Effects of Chemical and Biological Membrane Filtration Pre-treatment Processes on NOM Characteristics

By

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Abstract

Membrane filtration is commonly applied to reduce dissolved organic carbon (DOC) concentration to control trihalomethanes (THMs) formation; however, the high levels of DOC in the Canadian Prairies water sources can cause severe membrane fouling. Integrated biological and reverse osmosis membrane (IBROM) process is an RO membrane treatment unit utilizing primarily biological filtration pre-treatment. IBROM process claims to remove biodegradable DOC (BDOC), which allegedly should result in reduced fouling of the RO membranes. In this study, several pre-treatment methods, such as coagulation (with alum, polyaluminum chloride (PACl), aluminum chlorohydrate (ACH) and ferric chloride) and oxidation (with $KMnO_4$ and H_2O_2/UV) were evaluated for removal of DOC, BDOC, and THMs formation potential (THMFP). Moreover, BDOC change was measured in the biofiltration process using filters in the IBROM system. High-organic raw water source supplying the community of Herbert (Saskatchewan, Canada) was used in the experiments (DOC =17.5-22.7 mg/L and BDOC= 5.7-7.5 mg/L). The IBROM filters reduced DOC by 11% and increased the BDOC by 7%. Although the coagulation with PACl achieved the highest DOC and BDOC reduction (up to 57% and 58%, respectively), the coagulated water had the highest THMFP. H_2O_2/UV oxidation reduced the DOC only slightly by 10%, but the corresponding increase of BDOC and reduction of THMFP was very high (43% and 72%, respectively). Similar observations were made regarding oxidation with $KMnO_4$. Overall, the waters with a higher concentration of BDOC had lower THMFP.

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Structure of the Thesis

This is a manuscript (sandwich) style thesis with one manuscript that consists of contributions from Zahra Vojdani (author) and Dr. Beata Gorczyca (co-author). Both authors provided valuable inputs in the conception and design of the study.

Chapter 1 provides an introduction to the research, motivations, background, and objectives.

Chapter 2 is a literature review on the concepts discussed in this research, including NOM, BDOC, THMs, and the processes, including coagulation, oxidation, and the IBROM system.

Chapter 3 provides information on the materials and methods used in this research, including a description of the BDOC measurement method development, description of the IBROM case study, Herbert WTP, a summary of raw water quality and analytical methods used in this research.

Chapter 4 is the manuscript that is submitted to the Water Quality Research Journal for publication.

Chapters 5, 6, and 7 focus on the conclusion, engineering significance of this research, and recommendations for future work.

Contribution of Authors

The manuscript is included in chapter 4 of this thesis and authors' contribution is as follows:

Chapter 4: Vojdani, Z., Gorczyca, B., Preliminary investigation into the claims of the IBROM process, 2019. Submitted to *Water Quality Research Journal*, WQRJ-D-19-00017; Date submitted: 01 Oct. 2019; Status: Under review, 05 Nov. 2019.

i. Vojdani, Z.: Project conceptualization, methodology development, data acquisition, laboratory measurement, result interpretation, original draft, and editing.

ii. Gorczyca, B.: Project conceptualization, criticized methodology, supervision, review and editing, funding acquisition.

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List of Acronyms and Symbols

ACH	aluminum chlorohydrate
AOC	assimilable organic carbon
AOP(s)	advanced oxidation processes
Alum	aluminum sulfate
BAC	biological activated carbon
BDOC	biodegradable dissolved organic carbon
BOM	biodegradable organic matter
BOD	biochemical oxygen demand
$CHBr_3$	Bromoform
$CHBrCl_2$	bromodichloromethane
$CHCl_3$	Chloroform
CIP	cleaning-in-place
cm	Centimeter
DBP(s)	disinfection by-products
DOC	dissolved organic carbon
DI	deionized water
EC	expanded clay

EOM	extracellular organic matter
F	dilution factor
GAC	granular activated carbon
GDWQ	guidelines for drinking water quality
H_2O_2	hydrogen peroxide
HPI	Hydrophilic
HPO	Hydrophobic
IBROM	integrated biological and reverse osmosis membrane
J	Flux
$KMnO_4$	potassium permanganate
MAC	maximum acceptable concentration
MLSS	mixed liquor suspended solids
MWCO	molecular weight cut-off
MW	molecular weight
NF	Nanofiltration
NOM	natural organic matter
O_3	Ozone
PACl	polyaluminum chloride
POM	particulate organic matter
RDOC	refractory dissolved organic carbon
RO	reverse osmosis
Rpm	rounds per minute

SDI	silt density index
SEM	scanning electron microscope
TDS	total dissolved solids
THM(s)	Trihalomethanes
THMFP	THM formation potential
TOC	total organic carbon
UF	ultrafiltration
UV	ultraviolet
WHO	world health organization
WTP	water treatment plant
Λ	emission wavelength

Chapter 1: INTRODUCTION

1.1. Research Motivation

Herbert water treatment plant (WTP) located in Saskatchewan had been facing frequent membrane fouling issues. We were contacted by KGS Engineering Consultants Company and MITACS National Research Organization to further look into this plant's operational system and possibly find an explanation for the ongoing membrane fouling issues. While getting familiar with the plant's treatment process, we were introduced to a treatment system called IBROM that only utilizes biofiltration with Filtralite media and membrane filtration on poor-quality waters (with dissolved organic carbon (DOC(as high as 24 mg/L). The Herbert WTP was, therefore, called a modified-IBROM plant since it had coagulation and oxidation as additional pre-treatment steps.

According to Sapphire company, which is now the leading company to install IBROM or SIBROM (Sapphire IBROM) for treatment plants, IBROM process was reported to be operational in other installations (with more than 18 IBROM installations in Canada) showing low to no fouling at all in its membrane units. In a few papers that were published by IBROM's creator, we read that the main claim of IBROM was that by removal of biodegradable DOC (BDOC), membrane fouling would be heavily reduced.

BDOC removal by biological filtration was the key factor in the IBROM process. From this point, a project was conceptualized to measure BDOC removal in each treatment point of the Herbert WTP and also in lab-scale experiments with treatments other than biological treatment such as coagulation and oxidation that was also being used in Herbert WTP.

Moreover, as Herbert WTP had to often bypass the membranes, it was experiencing trihalomethanes (THMs(concentration higher than allowed by Canadian guidelines. While reading different studies on NOM characteristics and THMs formation, we were confronted with different stories about which fraction of NOM can contribute the most to THMs formation. This was particularly important since each different pre-treatment process in Herbert WTP could have increased/decreased a specific fraction of NOM significantly compared to other fractions. Therefore, THMs measurements were done in all the experiments to potentially find an explanation on which part of NOM, biodegradable or non-biodegradable, contributes more to THMs formation. As WTPs mainly focus on treatments that remove NOM in total rather than targeting a specific NOM fraction; the new information was going to help find out if one or a combination of pre-treatment processes can help reduce BDOC and THMs concentrations at the same time.

1.2. Background

Drinking water treatment involves removal of contaminants from raw water to produce water that is safe enough for human consumption and, i.e. has no short-term or long-term risk of any adverse health effect. Teatment processes have evolved over time from simple processes such as filtration, sedimentation, and chlorination of the final product to more advanced technologies such as membrane filtration. Reverse osmosis (RO) and nanofiltration (NF) membranes are widely being used in drinking water treatment processes as they can successfully produce a permeate that meets the current stringent drinking water quality guidelines and regulations.

Natural organic matter (NOM) is a complex mixture made up of organic matters with different molecular sizes, weight, structures, functional groups, and hydrophobicity (Lin & Wang, 2011). As carbon is the main component of NOM, dissolved and total organic carbon (DOC and TOC)

are historically considered as quantitative measures of dissolved and total organic matter, respectively.

Adverse impacts of NOM can include but are not limited to, the formation of harmful disinfection by-products (DBPs) such as potentially carcinogenic THMs, contribution to undesirable color, taste and odour in drinking water, and interfering with treatment processes like alleviating the level of membranes performance.

