prairies have exceptionally poor water quality due to high concentrations of dissolved organic carbon (DOC) of up to 25 mg/L and hardness exceeding 300 mg/L  $\text{CaCO}_3$  (Goss *et al.* 2017). Membrane filtration is commonly applied to reduce the DOC concentration and to control the formation of potentially carcinogenic trihalomethanes (THMs). However, reverse osmosis (RO) membranes, required to remove both DOC and total dissolved solids (TDS), experience serious fouling primarily due to extremely high concentration of DOC. One strategy to cope with fouling is to reduce DOC

levels in the pre-treatment processes prior to membrane filtration. American Membrane Technology Association (AMTA) recommends that RO membrane influent has less than 2 mg/L DOC (AMTA 2007; Badruzzaman *et al.* 2019).

#### Biodegradable DOC and membrane fouling

Baker & Dudley (1998) reported that biodegradable organic content made up 56–66% of the composition of the fouled RO membrane at a potable water treatment plant (WTP) that was used to treat high DOC surface water. The foulant

accumulated on these membranes was primarily composed of hydrophilic DOC fraction, which is typically more biodegradable. The readily biodegradable fraction of natural organic matter (NOM) can cause fouling by encouraging biofilm growth on the membrane surface (Al-Juboori & Yusaf 2012).

Biodegradable NOM is considered to be the dominant growth-limiting factor for bacteria and is often evaluated by biodegradable dissolved organic carbon (BDOC) (Siddiqui *et al.* 2017). BDOC is a measure of dissolved biodegradable organic carbon that can be mineralized by indigenous heterotrophic microorganisms within the water. Waters with a low concentration of BDOC are biologically stable, with low microbial regrowth and reduced or delayed fouling of the membrane (Al-Juboori & Yusaf 2012). Literature defines BDOC concentrations less than 0.15 mg/L at 20 °C as criteria for a biologically stable state of the treated water (Khan *et al.* 1999).

### BDOC and THMs formation potential

THMs formation is affected not only by the concentration of DOC but also by the DOC characteristics. However, it is not clear which characteristics of NOM are promoting THMs formation. There are inconsistent reports on the effects of NOM hydrophobicity and biodegradability on THMs concentration. Results of studies by Sadrnourmohamadi *et al.* (2013), Lin & Wang (2011) and Soh *et al.* (2008) report that hydrophobic NOM plays a greater role in the formation of THMs. On the other hand, Tubić *et al.* (2013) and Marhaba & Van (2000) report the hydrophilic fraction to have the highest specific THMs formation potential (THMs formation potential (THMFP) divided by DOC). These studies state that hydrophobic fraction may yield the greatest THMFP because this fraction is usually the dominant DOC fraction in raw waters.

Hydrophilic NOM has the highest biodegradability, while hydrophobic NOM is typically the least biodegradable NOM (Soh *et al.* 2008). The inconsistent reports on the NOM hydrophobicity and THMs formation make it difficult to observe if there is a relationship between the biodegradability of NOM and THMFP. Many studies have measured a BDOC change during conventional treatments such as coagulation, primarily to control biofilm growth in the distribution system; however, they have not discussed that how BDOC can affect THMFP.

## Processes used to reduce water DOC prior to membrane filtration

### Chemical coagulation

Effective DOC reduction via coagulation can directly influence downstream filtration processes, i.e., reduce membrane fouling. There have been many studies on the effectiveness of different coagulants on the removal of DOC and reduction of THMs; however, no study has looked closely at the effects of coagulation on DOC, BDOC and THMs all together in high DOC water.

### Oxidation

The addition of a strong oxidant, such as hydrogen peroxide, ozone, or UV irradiation, has been reported to protect the RO membranes from fouling by inhibiting biological activity (Siddiqui *et al.* 2017).

*Oxidation with potassium permanganate (KMnO<sub>4</sub>).* Experimental results have shown that potassium permanganate oxidation is particularly effective in improving filtration processes for waters with relatively high organic content. *In situ* formed manganese dioxide particles can adsorb naturally occurring organics and form bigger particulates, thus improving the removal of organic particulates by filtration and alleviating membrane fouling. Galvín & Rodríguez Melado (1998) reported that the use of permanganate as a pre-treatment in low dosages of about 0.45–0.8 mg/L in an RO membrane facility significantly improved the process through the elimination of algae and organic matter in the water (no DOC values were reported). Hidayah & Yeh (2018) reported that permanganate oxidation caused the breakdown of high molecular weight (MW) organics into low MW with a 10% increase in the DOC (DOC prior to oxidation of 4.2 mg/L). Despite the DOC increase, THMFP of the oxidized water was reported to decrease from 911.6 µg/L by 15%.

*Oxidation with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) coupled with UV (H<sub>2</sub>O<sub>2</sub>/UV).* H<sub>2</sub>O<sub>2</sub>/UV oxidation may cause partial oxidation of NOM by breaking large MW constituents into smaller and more biodegradable compounds such as aldehydes and

carboxylic acids (Sarathy & Mohseni 2009). Up to 20 mg/L of  $\text{H}_2\text{O}_2$  with UV fluence of  $1,500 \text{ mJ/cm}^2$  are typically applied in  $\text{H}_2\text{O}_2$ /UV commercial drinking water applications. Sarathy & Mohseni (2009) reported 15% mineralization of NOM for water with total organic carbon (TOC) equal to 2.18 mg/L during oxidation under these conditions. Toor & Mohseni (2007) reported 93% THMFP reduction (from 150 to 10  $\mu\text{g/L}$ ) by using 23 mg/L  $\text{H}_2\text{O}_2$  and UV fluence of  $2,500 \text{ mJ/cm}^2$ .

In comparison, it should be noted that DOC data from Environment Canada (2017) report a minimum average of 1.77 mg/L DOC, observed in Pacific Canada, and a maximum average of 12.89 mg/L, observed in the Prairies. To date, there is no literature reporting the use and effect of  $\text{KMnO}_4$  on drinking water sources with DOC higher than 6.8 mg/L (Godo-Pla *et al.* 2019). Moreover, the authors could not find any research reporting the effectiveness of  $\text{H}_2\text{O}_2$ /UV oxidation to control THMs in waters with DOC higher than 9.44 mg/L (Seo *et al.* 2019).

### Biological filtration – IBROM process

Biological removal of DOC is an attractive addition or alternative to chemical removal, especially for systems supplied by waters with a great deal of carbon since they may sustain biological activity and promote DOC biodegradation. The biological pre-treatment studied in this paper is the Integrated Biological and Reverse Osmosis Membrane or the IBROM process. This relatively novel process uses two filters connected in series using Filtralite media (Peterson *et al.* 2007). Filtralite media consist of lightweight expanded clay aggregates with high porosity and rough grain surfaces (Peterson *et al.* 2006). IBROM systems have been installed in 23 First Nation communities in the provinces of Saskatchewan and Alberta (Canada).

The IBROM process claims to remove any sources that provide energy and nutrients for bacterial growth from the water. BDOC may contain electron donors for biological processes and is considered to be one of the main nutrient sources. The IBROM process claims that the removal of BDOC alone would result in less fouling of the RO membranes. The IBROM system installed in the Yellow Quill WTP (Saskatchewan) reduced water DOC by 1 mg/L, resulting in RO membrane influent with DOC concentrations of 8.9 mg/L, i.e., more than four times higher than the 2 mg/L

concentration recommended for RO membrane influents. Yet, apparently, the RO membrane did not require chemical cleaning for up to 18 months (Peterson *et al.* 2006). It is worthwhile to note that chemical cleaning every 6 months or less is typically required to restore membrane performance (Ambrosi & Tessaro 2013).

The claims of IBROM systems have never been independently verified. There is no literature on the effectiveness of Filtralite filters in BDOC removal, and the reported DOC removal is very low – about 3 mg/L (Mitrouli *et al.* 2008).

This research is a short-term study on one of the IBROM installations; however, we believe that it is important to report our findings considering the large number of IBROM systems installed primarily in First Nations Reserves. According to Amnesty International Canada, at any one time, over one hundred of First Nations are under boil water advisories because their municipal water is not safe to drink (Amnesty International Canada 2018).

### Objectives

The main goal of this research was to conduct some preliminary investigation into the claims of the IBROM process by determining DOC and BDOC removal and THMFP at one of its installation in the Herbert WTP (Saskatchewan). This plant is supplied by an extremely high DOC and TDS water, composed of the dugout and groundwater blend with a DOC of 22.7 and 17.5 mg/L and TDS of 1,160 and 1,243 mg/L, respectively. The laboratory analyses and experiments were conducted using water collected from the plant.

Effectiveness of biological filtration (part of the IBROM process) and two conventional membrane pre-treatment processes installed at the Herbert WTP, i.e., coagulation and oxidation, in terms of BDOC removal and THMFP were analyzed. Correlations between DOC, BDOC concentration, and THMFP of the treated waters were investigated.

## MATERIALS AND METHODS

### General raw water quality

The Herbert WTP uses blended water consisting of the same ratio of water from a dugout (manmade pond) and

groundwater. General water quality parameters for both raw water supplies collected in August 2018 are summarized in Table 1. The oxidation experiments were conducted on the dugout water collected prior to water entering the treatment plant. This is an ideal oxidant addition location as it provides enough oxidation reaction time. At the Herbert WTP, oxidation and coagulation processes are applied to different water sources. Dugout water is oxidized first. Then, the water is blended with the groundwater and coagulated. Hence, in our laboratory experiments, oxidation was applied to the dugout water and coagulation on the blended water. Both dugout and blended raw water have high concentrations of DOC at approximately 22.7 and 17.5 mg/L, respectively. The hardness and TDS of the blended water are 376 mg/L  $\text{CaCO}_3$  and 1,243 mg/L, respectively, very similar to water quality across the Canadian Prairies.

Table 1 indicates that the blended water had lower hardness; however, it contained higher TDS concentrations. This could be due to the contribution of groundwater that is added to the dugout water and has TDS and hardness concentrations of 1,430 mg/L and 272 mg/L  $\text{CaCO}_3$ , respectively (data from August 2010). Since the groundwater has higher TDS and lower hardness values, the blended water, therefore, contains higher TDS and lower hardness concentrations compared to the dugout water.

### Biological filtration

The evaluation of the effectiveness of the IBROM process for the removal of DOC and BDOC was conducted on-site

at the Herbert WTP. Figure 1 demonstrates the unit processes comprising IBROM located at the plant, which includes two granular filters containing Filtralite HC and NC 0.8–1.6 mm clay media and one granular activated carbon filter followed by an RO membrane. Water samples were collected from before and after the IBROM filter units to measure DOC and BDOC removal efficiency. The results were based on triplicate measurements on two samples, collected on different days, from the plant under normal operating conditions.