Biodegradable organic matter (BOM) is a fraction of NOM that encourages biofilm growth in the distribution system and provides a habitat for the survival of pathogens. BOM is the dominant growth-limiting factor for bacteria and is often evaluated by biodegradable DOC (BDOC). Literature defines BDOC concentrations less than 0.15 mg/L at 20°C as criteria for a biologically stable state of the treated water (Yapsakli & Çeçen, 2009; Khan et al., 1998).

The NOM concentration, treatability, and reactivity vary considerably in Canada. Health Canada (2019a) guidelines for NOM report mean TOC concentrations of selected jurisdictions (Newfoundland and Labrador, Nova Scotia, New Brunswick, and Quebec) varying for surface water and groundwater from 4.8 to 7 mg/L and from 2 to 3.1 mg/L, respectively. Meanwhile, Canadian Prairies have drinking water sources with DOC concentration as high as 25 mg/L (Goss et al., 2017; Hiriart-Baer et al., 2013), almost five times higher than the DOC reported for the other jurisdictions. Therefore, these waters are considered waters with very high DOC values and multiple treatment processes may be needed for adequate removal of NOM since literature and membrane manufacturers recommend DOC levels lower than 2 mg/L in the membrane influent (Badruzzaman et al., 2019, AMTA, 2007).

RO membranes, though successful in removing NOM, hardness and other dissolved solids, are susceptible to fouling, which could lower the membrane performance and result in costly

replacements. A common approach to mitigate membrane fouling caused by organic matter is the pre-treatment of feed water before membrane filtration, in order to produce water with lower DOC concentration. Common pre-treatment methods before the membrane can be one or a combination of processes such as coagulation, oxidation, sand/anthracite filters, biologically activated filters, ultrafiltration and so on.

Coagulation is a process that is commonly used to agglomerate colloidal solids or slow-settling suspended solids to produce a rapid-settling floc. Most of the NOM can be removed by coagulation, although, the hydrophobic (HPO) fraction and high molecular weight (MW) compounds of NOM are removed more efficiently than hydrophilic (HPI) fraction and the low MW compounds (Matilainen et al., 2011).

Oxidation processes, which have been developed to remove NOM, Fe, or Mn from water, are established based on the formation of hydroxyl radical complexes. The oxidation process is reported to oxidize organic compounds with high MW into smaller MW ones (Gil et al., 2018). It is reported that oxidation alone can reduce THM formation potential (THMFP) since it decreases HPO fraction of DOC that is reported to be the main fraction of DOC to form THMs (Sadrnourmohamadi & Gorczyca, 2015a).

Biological filters are often integrated with membranes as a pre-treatment method in order to remove BDOC produced by oxidation processes, or any other nutrient source for the bacteria and other microorganisms in the water; this is to prevent further bacterial growth on the membrane surface or the distribution system. Integrated biological and RO membrane (IBROM) system, is a novel process mainly used in Canadian Prairies and First Nation communities, which usually have poor-quality water. As evidenced by the name, this process only uses biological filtration (with a

media called Filtralite) and an RO membrane, and is reported to be effective in the treatment of waters with the DOC concentration as high as 24 mg/L (Peterson et al., 2006 & 2007).

1.3. Problem Statement

Canadian Prairies have drinking water sources with inferior water quality, specifically regarding DOC concentration that is reported to be as high as 25 mg/L (Goss et al., 2017). Yapsakli & Çeçen (2009) suggest that BDOC values represent 10–30% of the TOC of the raw water. Therefore, with high DOC concentrations, Canadian Prairies waters will also have high BDOC concentration.

According to the Manitoba Office of Drinking Water, 50 to 70% of water treatment plants treating surface water are not in compliance with provincial THMs regulations (Sadrnourmohamadi et al., 2013). RO and NF membranes have been very efficient in the removal of divalent cations and NOM in surface waters (Jha et al., 2018). However, many WTPs in Canada, especially in rural communities, are facing frequent membrane fouling issues, causing costly recurrent replacement of the membranes. Nevertheless, this poor-quality water source, with such high DOC and BDOC concentrations, is more prone to bacterial growth. BDOC is reported to be considered the dominant growth-limiting factor for bacteria and an excess amount of it can cause fouling by encouraging biofilm growth on the membrane surface (Al-Juboori & Yusaf, 2012; Siddiqui et al., 2017).

The IBROM process claims that the removal of BDOC alone would result in less fouling of the RO membranes (Peterson et al. 2006). The IBROM system installed in Yellow Quill WTP (Saskatchewan) is reported to reduce DOC by 1 mg/L only, resulting in RO membrane influent with high DOC concentrations of 8.9 mg, i.e. more than four times higher than the recommended 2 mg/L concentration. Meanwhile, it is reported that the membranes used in the IBROM system do not require frequent cleaning with intervals between cleanings of up to 18 months (Peterson et al. 2006).

However, even with waters with a much better quality especially with lower DOC concentration, chemical cleaning is typically required every six months to restore membrane performance (Ambrosi and Tessaro 2013). There are no other literature reports or scientific justification on the performance of the IBROM system. Herbert WTP in Saskatchewan, Canada, is using a combination of coagulation, oxidation, and IBROM system. The plant experiences serious RO fouling.

The objective of this research is to investigate claims of the IBROM process effectiveness for removal of BDOC. Furthermore, the effectiveness of DOC, BDOC removal and THMFP by all RO pre-treatment processes applied in Herbert WTP (i.e. coagulation, oxidation) was studied.

1.4. Research Objectives

The first objective of this study was to evaluate the effectiveness of biological filters in the IBROM process of Herbert WTP regarding BDOC removal.

Furthermore, two other membrane pre-treatment processes, coagulation and oxidation, were investigated in terms of DOC, BDOC, and THMFP. The research was conducted at a laboratory-scale using water collected from Herbert WTP with a DOC of 17.5-22.7 mg/L. No study has ever investigated NOM characteristics and concentration change for water with such high DOC amounts and with these pre-treatment methods.

The objectives of the laboratory-scale experiments was to observe BDOC removal efficiency in treatment methods other than biological treatments. Coagulation was conducted using aluminum sulfate (alum), polyaluminum chloride (PACl), aluminum chlorohydrate (ACH) and ferric chloride, while oxidation was conducted with $KMnO_4$ and UV/H_2O_2 in different dosages as later explained in chapter 3.

The third objective of this study was to investigate a potential correlation between BDOC concentration and THMFP of the laboratory treated waters. Literature reports do not present a consistent story on which fraction of NOM, biodegradable or non-biodegradable, contributes more to THMs formation. This correlation, if existed at all, can be beneficial to water treatment plants that deal with high DOC waters since they potentially face both problems of elevated THM concentration and membrane fouling. It has been noted that a treatment process that is routinely used to reduce THMs (such as oxidation) may cause extreme membrane fouling. This correlation will help choose the process that can meet each plant's specific removal goals.

CHAPTER 2: LITERATURE REVIEW

This literature review consists of an introduction to NOM, its different fractions, variability, and guidelines of NOM in Canada. Furthermore, the concepts of coagulation and oxidation were explained along with summary tables of the reported effectiveness in removal of DOC, THMs and BDOC by these processes. The next section was concentrated on the IBROM system and Filtralite media used in its filters.

Furthermore, BDOC measurements were done for the first time in the Environmental Engineering Water Lab of the University of Manitoba for this research. Therefore, a literature review of the different methods used for BDOC measurement is included at the end of this chapter. The Method itself is discussed in Chapter 3, Materials and Methods.

2.1. Natural Organic Matter (NOM)

Natural water sources contain suspended, dissolved organic and/or inorganic matter, as well as biological organisms, such as bacteria, protozoa, algae, or viruses. These particles are mainly differentiated as suspended (> 0.45 μm) and dissolved (< 0.45 μm) particles. The presence of these particles can (i) deteriorate water quality by increasing turbidity or color, (ii) carry waterborne pathogenic organisms or toxic compounds, and potentially transmit them to the consumer and (iii) interfere with the treatment processes (Matilainen et al., 2011).