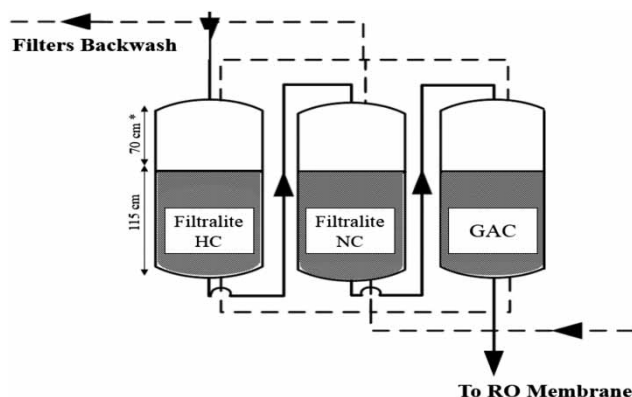
### Bench-scale coagulation and oxidation experiments

Laboratory bench-scale coagulation tests were conducted using the blended water with aluminum sulfate (alum), poly-aluminum chloride (PACl), aluminum chlorohydrate (ACH) and ferric chloride. Based on the study by Sadrnourmohadi *et al.* (2013) on the water with similar DOC, coagulant doses of 20–120 mg/L were selected. Herbert WTP source water had very high alkalinity (Table 1). The adjustment of pH required an excessive amount of acids, which was not economically feasible in this plant. Therefore, the pH was intentionally not adjusted in our experiments. The coagulation experiments were carried out at room temperature using the conventional method in a six paddle PB-700TM standard jar tester by Phipps & Bird (Richmond, USA). One liter of water was coagulated for each coagulation dose; the rapid mix was at 100 rpm for 1 min followed by slow mixing at 30 rpm for 15 min. The samples were then allowed to settle for 30 min.

**Table 1** | Dugout and blended water quality parameters for the Herbert WTP (29 August 2018)

Parameter	Unit	GCDWQ <sup>a</sup> (treated water)	Dugout water	Blended water
pH	–	7–10.5	8–8.8	7.9–8.5
Alkalinity	mg/L $\text{CaCO}_3$	–	234	350.5
THMFP	µg/L	≤100	809.8 ± 60	865.9 ± 39
Hardness	mg/L $\text{CaCO}_3$	80–100	495	376
TDS	mg/L	≤500	1160	1243
DOC	mg/L	–	22.7 ± 0.4	17.5 ± 0.7
BDOC	mg/L	–	7.5 ± 0.8	5.75 ± 0.3
Iron	mg/L	≤0.3	0.105	0.77
Manganese	mg/L	<0.12	0.06	0.01

<sup>a</sup>Guidelines on Canadian Drinking Water Quality (Health Canada 2019).



**Figure 1** | Schematic diagram of the on-site IBROM biofiltration set-up (\* indicates empty space for hydrostatic head development).

The oxidation experiments were conducted on the dugout water collected from the Herbert WTP. Depending on the water quality and the removal target, literature reports dosages in the range of 0.1–5 mg/L of  $\text{KMnO}_4$  (Ma *et al.* 2001). Considering the high dugout DOC (22.7 mg/L), 0.25, 0.5, 1, 1.5 and 2 mg/L of  $\text{KMnO}_4$  were used in the oxidation experiments. The experiment was carried out with a Six-Beaker Jar Test Apparatus. Permanganate solution was added into 1-L beakers. Fast mixing was for 30 s at 300 rpm followed by slow mixing for 5 min at 35 rpm, and then the water was allowed to stand for 15 min. The residual Mn concentrations were measured by inductively coupled plasma mass spectrometry. To avoid any interference of the oxidant in the BDOC and DOC measurements, the samples were quenched using sodium thiosulfate before further analysis.

Hydrogen peroxide doses of 20, 40, 60, 80 and 100 mg/L and UV fluence of 2,000  $\text{mJ}/\text{cm}^2$  were applied in the  $\text{H}_2\text{O}_2$ /UV experiments. The concentrations of  $\text{H}_2\text{O}_2$  were selected based on the studies by Goslan *et al.* (2006) working with DOC concentrations of 15.7, close to the DOC of raw water in this study. UV radiation was conducted using an annular reactor with a working volume of 1 L using a centrally mounted low-pressure UV lamp (Jelight Company, Inc., Irvine, CA, USA). The samples were quenched using bovine liver catalase (lyophilized powder  $\geq 10,000$  units  $\text{mg}^{-1}$  protein) at a concentration of 0.2 mg/L in the sample. This concentration of catalase has proved to be effective for removing  $\text{H}_2\text{O}_2$  within 10 min (Sarathy & Mohseni 2009).

DOC concentration was determined using a SkalarHT Formacs TOC Analyzer (Skalar, GA, USA). The TOC analyzer had a detection limit of 0.05 mg/L C and reproducibility within 2% of full scale. DOC is defined as the organic carbon concentration of sample water that has been filtered through a 0.45- $\mu\text{m}$  membrane filter. DOC was determined by measuring total carbon and subtracting the measurement for total inorganic carbon through the acidification of all forms of inorganic carbon.

THMFP measurements were conducted according to *Standard Methods 5710B* (APHA 2012). The chlorine demand was not determined prior to the THMFP tests due to the small sample volumes of the coagulated and oxidized water (1 L). Instead, all samples were chlorinated with 20 mg/L sodium hypochlorite. Our previous experience with high DOC waters indicated that this chlorine dose is sufficient to react with the organics. The samples were then buffered to pH 7. Sample vials were sealed with TFE caps and kept in the dark at 20 °C for 7 days. THMs concentrations were determined with a liquid–liquid extraction method according to *Standard Methods 6232B* (APHA 2012), using an Agilent 7890A GC System (Agilent Technologies, California, USA) equipped with a CombiPAL CTC Analytics auto-sampler and electron capture detection.