NOM is a complex matrix of organic material present in surface or groundwater and can include proteins, amino acids, hydrocarbons, phenols, humic and fulvic acids, and so on. NOM generally

originates from three primary sources: (i) terrestrial material from soils, (ii) derived from algal or phytoplankton origin in the water, and (iii) synthetic organic substances of man-made or industrial origin (Edzwald, 2010).

2.1.1. NOM Different Fractions

NOM is an extremely complex mixture of organic compounds varying in size, polarity, charge density, molecular mass and biodegradability. In general, NOM in water is composed of two major fractions: dissolved and non-dissolved organic matter. Since carbon is the main constituent of NOM, DOC and TOC are considered as quantitative measures of dissolved and total organic matter, respectively. While TOC is defined as a measure of the total amount of organic carbon that is present in the water, DOC is the fraction of organic carbon that can pass through a 0.45 μm filter, with particulate organic matter (POM) remaining on the filter. In the focus of water treatment, POM is largely ignored as it can be removed during conventional water treatments such as coagulation and filtration. Therefore, DOC is the focus of THMs precursor studies as it is more difficult to remove, and it remains in the treated water to react with chlorine during chlorine disinfection.

From the biodegradability point of view, DOC is divided into biodegradable DOC (BDOC) and refractory DOC (RDOC), which is the fraction of DOC that is not biodegradable.

Moreover, NOM can be categorized based on its polarity (i.e., hydrophobic or hydrophilic) and acid/neutral/base properties. The smaller NOM fractions (<0.5 kDa) tend to be hydrophilic compounds. The most biodegradable fraction of NOM includes carbohydrates and amino acids, which are hydrophilic compounds. It is reported that the hydrophilic fraction of NOM is generally the biodegradable fraction of NOM (Soh et al. 2008).

2.1.2. NOM Variations and Guidelines in Canada

The treatability and reactivity of NOM vary significantly in Canada, as each water source has unique features. The Health Canada (2019a) guidance document for NOM reports mean TOC concentrations of selected jurisdictions (Newfoundland and Labrador, Nova Scotia, New Brunswick, and Quebec) varying for surface water and groundwater in the range of 4.8-7 mg/L and 2 to 3.1 mg/L, respectively. Moreover, the national survey (2009-2010) of Health Canada (2019a) indicates mean DOC values of 1.8 mg/L for raw well water and 7.3 mg/L for raw lake water. These data demonstrate that there is significant variability in NOM concentrations spatially.

DOC data from Environment Canada (2017) during the years of 2000 to 2015 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 Prairies).

Studies report higher NOM concentration in Canadian Prairies that include Manitoba, Alberta, and Saskatchewan. Canadian Prairies have drinking water sources with an inferior water quality specifically regarding DOC concentration that is reported to be as high as 25 mg/L (Goss et al., 2017; Hiriart-Baer et al., 2013); this is almost five times higher than the DOC reported for the other jurisdictions.

This water is considered as one with very high DOC values, and multiple treatment processes may be needed to adequately remove NOM.

There is no practical health-based value or numerical limit to define adequate removal of NOM. International organizations have not established numerical limits for NOM in drinking water. The U.S. Environmental Protection Agency's (U.S. EPA, 2016) rule for disinfectants and DBPs requires removal of TOC levels of above 2 mg/L from surface water while the World Health Organization (WHO, 2014) only suggests optimized NOM removal to minimize biofilm growth in the distribution system without providing an operational minimum TOC value.

Therefore, the main criteria in determining minimum TOC residual in water are the suggestions made by membrane manufacturers and membrane-related studies. Literature and membrane manufacturers advise that any DOC concentration higher than 2 mg/L in the membrane influent can cause early periods of membrane cleaning and eventually fast replacement due to fouling (Badruzzaman et al., 2019; AMTA, 2007).

2.1.3. Biodegradable Dissolved Organic Carbon (BDOC)

Biodegradable NOM is the dominant growth-limiting factor for bacteria and is often evaluated by BDOC and/or assimilable organic carbon (AOC) concentrations (Chen et al., 2018; Siddiqui et al., 2017). BDOC is a measure of dissolved biodegradable organic carbon that can be mineralized by indigenous heterotrophic microorganisms within the water (Huck, 1990).

AOC and BDOC are theoretically different parameters. AOC is based on the metabolic capability of two bacteria species that are i.e., Pseudomonas fluorescens P-17 and Spirillumstrain NOX. The parameter measured to determine AOC is the biomass formed due to biodegradable carbon assimilation. Meanwhile, BDOC is based on the metabolic activities of an unknown but much larger number of species. BDOC is determined from direct measurements of DOC and provides the values in units of carbon; also, information on the proportion of DOC that is non-biodegradable or RDOC can be provided (Volk & Lechevallier, 2002; Frías et al., 1992).

BDOC is often used as a measure of NOM biodegradability (Tubić et al., 2013). Waters with a low concentration of BDOC are biologically stable, with low microbial regrowth and reduced or delayed membrane fouling (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 (Yapsakli & Çeçen, 2009; Khan et al., 1998).

2.1.4. Problems Associated with NOM in Drinking Water Treatment

Organic matter present in the water can cause aesthetical issues affecting the colour, taste, and odour of the water. Moreover, microorganisms can consume NOM as a substrate and increase regrowth in the treatment units and distribution systems, especially when there is a lack of sufficient disinfectant residual (Sadrnourmohamadi & Gorczyca, 2015b). NOM can also have a deteriorative effect on treatment processes. Organic carbon has been reported as the main membrane foulant (Bucs et al., 2018; Baker & Dudley, 1998). Autopsies of several fouled membranes by surface waters of Canadian Prairies report that DOC is the main component of the membrane foulant (Avista Technologies, 2012, 2013, 2015).

Excess concentration of DOC increases the dosage of required oxidant, coagulant, and disinfectant for drinking water treatment. Besides, some NOM fractions may promote corrosion in the distribution system (Goss, 2011). These adverse effects overall increase the total operational cost of water treatment.

2.1.5. THMs Definition and Applicable Guidelines

One of the main problems with NOM is the consequent formation of DBPs. The most widely regulated chlorine DBPs - THMs that are known as potential carcinogens (Sadrnourmohamadi & Gorczyca, 2015b). The four regulated and most commonly occurring THMs are chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$).

Other chlorination by-products, such as haloacetic acids and halonitriles, can be formed during the relatively slow organic reactions that occur between free chlorine and naturally occurring organic precursors such as humic and fulvic acids.

The concentrations of THM compounds produced by chlorination are a function of pH, temperature, free chlorine concentration, contact time, and concentration and nature of oxidizable organic material in the water (Health Canada, 2019b; Morris et al., 1980).

Although there is no specific value for NOM concentration in standards and regulations, the amount of THMs is strictly limited by authorized organizations. *Table 1* shows some regulated values for THMs in the drinking water.

Table 1. Current regulatory standards for trihalomethanes (THMs)

Guidelines / Standards	$CHCl_3$ (mg/l)	$CHBrCl_2$ (mg/l)	$CHBr_2Cl$ (mg/l)	$CHBr_3$ (mg/l)
WHO (WHO, 2005)	0.3	0.06	0.1	0.1
Canada (Health Canada, 2019b)	0.1 mg/l for total THMs			
Manitoba (Manitoba WS, 2009)				

For total THMs, world health organization (WHO, 2005) recommends a fractionation approach to account for additive toxicity as follows in Equation 1:

$$\frac{C_{Chloroform}}{300\ \mu g/l} + \frac{C_{Bromodichloromethane}}{60\ \mu g/l} + \frac{C_{Dibromochloromethane}}{100\ \mu g/l} + \frac{C_{Bromoform}}{100\ \mu g/l} < 1$$

(Eq.1)

2.1.6. Effect of Different NOM Fractions on THMFP

THMs formation is affected not only by the concentration of DOC but also by the DOC characteristics. 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 is the main fraction in the formation of THM. On the other hand, Tubić et al. (2013) and Marhaba & Van (2000) report

the hydrophilic fraction to have the highest specific THMFP (THMFP divided by DOC). They report hydrophilic fraction as the main contributor to THMs formation. The 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 NOM hydrophobicity and THMs formation make it difficult to observe a relationship between the biodegradability of NOM and THMFP. Many studies have measured BDOC change during conventional treatment processes such as coagulation, primarily to control biofilm growth in the distribution system (Umar et al. 2014); however, they have not discussed how BDOC can affect THMFP.