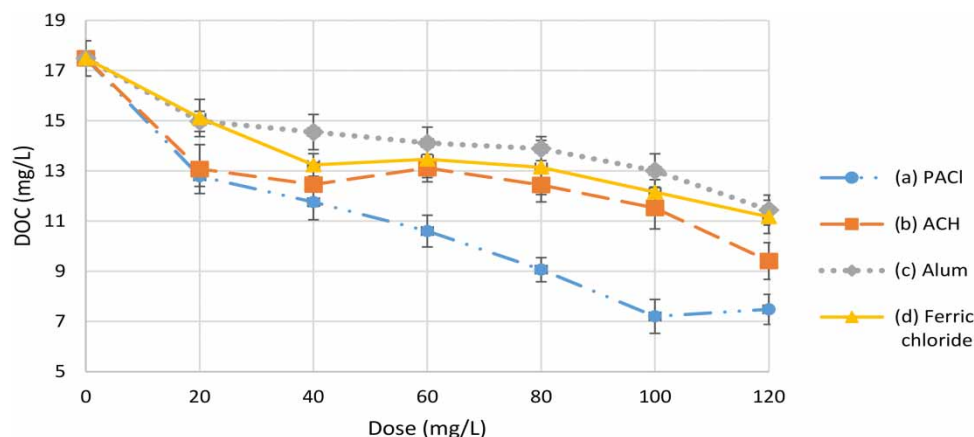
The BDOC test was performed according to a batch procedure by Khan *et al.* (1999) using a bacterial inoculum. In this test, 230 mL samples were filtered through a 0.7  $\mu\text{m}$  glass-fiber filter (GF/F, Whatman), inoculated with biologically active BOD seeds (Bio-Systems Corporation, Illinois, USA), and incubated at 20 °C for 28 days. After incubation, the samples were analyzed for DOC. For the blank sample, deionized water was inoculated with the same seed and kept at the same conditions. Eventually, BDOC concentration was calculated based on the difference in DOC reduction in the test samples and the blank sample after the incubation period.

## RESULTS AND DISCUSSION

### DOC, BDOC, and THMFP in coagulation experiments

Figure 2 shows the DOC removal by the four coagulants used in this study. For all coagulants, the removal of DOC

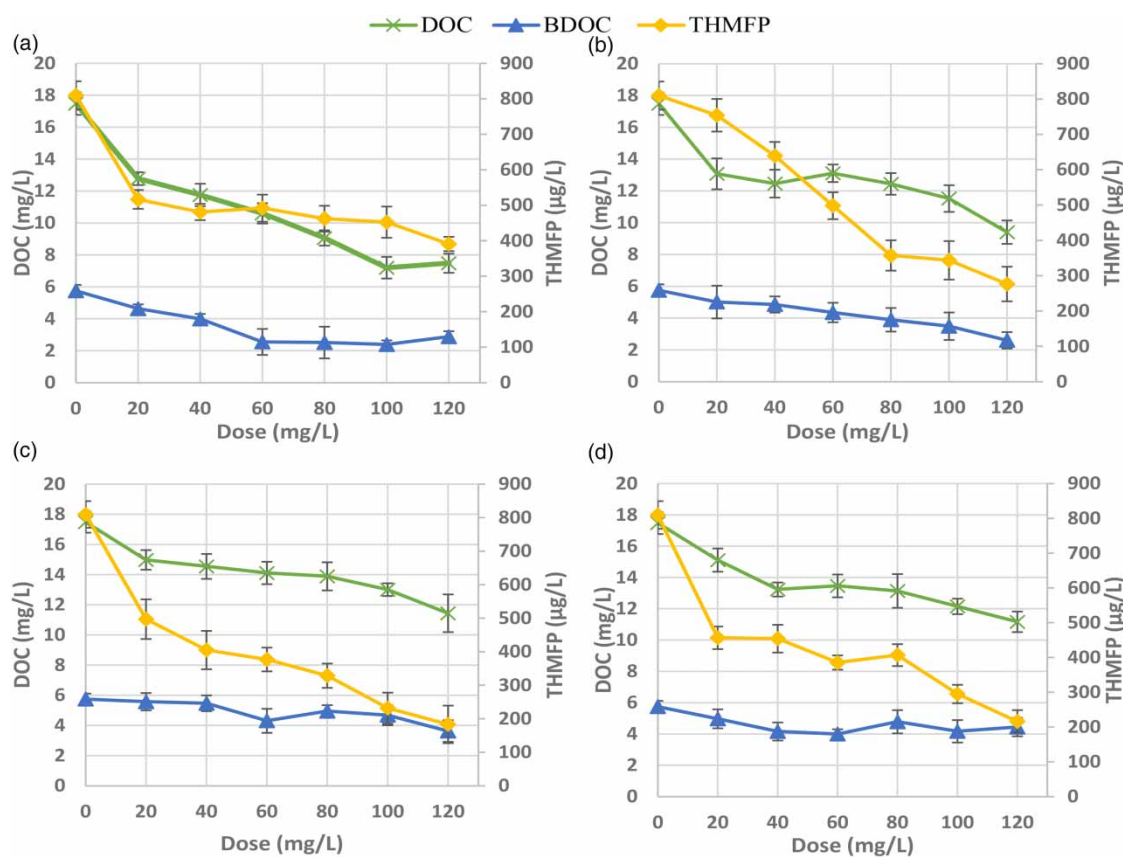




**Figure 2** | Removal of DOC for (a) PACI, (b) ACH, (c) alum and (d) ferric chloride at varying coagulant doses.

increased with the increased coagulant dose as expected. PACI is an optimum coagulant for this water in terms of DOC reduction. At the optimum dose of 100 mg/L, the coagulated water had a DOC of 7.5 mg/L and a pH of 7.2.

BDOC in the raw water was 5.75 mg/L (Table 1). Figure 3 shows changes in DOC, BDOC and THMFP in the coagulated waters. BDOC removal in bench-scale coagulation tests ranged from 20% to 60% for different



**Figure 3** | DOC, BDOC and THMFP for (a) PACI, (b) ACH, (c) alum and (d) ferric chloride at varying coagulant doses.

coagulants. Maximum BDOC removal was observed with 60 mg/L of PACl, reducing the BDOC by 58% down to 2.4 mg/L.

The raw blended water had a THMFP of 809.8 µg/L. In Canada, THMs are regulated at a maximum acceptable concentration (MAC) of 100 µg/L (Health Canada 2019). Figure 3 demonstrates THMFP for all coagulants and dosages used in the experiments. Water coagulated with 120 mg/L of alum had the lowest THMFP of 183.5 µg/L. Of the four coagulants tested, alum showed the greatest average reduction in THMFP while having lower DOC removal compared to other coagulants.

Reduction of water THMFP by coagulation is thought to be due to the reduction of the concentration of total DOC; however, factors other than DOC concentration seem to play a role here. Although PACl reduced water DOC the most, this coagulant had the least reduction in THMFP (THMFP of 452.3 µg/L at 100 mg/L dose of coagulant). Figure 3 shows that alum and ferric chloride were not as effective in the removal of BDOC as PACl while they had the highest reduction in THMFP. Our measurements indicated an inverse relationship between biodegradability and THMFP of the raw waters studied.

Overall, PACl showed the highest DOC removal according to laboratory-scale coagulation tests. DOC and BDOC in the optimally coagulated water, with 100 mg/L of PACl, were 7.5 and 2.4 mg/L, respectively. The DOC was still

higher than the recommended 2 mg/L, and therefore, this water is likely to cause serious RO membrane fouling. None of the water samples coagulated by different coagulants and doses met the criterion recommended for biologically stable water (BDOC less than 0.15 mg/L). Thus, it can be concluded that in the case of waters with high DOC, coagulation alone is not capable of lowering DOC sufficiently to mitigate RO membrane fouling or making the water biologically stable; however, it can reduce THMFP close to the MAC of 100 µg/L.

High values obtained for the optimum coagulant dosages are due to the high value of the original DOC. Adjusting pH can lower required coagulant doses; however, it is not a viable option when dealing with high alkalinity. The high coagulant dosages may affect RO membrane performance, but, in this study, we did not investigate the performance of the RO membrane.

#### Oxidation experiments with $\text{KMnO}_4$ and $\text{H}_2\text{O}_2/\text{UV}$

Figure 4 shows the change in the DOC concentration by oxidation for different dosages of  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2/\text{UV}$ . None of the oxidants were able to effectively reduce DOC concentration. Oxidation with 0.5 mg/L of  $\text{KMnO}_4$  had the maximum DOC removal of 8% (reducing DOC from initial 22.7 to 20.8 mg/L). 40 mg/L of  $\text{H}_2\text{O}_2/\text{UV}$  showed maximum removal of 15% (reducing DOC from initial 22.7 to 19.3 mg/L).

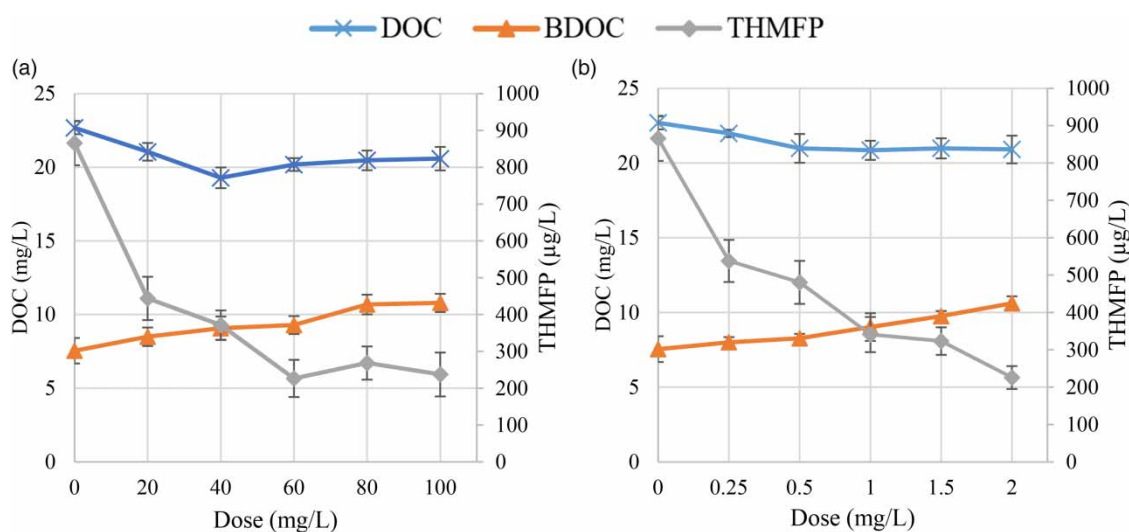


Figure 4 | Changes in DOC, BDOC and THMFP in oxidation with (a)  $\text{H}_2\text{O}_2/\text{UV}$  and (b)  $\text{KMnO}_4$ .

These results demonstrate that oxidation is not able to remove a significant amount of DOC.

However, oxidation with  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2/\text{UV}$  significantly reduced the THMFP of the water (Figure 4(b)). THMFP was decreased from an initial concentration of 865.9 down to 225.8  $\mu\text{g/L}$  (74% reduction) at a dose of 2 mg/L  $\text{KMnO}_4$ . In the case of  $\text{H}_2\text{O}_2/\text{UV}$ , THMFP was decreased to 237.5  $\mu\text{g/L}$  (72% reduction) with 100 mg/L of  $\text{H}_2\text{O}_2$ .