2.2. Total Dissolved Solids (TDS)

Total dissolved solids (TDS) comprise inorganic salts and small amounts of organic matter that are dissolved in water. The principal constituents are usually sodium, chloride, calcium, magnesium, potassium, sulfates, and bicarbonates. (Health Canada, 1991)

Health Canada (1991) reports that TDS levels vary significantly spatially. Levels of TDS in Newfoundland and Labrador were in the range of 10 to 2263 mg/L. In Manitoba, TDS concentrations measured during 1988 in the treated water of 168 communities ranged from 56 to 2510 mg/L; Levels of TDS in drinking water taken between 1970 and 1989 in Saskatchewan ranged from 6.5 to 5376 mg/L.

An aesthetic objective of ≤500 mg/L has been established for TDS in drinking water. At higher levels, excessive hardness, unpalatability, mineral deposition, and corrosion may occur.

The TDS of the raw water source used in this research (from Saskatchewan) was 1160-1243 mg/L, which is lower than the average reported for Saskatchewan. Saskatchewan surface water sources generally have very high concentration of TDS. As a metter of fact, the Saskatchewan Ministry of the Environment's Drinking Water Quality Standards have increased the aesthetic objective for TDS to 1500 mg/L (SaskH_2O, 2008).

TDS is not appreciably removed using conventional water treatment processes. As a matter of fact, with the chemicals added during conventional water treatment, it can generally increase the concentration of the TDS. Reverse osmosis process is typical for removing TDS from raw water as it can remove virtually all dissolved substances (Health Canada, 1991).

2.3. Treatment Strategies to Reduce NOM Concentration

2.3.1. Removal of NOM Using Coagulation Process

Coagulation has been conventionally applied in water treatment to decrease NOM, turbidity, color and remove suspended particles and pathogens. Coagulation is used to agglomerate colloidal solids or slow-settling suspended solids to produce rapid-settling flocs, by adding a floc-forming coagulant (commonly aluminum or ferric salts) (Matilainen et al., 2010).

Coagulants dissociate in water to form metallic ion (Al^{3+} or Fe^{3+}), which undergoes hydrolysis and creates positively charged hydroxo-metallic ion complexes. These complexes are polyvalent ions possessing high positive charges and are adsorbed to the surface of the negative colloids. This results in a reduction of the zeta potential to a level where the colloids are destabilized. The destabilized particles, along with their adsorbed hydroxo-metallic complexes, aggregate by inter-particulate attraction due to van der Waals forces. The aggregation of the destabilized particles also occurs by inter-particulate bridging involving chemical interactions between reactive groups on the destabilized particles. These forces are supported by the agitation or mixing provided in the

water, which further causes the destabilized particles to come in close vicinity and aggregate into flocs large enough to settle or be filtered from the solution (Santos et al., 2014; Edzwald, 2010). *Figure 1* illustrates the process of decreasing repulsive forces between particles by using coagulants in aqueous solutions.

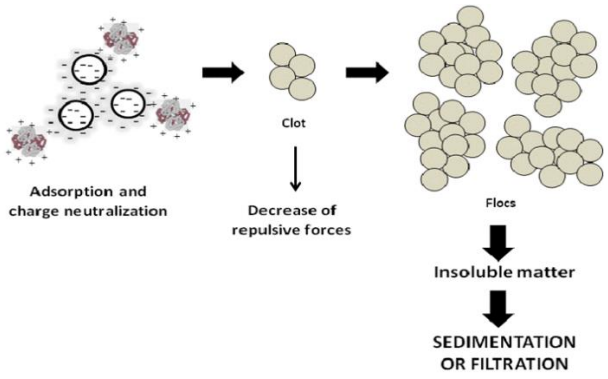


Figure 1. Coagulation process in water and wastewater treatments (Santos et al., 2014)

Coagulation-flocculation is generally used as a pre-treatment method before sedimentation and filtration. There have been many studies on the effectiveness of different coagulants on the removal of DOC, BDOC, and reduction of THMs and a number of them are summarized in Table 2.

The author could not find any study that has analyzed the effects of different coagulation conditions on DOC, THMFP, and BDOC, all together. The studies mentioned in Table 2 are a summary of studies on drinking water with DOC concentrations close to the DOC of the raw water studied in this research. The raw water used in our study had a DOC of 17.5-22.7 mg/L. 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 Prairies).

Table 2. Selected research studies on the removal of NOM for drinking water purposes by coagulation.

Reference	Water Source Quality	pH Adjustment	Coagulant Type and Dose	Results
(Zhao et al., 2014)	Turbidity: 6.2-9.4 NTU DOC: 3.9-4.55 mg/L	4 to 8	Alum ($Al_2(SO_4)_3$) Dose: 5-50 mg/L	The optimum pH of 7 and coagulant dose of 30 mg/L. DOC removal of 43%
(Jarvis et al., 2012)	Turbidity: 3.5 NTU DOC: 12.9 mg/L	5 to 9	Alum Dose: 5-15 mg/L	The optimum pH of 5 and coagulant dose of 5 mg/L. DOC removal of 76%
(Soh et al., 2008)	Turbidity: 2.16 NTU DOC: 12.67 mg/L THMFP: 475 µg/L	Adjusted to 6 from 7.4	Alum Dose: 50-200 mg/L	The optimum dose of 100 mg/L. DOC removal of 58%. THMFP removal of 66%
(Zhao et., al 2014)	Turbidity: 6.2-9.4 NTU DOC: 3.9-4.55 mg/L	5 to 10	Ferric chloride ($FeCl_3$) Dose: 15-90 mg/L	The optimum pH of 7 and dose of 65 mg/L. DOC removal of 58%
(Tubic et al., 2013)	DOC: 9.44 mg/L BDOC: 2.5 mg/L	Adjusted to 7	Ferric chloride Dose: 200 mg/L	DOC removal of 56% and BDOC removal 58%
(Hussain et al., 2013)	Turbidity: 91.3 NTU DOC: 14.1 mg/L	5.5 to 8.5	PACl Dose: 5-16 mg/L	The optimum pH of 6 and dose of 11 mg/L. DOC removal of 20%
(Sadrnourmohamadi et al., 2013)	Turbidity: 0.5 NTU	6 to 8	Alum, ferric sulfate,	The optimum pH of 6 and a dose of 120 mg/L.

	DOC: 8-12 mg/L THMFP 327 μg/L		ferric chloride, titanium sulfate Doses of 20-120 mg/L	Ferric chloride: greatest THMFP reduction by 86% and lowest DOC reduction by 54% Ferric sulfate: Greatest DOC reduction by 66%

2.3.2. Removal of NOMs Using Oxidation Processes

Oxidation processes result in the formation of hydroxyl radical complexes that are highly reactive and do not remain in the water for a long time. Hydroxyl radical oxidize organic compounds with high molecular weight (MW) into smaller ones (Gil et al., 2018). It is reported that oxidation alone can reduce THMFP since it decreases the hydrophobic (HPO) fraction of DOC that is main fraction of DOC to form THMs (Sadrnourmohamadi & Gorczyca, 2015a).