According to Figure 4, while the reduction in THMFP treated with  $\text{H}_2\text{O}_2/\text{UV}$  averaged 64%, the corresponding decrease of DOC was only 10%. The same was observed in  $\text{KMnO}_4$  with 56% and 7% average reduction in THMFP and DOC, respectively. Therefore, the total DOC cannot be the main factor contributing to THMFP.

Although the DOC of the water was relatively unchanged by oxidation, the water BDOC increased with the oxidant dose (Figure 5(a)). The original BDOC content of the water was 7.54 mg/L. Oxidation with 2 mg/L of  $\text{KMnO}_4$  resulted in the greatest increase of BDOC by 28% and to 10.6 mg/L. 100 mg/L of  $\text{H}_2\text{O}_2$  with 2,500  $\text{mJ/cm}^2$  UV fluence had greatest BDOC equal to 10.8 mg/L. This confirms the trend observed between BDOC and THMFP in coagulation. Higher BDOC water has lower THMFP following oxidation.

$\text{H}_2\text{O}_2/\text{UV}$  showed to be more effective in terms of control of THMs than permanganate. Although the DOC change was very similar for both oxidants tested (Figure 4), the water

oxidized with  $\text{H}_2\text{O}_2/\text{UV}$  always contained more BDOC. Also, water oxidized with  $\text{H}_2\text{O}_2/\text{UV}$  had lower THMFP compared to water oxidized with  $\text{KMnO}_4$  (Figure 5(b)).

It appears that oxidation of NOM, whether by  $\text{KMnO}_4$  or  $\text{H}_2\text{O}_2/\text{UV}$ , is changing NOM chemical characteristics and increasing its biodegradability. Spectroscopic studies of NOM and humic substances in drinking water report a significant reduction of aromatic and highly conjugated and hydrophobic compounds (constituting primarily the non-biodegradable fraction) after oxidation (Sadrnourmohamadi & Gorczyca 2015). Therefore, the concentration of hydrophobic NOM is reduced after oxidation, indicating that oxidants mainly react with hydrophobic NOM. The concentration of hydrophobic NOM in the pre-oxidized water will be relatively low. Therefore, when another strong oxidant, like chlorine, is added to already oxidized water, fewer oxidation reactions will take place and the formation of THMs will be reduced.

### BDOC change by the biological filtration

Table 2 summarizes the DOC and BDOC before and after the IBROM filters in the plant. The dugout water had a high DOC level of 22.7 mg/L and when blended with the groundwater, DOC concentration dropped to an average of 17.5 mg/L. The BDOC measurement of the blended water indicates that 5.75 mg/L or 34% of the DOC in the raw water is biodegradable.

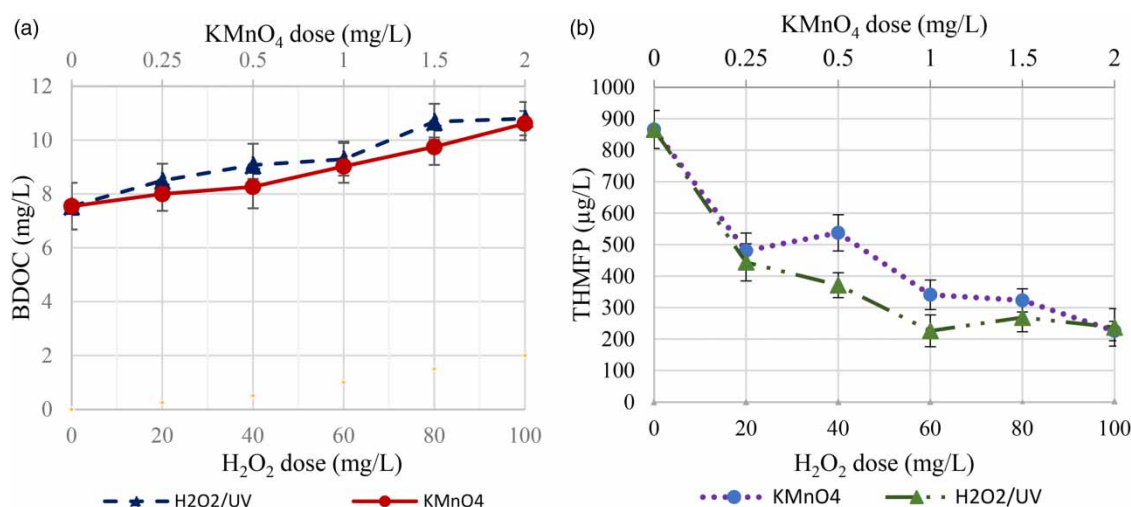


Figure 5 | Changes in (a) BDOC and (b) THMFP compared in oxidation with  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2/\text{UV}$ .



**Table 2** | DOC and BDOC concentration change along the treatment train of the Herbert WTP

Sample water	Dugout	Blended	Clarifier	IBROM filters (Filtralite)
DOC (mg/L)	22.7 ± 0.4	17.5 ± 0.7	15.4 ± 0.6	13.6 ± 0.9
BDOC (mg/L)	7.54 ± 0.8	5.75 ± 0.3	5.56 ± 0.7	5.96 ± 0.4

Table 2 indicates that the two Filtralite filters have 11% DOC removal. (DOC decreases from 15.4 to 13.68 mg/L.) No significant change of BDOC was observed in the IBROM effluent at the Herbert WTP. The results indicate that the IBROM process installed at the Herbert WTP is not effective in the removal of BDOC or DOC.

## DISCUSSION

This study was supported by the KGS Group involved in the upgrade of the Herbert WTP. Oxidation and coagulation processes are applied to different water sources in this system. Dugout water is oxidized first. Then, the water is blended with the groundwater and coagulated. Hence, in our laboratory experiments, oxidation was applied to the dugout water and coagulation on the blended water. Since the two water sources had different DOC, pH, hardness, therefore, the results in terms of BDOC removals and THMFP should not be compared.