Oxidation processes, which have been developed to remove NOM and various other pollutants, mainly include ozone (O_3), hydrogen peroxide (H_2O_2), $KMnO_4$, UV/chlorine, UV/H_2O_2, UV/O_3, and H_2O_2/O_3 (Sillanpää, Ncibi, & Matilainen, 2018).

The mechanism of organic matter oxidation is different, depending on the applied oxidant and the point of oxidant addition in the water treatment process (Yates et al., 2014). For example, in pre-oxidation to aid coagulation, oxidants destroy the organic coatings on the particles which reduces their negative charge and repulsive forces and improves DOC removal by coagulation (Xie et al., 2016).

2.3.2.1. Removal of NOM by $KMnO_4$ Oxidation

Potassium permanganate ($KMnO_4$) is an oxidant commonly used in water treatment processes. Compared to the other oxidation processes, such as chlorination, $KMnO_4$ oxidation produces fewer by-products and has been reported to improve the next treatment processes such as coagulation. $KMnO_4$ has been used for the removal of iron, manganese, algae, cyanobacteria, and particles, etc. (Godo-Pla et al., 2019; Elsheikh et al., 2018; Liu et al., 2013).

When added to the water, $KMnO_4$ reacts with reductive species such as NOM, Fe (II), and Mn (II) and forms hydrous manganese dioxide (δMnO_2) (Equation 2).

$$MnO_4^- + 4H^+ + 3e \rightarrow MnO_2 + 2H_2O \quad \text{(Eq.2)}$$

δMnO_2 can act as an electron acceptor in the oxidation of NOM:

$$MnO_2 + NOM \rightarrow Mn^{2+} + NOM' \quad \text{(Eq.3)}$$

$KMnO_4$ pre-oxidation can improve proceeding coagulation processes. MnO_2 formed during oxidation absorbs the small hydrophobic organic molecules and thus improving the total removal of NOM.

Moreover, recent studies indicate that pre-oxidation with $KMnO_4$ can considerably mitigate the membrane fouling, especially the irreversible fouling that cannot be removed by hydraulic backwashing. It has been reported that total membrane resistance (R) is reduced when $KMnO_4$ is added to the membrane influent since MnO_2 nanoparticles adsorb small organic molecules and cationic ions and prevent them from entering membrane pores (reducing irreversible fouling). Therefore, the narrowing and blocking of membrane pores caused by NOM can be alleviated. These MnO_2/NOM complexes that accumulate on the membrane surface form a loose fragment on the cake layer that can be removed (reducing reversible fouling) (Zhao et al., 2018; Lin et al., 2012).

Zhao et al. (2018) investigated the influence of $KMnO_4$ dosing in a coagulation/ultrafiltration process. They reported that by destroying humic substances in the water, through 0.5 mg/L $KMnO_4$ pre-oxidation, reduced DOC from initial DOC of 5 mg/L to 3 mg/L with a total hydrophobic fraction decrease by 28%. The irreversible resistance of the membrane was smaller when the $KMnO_4$ was applied before the coagulation.

Hidayah et al. (2019) reported that pre-oxidation/coagulation performance was better than coagulation alone regarding organic removal; TOC was reduced from 6.9 mg/L to 4.2 mg/L after pre-oxidation with 1 mg/L $KMnO_4$ followed by $FeCl_3$ coagulation. However, when $KMnO_4$ pre-oxidation was applied alone, a slight increase (15%) in the TOC concentration was observed. The NOM concentration increase by $KMnO_4$ is reported by other researchers as well (Jian et al., 2019; Shi et al., 2019; Ma et al., 2018). It has been reported that the increasing $KMnO_4$ dosage up to 1 mg/L, firstly motivates the release of extracellular organic matter (EOM) from potential algae cells in the water, which eventually leads to the increase of DOC in the sample. However, at higher $KMnO_4$ dosage up to 2 mg/L, the MnO_2 aggregates were large enough to adsorb DOC (Shi et al., 2019).

Optimization of the $KMnO_4$ dosing is necessary in order to maximize the oxidation capacity and at the same time, keep the Mn residual concentration in the treated water less than the maximum acceptable concentration (MAC) of Mn that is 0.12 mg/L. More than MAC of Mn can cause an undesirable taste, order, and colour and can lead to the accumulation of deposits in the distribution system (Health Canada, 2019b). *Table 3* summarizes effects of $KMnO_4$ oxidation on removal of DOC and THMFP in water treatment. The dose of $KMnO_4$ depends on point of addition and water quality. The typical dose varies between 0.5 mg/L to 3 mg/L, with at least 1 hour of contact time (Godo-Pla et al., 2019).

It should be noted that the authors are not aware of any literature reporting use and effect of $KMnO_4$ on a drinking water source with DOC concentration higher than 6.8 mg/L (Godo-Pla et al., 2019; Shi et al., 2019; Ma et al., 2018).

Table 3. Selected research on the use of $KMnO_4$ in combination with the different processes in drinking water treatment.

Reference ($KMnO_4$ combined with …)	$KMnO_4$ Dose (mg/L)	Source Water Quality	Results
(Hidayah & Yeh, 2018) (stand-alone)	2	DOC: 4.19 mg/L THMFP: 911.6 ug/L	DOC increased by 10% THMFP reduced by 15%
(Xie et al., 2013) (stand-alone)	0.4 – 2	DOC: 0.42 mg/L	DOC was unchanged
(Zhao et al., 2018) (Coagulation/ultrafiltration)	0.5	DOC: 5 mg/L	up to 40% TOC removal
(Hu et al., 2018) (Coagulation)	1	DOC: 6 mg/L THMs: 146 ug/L	THMs reduction by 41%
(Ma et al., 2018) (Coagulation)	0.94	DOC: 3.8 - 6.8 mg/L	DOC removal by 63.8%
(Lu et al., 2015) (ultrafiltration)	0.4	DOC: 2.54 mg/L	DOC removal by 3.5% 31% reduction in resistance
(Zhang et al., 2017) (Coagulation/membrane)	0.5	TOC: 3.35 mg/L	DOC removal by 3.5%

2.3.2.2.Removal of NOM with UV/H_2O_2 Oxidation

UV based advanced oxidation processes (AOPs) have great potential for drinking water production due to the wide acceptance and application of UV as an effective disinfectant. According to Toor & Mohseni (2007), UV/H_2O_2 process can be used as a rigorous or moderate treatment method to decrease the formation of DBPs in drinking water. In rigorous treatment (UV fluence> 3000 mJ/cm^2), complete oxidation or mineralization of NOM to CO_2 reduces the DBPs formation potential irrespective of the NOM properties.

In the moderate UV/H_2O_2 treatment (UV fluence of 500 to 3000 mJ/cm^2), NOM is partially oxidized, and its bigger hydrophobic molecules are degraded into smaller and more biodegradable compounds with small MW such as aldehydes and carboxylic acids. That is because larger MW compounds (such as the humic matters) have chemical bonding that is relatively easy to break by the catalyzed UV oxidation. Rigorous treatment comes with a high cost of energy, while moderate treatment may result in insignificant reductions of DBPs precursors. Moreover, the overall impact of oxidation on DBPs formation in the raw water is determined by the original chemical characteristics and composition of NOM. Therefore, it is crucial to optimize the process for each individual raw water quality.

Oxidation processes mainly change the characteristics of NOM rather than its concentrations. Researchers report that after UV/H_2O_2 oxidation, the hydrophobic NOM is converted to more biodegradable hydrophilic NOM, and thus reducing hydrophobic NOM concentration (Lin & Wang, 2011). THMFP tests show that the hydrophobic portion is the main contributor to THMs formation after the chlorination process (Sadrnourmohamadi & Gorczyca, 2015b).

Toor and Mohseni (2007) report that with UV fluence of 3000 mJ/cm^2 and 23 mg/L H_2O_2, the DOC was changed insignificantly (1.59 mg/L to 1.27 mg/L), however, it significantly reduced the

THMFP down to 59 μg/L from 198 μg/L. The same trend was observed in the works of (Chu et al. (2014), Liu et al. (2012) and Wan et al. (2019) when UV/H_2O_2 oxidation successfully transformed the DBPs precursors to less chlorine reactive species without the need for significant NOM mineralization.

Table 4 is summarizing some of the selected studies on drinking water treatment application of UV/H_2O_2. The authors are not aware of any research reporting on the effectiveness of H_2O_2 /UV oxidation to control THMs in DOC water higher than 9.44 mg/L (Seo et al., 2019; Wan et al., 2019; Čehovin et al., 2017; Tubić et al., 2013).

Table 4. Selected research on the application of the UV/H_2O_2 process in drinking water treatment

Reference	H_2O_2 dose (mg/L)	UV Fluence	Source Water Quality	Results
(Wang et al., 2006)	280	40W (50 min)	DOC: 6.6-8 mg/L THMFP: 589 μg/L Hardness: 220 mg $CaCO_3$/L	DOC reduction by 84% THMFP reduction to 37 μg/L
(Toor & Mohseni, 2007)	23	3000 mJ/cm^2	DOC: 1.59 mg/L BDOC: 1.6 mg/L THMFP: 198 μg/L	THMFP reduction to 59 μg/L DOC to 1.27 mg/L BDOC increase by 45%
(Sarathy & Mohseni, 2010)	15	2000 mJ/cm^2	TOC: 2.53 mg/L THMFP: 397 μg/L	Insignificant TOC change THMFP Reduction to 80 μg/L
(Lamsal et al., 2011)	23	1140 mJ/cm^2	DOC: 2.8 mg/L THMFP: 330 μg/L	DOC reduction of 60% THMFP decrease to 70 μg/L
(Lin & Wang, 2011)	-	450W (60 min)	DOC: 8.5, 3.1 and 0.9 mg/L	THMFPs reductions of 48.3%, 46.7% and 50%, respectively

(Chu et al., 2014)	50	585 mJ/cm^2	DOC: 2.3 mg/L	DOC reduction of 15% THMFP reduction of 70%

2.3.3. Membrane Filtration Processes for NOM Removal

In potable water treatment, there is much interest in the use of membranes for the removal of DBPs precursors, particles (turbidity), and microorganisms, with the potential use of free chlorine as a post-disinfectant. Membrane processes use hydraulic pressure to force water through a semi-permeable surface that rejects most contaminants. Variations of this technology include RO, nanofiltration (low-pressure RO), and microfiltration membranes with a bigger pore size. Most of the water treatment plants have replaced their elaborate conventional treatment processes with a membrane system, due to its high NOM removal efficiency and much lesser use of chemicals. The reduction in NOM concentration using membranes before disinfection with chlorine automatically reduces the THMs formation (Goss, 2011).

For waters with high DOC values, multiple pre-treatment processes are required to adequately lower DOC levels before RO membrane treatment since literature and membrane manufacturers advise DOC levels lower than 2 mg/L in the membrane influent (Badruzzaman et al., 2019, AMTA, 2007).

2.3.4. Biological Filtration for NOM Removal

Biofiltration is a biologically active media filtration process developed mainly as a pre-treatment step to enhance the performance of the next treatment steps and improve finished water quality. The filters can contain different types of aggregates for microbial adhesion. Biological treatment is based on the use of microbes that will need to obtain energy (bio-oxidation) from the conversion of compounds that are aimed to be removed from the water. Bio-oxidizing processes happening in

these aggregates transform the ions from reduced state to oxidized state (e.g. from Fe^{2+} to Fe^{3+} or Mn^{2+} to Mn^{3+}).

Any raw water source has different compounds that can be nutrient and energy sources for bacteria. The objective is to convert these compounds into biomass particulates or organic/inorganic flocs and then quickly separate them. Therefore, the redox potential of the water should be increased to the point where bacteria can start the biological oxidation of the removal target (Fe, Mn, NOM, etc.), which can be done by adding a redox agent such as air or oxygen ahead of the biological filters.

A biofiltration unit is reported to improve the water quality, such as reduction of BDOC, precursors of disinfection by-products, bivalent species of iron, and manganese (Persson et al., 2005).

Anthracite, sand, granular activated carbon (GAC), and biological activated carbon (BAC) are conventional filter media in the biofilters. Chen et al. (2016) used two separate columns of dual-media, sand, and anthracite, operated in series as biofilters. De Vera et al. (2016) carried out biofiltration using anthracite and BAC to compare the biodegradability of non-ozonated and ozonated water. Other studies used BAC media in their biofiltration unit (Korotta-Gamage & Sathasivan, 2017; Black & Bérubé, 2014) or sand/anthracite biofilters followed by a biologically-active GAC contactor (Fu et al., 2017).

2.4. Integrated Biological and Reverse Osmosis Membrane (IBROM)

Integrated Biological and Reverse Osmosis Membrane (IBROM) treatment process is a combination of a biological filtration unit followed by an RO membrane unit. The IBROM has been currently installed in 18 WTPs, mostly in Saskatchewan and first nations communities (SDWF, 2018; Peterson et al., 2015).

The biological filtration in the IBROM process takes place in the Filtralite filters (Filtralite, 2019) that are made from a natural clay material with high porosity and rough grain surfaces. Table 5 is a summary of physical properties of Filtralite HC and NC used in Herbert WTP compared to other filtration media.

Table 5 Physical characteristics of sand, anthracite, Filtralite HC and NC filter media (Mitrouli et al., 2009)

Parameter	**Sand**	**Anthracite**	**GAC (Filtrasorb 400 Calgon)**	**Filtralite HC**	**Filtralite NC**
a	0.8–1.25	1.2–2.5	0.3 – 4.7	0.8–1.6	1.5–2.5
Bulk density, kg/m^3	1550	730	540	700 ± 75	235 ± 75
Particle density, kg/m^3	2650	1400	2000 - 2100	1650 ± 150	720 ± 150
Effective size (d_{10}), mm	0.9	1.55	0.55–0.75	0.9	1.7 ± 0.3
Coefficient of uniformity	<1.5	1.3	1.9 (max)	<1.5	<1.5
Particle porosity, %	–	–	-	40	73
Filter bed void fraction, %	43	48	-	62	67

The primary purpose of biological filtration in the IBROM process is the biological removal of sources that provide energy and nutrients for bacteria, which include phosphorus, nitrogen, dissolved organics, iron, etc. These sources would encourage bacterial growth on the membrane surface and cause fouling. The pilot process developed for Yellow Quill WTP (first IBROM plant, 2005) that is depicted in *Figure 2* included one contactor providing air as a redox agent and requirement for aerobic growth, followed by three filters running in series and an RO membrane unit as the last treatment step.

The key and distinguishing unit of the IBROM process is perhaps the media inside the biofilters that are aggregates for microbial adhesion and named Filtralite.

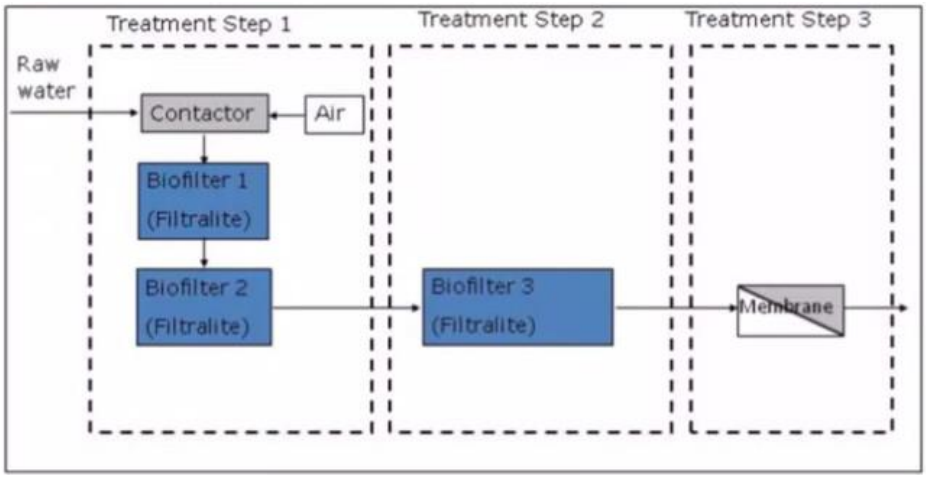


Figure 2. Flow diagram of the IBROM process as implemented at Yellow Quill First Nation)SDWT, 2018(

2.4.1. Filtralite Media

The biological filters in the IBROM process contain Filtralite media, made from lightweight expanded clay (EC) aggregates with high porosity and rough grain surfaces, originally sourced from the grounds in Oslo, Norway. Lightweight EC aggregates are manufactured from burning clay at high temperatures up to 1200°C followed by crushing and sieving to reach the preferred size fractions (Eikebrokk & Saltnes, 2002; Saltnes et al., 2002). The Filtralite media is categorized by the density of the clay aggregates in groups of NC, MC, and HC (N= Normal, M= Medium and H= High density, C= Crushed).