## CONCLUSIONS

The removal of DOC, BDOC and THMFP from the high DOC and TDS water by IBROM, chemical coagulation and oxidation was evaluated. A blend of dugout and groundwater collected from the Herbert WTP (Saskatchewan) was used. The dugout water had a DOC of 22.7 mg/L and TDS of 1,160 mg/L, respectively, while blended raw water had a DOC of 17.5 mg/L and TDS of 1,243 mg/L. The following conclusions can be made from this study:

1. Biological filters constituting the IBROM system operating at the Herbert WTP were found to be ineffective in removing BDOC or DOC.

2. Laboratory-optimized coagulation was found to be quite successful in reducing water DOC and BDOC in blended water. Maximum DOC and BDOC reductions by coagulation were observed with 100 mg/L of PACl, which reduced DOC and BDOC to 7.5 and 2.4 mg/L, respectively.
3. Alum and ferric chloride showed the most significant reduction in THMFP from 809.8 µg/L to 183.5 µg/L and 216.2 µg/L with the total DOC reduction of 34% and 36%, respectively. The removal of DOC and the formation of THMs varied for different coagulants.
4. Oxidation tests conducted on dugout water resulted in a decrease in THMFP and an increase in BDOC concentration. H<sub>2</sub>O<sub>2</sub>/UV oxidation reduced the DOC by 15% while increasing the formation of BDOC up to 30%. Oxidation with KMnO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>/UV significantly reduced the THMFP from the initial THMFP of 865.9 µg/L to 225.8 µg/L and 237.5 µg/L, respectively.
5. Oxidation most likely degraded the large hydrophobic NOM into smaller hydrophilic NOM that is less prone to form THMs and more biodegradable than the other fractions. It appears that by applying pre-oxidation before chlorine addition, the concentration of the hydrophobic fraction of NOM, that is the main fraction reacting with chlorine, is reduced. Consequently, since there is less hydrophobic NOM to react with chlorine, the THMFP is reduced.

Overall, the IBROM system studied here was ineffective in the removal of DOC or BDOC, which has been reported as the key reasons for RO fouling in the literature. At the Herbert plant, the conventional coagulation and oxidation were much more effective in the removal of DOC and reduction of BDOC than the IBROM system. Conventionally coagulated and oxidized water samples with high BDOC concentration formed less THMs. This suggests that the formation of THMs can be effectively controlled by changing water DOC characteristics rather than removing DOC entirely with RO filtration.

## ACKNOWLEDGEMENTS

The authors thank KGS Group Inc. and the operators of the Herbert WTP for providing assistance and insight into the

project and plant operations. This work was supported by the MITACS Accelerate Program with assistance from KGS Group Inc. and additional funding provided by NSERC Canada.