There has been considerable interest in Filtralite as an alternative to sand/anthracite filter media. Rough and angular surface, sharp edges, and high porosity of crushed EC aggregates offer a large surface area for microbial growth (Melin & Ødegaard, 1999). *Figure 3* is SEM images of Filtralite and anthracite media, well depicting the difference in the porosity of the grains.

A few of those studies which have compared the performance of traditional biofilter media with Filtralite media will be further reviewed. It should be noted that these studies limited the

water quality analysis to TOC and turbidity measurement and not other qualities such as BDOC that is the main target for removal in the IBROM process.

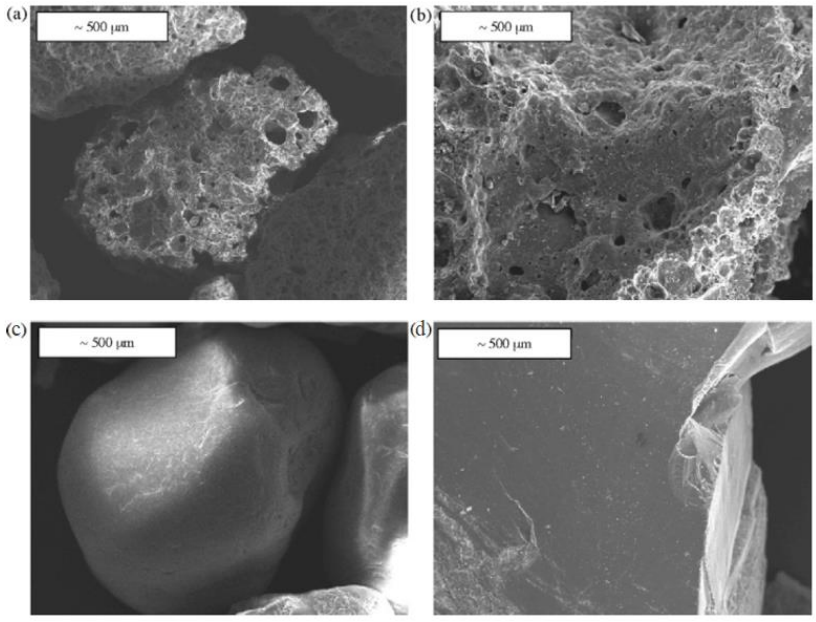


Figure 3. SEM images of (a) Filtralite HC 0.8–1.6 mm, (b) Filtralite NC 1.5–2.5 mm, (c) sand grains 0.8–1.2 mm and (d) anthracite 1.2–2.5 mm with 80x magnification (Mitrouli et al., 2009)

Melin & Odegaard (1999) studied a pilot-scale ozonation/biofiltration treatment plant for synthetic raw water with TOC concentrations of 3.2 – 5 mg/L, using Filtralite NC and HC 0.5-2.5 mm filters. Before these experiments, the Filtralite NC filter had been in operation for 11 months to develop the biomass. Like the Yellow Quill's process, the Filtralite filters were reported to remove low levels of organic carbon with TOC removals of less than 2 mg/L. In this case, the removal amount of 2 mg/L can be enough since the original TOC itself is less than 5 mg/L.

Eikebrokk & Saltnes (2002) conducted a study using different coagulants in a pilot-scale treatment to compare the performance of two identical and parallel filter columns, one filled with sand/anthracite media and the other filled with Filtralite HC and NC media. The raw water had a DOC level of 2.3 - 5 mg/L and a maximum turbidity of 0.2 NTU. The results indicated that regardless of the coagulant type, the Filtralite filters had lower initial head loss and a lower rate of

head loss increase compared to sand/anthracite. Both filters had comparative organic carbon removal, 36-65%, and 34-62%, respectively.

Mitrouli et al. (2009) compared sand/anthracite media with Filtralite NC and HC as pre-treatment for RO desalination installation (that is 15-min silt density index (SDI_{15}) values lower than 5). The seawater had a TDS concentration of 38,000 mg/L, the turbidity of 1–2 NTU, and TOC in the range of 1.9-4 mg/L. PACl coagulation was conducted before the filters. It was demonstrated that both filters produced filtrate of satisfactory quality for feeding RO systems with SDI_{15} values lower than 4.2. TOC removal of the filtration through Filtralite and sand/anthracite were on average, 49% and 35%, resulting in TOC in RO influent of 2.04 and 2.6 mg/L, respectively.

It is worthy to note that in their study, an initial set of experiments was conducted without the use of coagulant before the biofiltration unit. The SDI_{15} values in both filters' effluent were extremely high, rendering the product water quality not acceptable for RO feed water criteria (Mitrouli et al., 2009). Moreover, TOC removals reported in the literature vary widely in accordance with the source water, oxidant dosage and the Filtralite density, ranging from 18-50% (or maximum of 2 mg/L) which is an evidence that use of biofiltration alone as a pre-treatment is not enough to lower high DOC concentrations to 2 mg/L required for RO membrane influent.

However, the IBROM process uses only biofiltration as its pre-treatment before the RO membrane and is reported to be effective in producing water suitable to be fed to RO membrane (Peterson et al., 2006; Peterson et al., 2007a; Peterson et al., 2007b). Yellow Quill's treated water quality is the only data published on the performance of the IBROM process. The data shows that the Filtralite filter is reducing DOC by 1 mg/L only (that is BDOC), resulting in RO membrane influent DOC of 8.9 mg/L (Peterson et al., 2006). They report that with this DOC, the membranes were fully operational for 18 months until the need for a cleaning in place (CIP) session. Meanwhile, literature

reports that DOC concentrations higher than 2 mg/L in influent of the membrane will quickly clog the membrane pores requiring chemical cleaning every six months to restore membrane performance (Ambrosi and Tessaro 2013).

Another case is the Saddle Lake First Nation community with raw water DOC concentration of up to 24 mg/L and THMs concentrations in the treated water above 200 µg/L. It is reported that after the IBROM process installation, the plant has operated for five years in a row without the RO membranes needing a CIP (Peterson et al., 2015).

It should be noted that even if biofilters of the IBROM process remove all the BDOC concentrations and there would be no bacterial growth, high concentration of NOM can still cause organic and colloidal fouling on the membrane surface.

These facts lead to doubt the claims of the IBROM process while increasing numbers of WTPs using the IBROM process is evidently a proof for high efficiency of the IBROM process.

2.4.2. BDOC Measurement Methods

BDOC is an operationally defined parameter that depends on the protocol of measurement and experimental conditions such as contact time, microbial diversity, etc. Over the years, different methods and protocols have been developed to effectively measure BDOC. In the method developed by Servais et al., (1989), the biodegradation was simulated by using unfiltered raw water collected from the same location as the sample. Samples were incubated at 20 °C in the dark for a period of up to 30 days. The difference between the initial and final DOC of the water samples was the BDOC of the sample water.