## REFERENCES

- Al-Juboori, R. A. & Yusaf, T. 2012 [Biofouling in RO system: mechanisms, monitoring and controlling](#). *Desalination* **302**, 1–23. <https://doi.org/10.1016/j.desal.2012.06.016>.
- Ambrosi, A. & Tessaro, I. C. 2013 [Study on potassium permanganate chemical treatment of discarded reverse osmosis membranes aiming their reuse](#). *Separation Science and Technology* **48** (10), 1537–1543. <https://doi.org/10.1080/01496395.2012.745876>.
- American Membrane Technology Association (AMTA) 2007 *Pretreatment for Membrane Processes*. Available from: [https://www.amtaorg.com/wp-content/uploads/12\\_Pretreatment.pdf](https://www.amtaorg.com/wp-content/uploads/12_Pretreatment.pdf) (accessed 22 March 2019).
- Amnesty International Canada 2018 *The Right to Water, Our Work: Issues: Indigenous Peoples: Indigenous Peoples in Canada*. Available from: <https://www.amnesty.ca/our-work/issues/indigenous-peoples/indigenous-peoples-in-canada/the-right-to-water> (accessed 14 January 2019).
- APHA/AWWA/WEF 2012 *Standard Methods for the Examination of Water and Wastewater*, 22nd edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.
- Badruzzaman, M., Voutchkov, N., Weinrich, L. & Jacangelo, J. G. 2019 [Selection of pre-treatment technologies for seawater reverse osmosis plants: a review](#). *Desalination* **449**, 78–91. <https://doi.org/10.1016/j.desal.2018.10.006>.
- Baker, J. S. & Dudley, L. Y. 1998 [Biofouling in membrane systems: a review](#). *Desalination* **118** (1–3), 81–89. [https://doi.org/10.1016/S0011-9164\(98\)00091-5](https://doi.org/10.1016/S0011-9164(98)00091-5).
- Environment Canada 2017 *National Long-Term Water Quality Monitoring Data*. Available from: <http://donnees.ec.gc.ca/data/substances/monitor/national-long-term-water-quality-monitoring-data/> (accessed 10 December 2019).
- Galvín, R. M. & Rodríguez Mellado, J. M. 1998 Potassium permanganate as pre-oxidant in a reverse osmosis water plant. *Water SA* **24** (4), 361–363.
- Godo-Pla, L., Emiliano, P., Valero, F., Poch, M., Sin, G. & Monclús, H. 2019 [Predicting the oxidant demand in full-scale drinking water treatment using an artificial neural network: uncertainty and sensitivity analysis](#). *Process Safety and Environmental Protection* **125**, 317–327. <https://doi.org/10.1016/j.psep.2019.03.017>.
- Goslan, E. H., Gurses, F., Banks, J. & Parsons, S. A. 2006 [An investigation into reservoir NOM reduction by UV photolysis and advanced oxidation processes](#). *Chemosphere* **65** (7), 1113–1119. <https://doi.org/10.1016/j.chemosphere.2006.04.041>.
- Goss, C. D., Wiens, R., Gorczyca, B. & Gough, K. M. 2017 [Comparison of three solid phase extraction sorbents for the isolation of THM precursors from Manitoban surface waters](#). *Chemosphere* **168**, 917–924. <https://doi.org/10.1016/j.chemosphere.2016.10.118>.
- Health Canada 2019 *Guidelines for Canadian Drinking Water Quality- Summary Table*, Vol. 2006. Healthy Living. Retrieved from: <https://www.canada.ca/en/health-canada/services/environmental-workplace-health/reports-publications/water-quality/guidelines-canadian-drinking-water-quality-summary-table.html>.
- Hidayah, E. N. & Yeh, H. H. 2018 [Effect of permanganate preoxidation to natural organic matter and disinfection by-products formation potential removal](#). *Journal of Physics: Conference Series* **953**, 1–6. <https://doi.org/10.1088/1742-6596/953/1/012218>.
- Khan, E., King, S., Babcock, R. W. & Stenstrom, M. K. 1999 [Factors influencing biodegradable dissolved organic carbon measurements](#). *Journal of Environmental Engineering* **125** (6), 514–521.
- Lin, H. C. & Wang, G. S. 2011 [Effects of UV/H<sub>2</sub>O<sub>2</sub> on NOM fractionation and corresponding DBPs formation](#). *Desalination* **270** (1–3), 221–226. <https://doi.org/10.1016/j.desal.2010.11.049>.
- Ma, J., Li, G. B., Chen, Z. L., Xu, G. R. & Cai, G. Q. 2001 [Enhanced coagulation of surface waters with high organic content by permanganate preoxidation](#). *Water Science and Technology: Water Supply* **1** (1), 51–61.
- Marhaba, T. F. & Van, D. 2000 [The variation of mass and disinfection by-product formation potential of dissolved organic matter fractions along a conventional surface water treatment plant](#). *Journal of Hazardous Materials* **74** (3), 133–147. [https://doi.org/10.1016/S0304-3894\(99\)00190-9](https://doi.org/10.1016/S0304-3894(99)00190-9).
- Mitrouli, S. T., Yiantios, S. G., Karabelas, A. J., Mitrakas, M., Fóllesdal, M. & Kjolseth, P. A. 2008 [Pretreatment for desalination of seawater from an open intake by dual-media filtration: pilot testing and comparison of two different media](#). *Desalination* **222** (1–3), 24–37. <https://doi.org/10.1016/j.desal.2007.02.062>.
- Peterson, H., Pratt, R., Neapetung, R. & Sortehaug, O. 2006 Integrated biological filtration and reverse osmosis treatment of cold poor quality groundwater on the North American prairies. *Safe Drinking Water Foundation*, IWA Publishing, London, **5**, 424–432.
- Peterson, H., Pratt, R., Neapetung, R. & Sortehaug, O. 2007 Biological filtration of poor quality brackish water reducing reverse osmosis membrane fouling. IDA World Congress, Maspalomas, Gran Canaria 1–18.
- Sadrnourmohamadi, M., Gorczyca, B. & Goss, C. D. 2013 [Removal of DOC and its fractions from the high DOC and hardness surface waters of the Canadian Prairie](#). *Water Science and Technology: Water Supply* **13** (3), 864–870.

- Sadrnourmohamadi, M. & Gorczyca, B. 2015 Effects of ozone as a stand-alone and coagulation-aid treatment on the reduction of trihalomethanes precursors from high DOC and hardness water. *Water Research* **73**, 171–180. <https://doi.org/10.1016/j.watres.2015.01.023>.
- Sarathy, S. & Mohseni, M. 2009 The fate of natural organic matter during UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation of drinking water. *Canadian Journal of Civil Engineering* **36** (1), 160–169. <https://doi.org/10.1139/S08-045>.
- Seo, C., Shin, J., Lee, M., Lee, W., Yoom, H., Son, H., Jang, S. & Lee, Y. 2019 Elimination efficiency of organic UV filters during ozonation and UV/H<sub>2</sub>O<sub>2</sub> treatment of drinking water and wastewater effluent. *Chemosphere* **230**, 248–257.
- Siddiqui, A., Pinel, I., Prest, E. I., Bucs, S. S., van Loosdrecht, M. C. M., Kruithof, J. C. & Vrouwenvelder, J. S. 2017 Application of DBNPA dosage for biofouling control in spiral wound membrane systems. *Desalination and Water Treatment* **68**, 12–22. <https://doi.org/10.5004/dwt.2017.20370>.
- Soh, Y. C., Roddick, F. & Van Leeuwen, J. 2008 The impact of alum coagulation on the character, biodegradability and disinfection by-product formation potential of reservoir natural organic matter (NOM) fractions. *Water Science Technology* **58** (6), 1173–1179. <https://doi.org/10.2166/wst.2008.475>.
- Toor, R. & Mohseni, M. 2007 UV-H<sub>2</sub>O<sub>2</sub> based AOP and its integration with biological activated carbon treatment for DBP reduction in drinking water. *Chemosphere* **66** (11), 2087–2095. <https://doi.org/10.1016/j.chemosphere.2006.09.043>.
- Tubić, A., Agbaba, J., Dalmacija, B., Molnar, J., Maletić, S., Watson, M. & Perović, S. U. 2013 Insight into changes during coagulation in NOM reactivity for trihalomethanes and haloacetic acids formation. *Journal of Environment Management* **118**, 153–160. <https://doi.org/10.1016/j.jenvman.2012.11.046>.

First received 12 September 2019; accepted in revised form 13 February 2020. Available online 19 March 2020