The BDOC test was modified over the years in order to shorten the measurement time and increase the microorganisms' diversity in the water sample. Higher microbial diversity and quantity in the inoculum can help exert the maximum of the BDOC that is in the water.

All BDOC procedures are based on the reduction of DOC following the exposure of water samples to a bacterial inoculum. In general, based on the type of inoculum and exposure method, BDOC measurements methods are divided into two different protocols:

- Adding suspended bacteria (an inoculum) to a limited amount of sample and incubation of the sample (Khan et al., 2005; Volk et al., 1994; Servais et al., 1989, 1985)
- Utilizing attached bacteria in plug-flow reactors or sand columns (Babcock et al., 2011; Frías et al., 1992; Volk et al., 1994).

These methods share the same concept, which is measuring the initial and final DOC concentration during a period of controlled biochemical reaction.

The original method by Khan (1988) was based on using indigenous suspended microorganisms (i.e. unfiltered water samples) under oxic conditions in a mixed batch test (*Figure 4*). This method was easy to develop and repeat; however, the time required to complete the test was long, almost 30 days. Moreover, it was not certain that the unfiltered water samples have enough bacteria diversity and quantity to reflect all the biodegradable parts of DOC. To address this issue, researchers have suggested testing different types, and amounts of inoculum on the samples, including mixed liquor suspended solids (MLSS) or biochemical oxygen demand (BOD) commercial seeds.

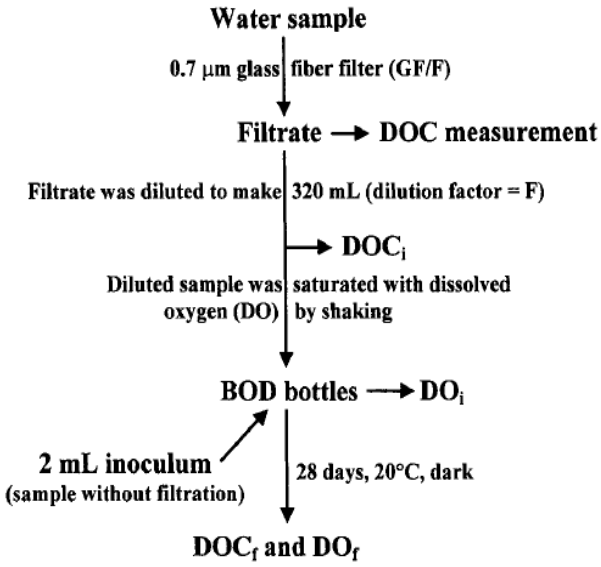


Figure 4. Modified bioassay protocol for measuring BDOC developed by Khan et al. (1999).

Khan et al. (1998) studied different types of inoculum, including unfiltered secondary effluent, BOD seed, and MLSS. The water samples examined were standard solutions of known DOC, treatment plant effluents, and ozonated treatment plant effluents. For all the inoculums tested it was possible to measure BDOC within five days using a larger volume of inoculum.

Khan et al. (2005) compared different BOD seeds with indigenous seed and MLSS to measure BDOC of standard solutions. Acetate standard solution is an entirely biodegradable solution, and therefore, the BDOC recovery that is defined as the $BDOC/DOC_{initial}$ ratio should be equal to 1 or 100%. The results indicated that MLSS had slightly higher BDOC recovery values (~1.04) while inoculums with the BOD seed and indigenous seed provided similar recovery values (~0.93). This could be explained by higher microbial diversity and quantity in the MLSS compared to the other inoculums.

Yapsakli & Çeçen (2009) used suspended bacteria originating from a dam reservoir. Different seeding ratios, 1:100, 1:250, and 1:500 ($V_{inoculum}/V_{sample}$) were tested on standard acetate solutions,

raw and ozonated waters of the same reservoir. In all the water samples, higher BDOC readings were achieved at a seeding ratio of 1:100, the one with the highest microbial density.

Cell lysis can occur if the bacterial concentration in the inoculum is very high. This occurs because the cell contents become soluble and hence increase DOC concentration in the solution. In this case, the BDOC values would be mathematically negative and, therefore, wrong. Consecutively, different inoculum amounts should be tested in order to avoid such situations. Furthermore, DOC should be measured at different time intervals to observe a decreasing trend in DOC (Yapsakli & Çeçen, 2009).

Another method used to evaluate BDOC is the use of recirculating plug-flow reactors (De Vittor et al., 2009; Søndergaard et al., 2001, 2004; Volk et al., 1997). In this method, a relatively large culture of microorganisms is attached to media in a plug-flow reactor, allowing for rapid measurement of BDOC. The plug-flow reactors can measure BDOC over a much shorter period compared to the original batch method (one day vs. 28 days). However, it can take months for media colonization of adapted microorganisms. The complexity of maintaining the reactors and minimizing variability of the conditions decreases the reliability and reproducibility of the method.

Columns containing media such as sand with the attached microbial population can also be used to measure BDOC. Volk et al. (1997) determined BDOC levels using bacteria fixed on the sand. In this test, 300 mL water samples were inoculated with 100 g of biologically active sand and incubated at 20°C under a 4 L/h aeration rate. DOC values were analyzed daily in duplicate until minimum DOC values were reached. BDOC concentrations were derived from the difference between initial DOC and minimum DOC.

Volk et al. (1994) studied the effect of operating conditions such as inoculum size, incubation period, and aeration in both suspended bacteria method and sand column method. BDOC values

were higher when using sand columns, probably resulting from greater bacterial diversity in the sand column than in unfiltered water inoculum and a higher biodegradation ability for fixed bacteria than for suspended bacteria. However, the development and maintaining of the bacterial population in the sand column is a complex and time-taking process. Volk et al. (1994) reported that aeration, when used with attached bacteria, accelerated the biodegradation process and increased the accuracy of BDOC results; however, it did not affect the BDOC values for suspended bacteria.

The sand column allows many replicates to run since the measurement time is reduced to less than one day. However, like plug-flow reactors, development and maintaining of the microbial population can take months and make it difficult to obtain reproducible results.

Currently, there is no absolute measure of BOM that can be used as a standard for all other assays since all methods differ in their minimum detection limits and applicability. All BDOC measurement protocols attempt to quantify as much of the biodegradable organic matter within the water as possible.

In general, all BDOC measurement methods take a long time whether during incubation or the development of the microbial population. However, a batch system, using an optimum amount of BOD seed as the suspended bacteria, can provide sufficient microbial diversity and quantity, which in return results in shortened measurement time and accurate BDOC values (Yapsakli & Çeçen, 2009). BOD seed inoculum can provide a uniform bacterial culture and condition, providing the same condition for each of the samples at any time. The batch method can be easily used to provide reproducible and reliable results without having to deal with complex biological reactors or columns.

The procedure used in this research will be discussed in detail in Chapter 3.5.

CHAPTER 3: MATERIALS AND METHODS

3.1. Water Source

Raw water used in this research was collected from Herbert WTP. Herbert Town is in southwestern Saskatchewan, with a population of 856 as of 2016. The Herbert WTP, with an average daily capacity of 650 m^3/day, utilizes a groundwater and surface water supply. The blended water ratio is of 70% surface water to 30% groundwater during the summer season and 50% to 50% ratio during the winter season. The plant employs a modified IBROM process that is preceded by coagulation/sedimentation and post-oxidation (*Figure 5*).

As demonstrated in *Figure 5*, the first treatment step is chemical coagulation carried out with polyaluminium chloride (ClearPac180 or PACl) at the dosage of 90-100 mg/L in the winter, and 100-120 mg/L in the summer.

Then, potassium permanganate dosed at 0.37 mg/L is added to the water. The coagulation and oxidation are done almost at the same time followed by flocculation and sedimentation in the clarifier.

The next step is the unit processes comprising IBROM, which are two Filtralite filters and one GAC filter followed by a membrane. The membrane is a RO membrane system model # SWM 8040-40-4 that is a single pass membrane treatment system designed to operate at a recovery of

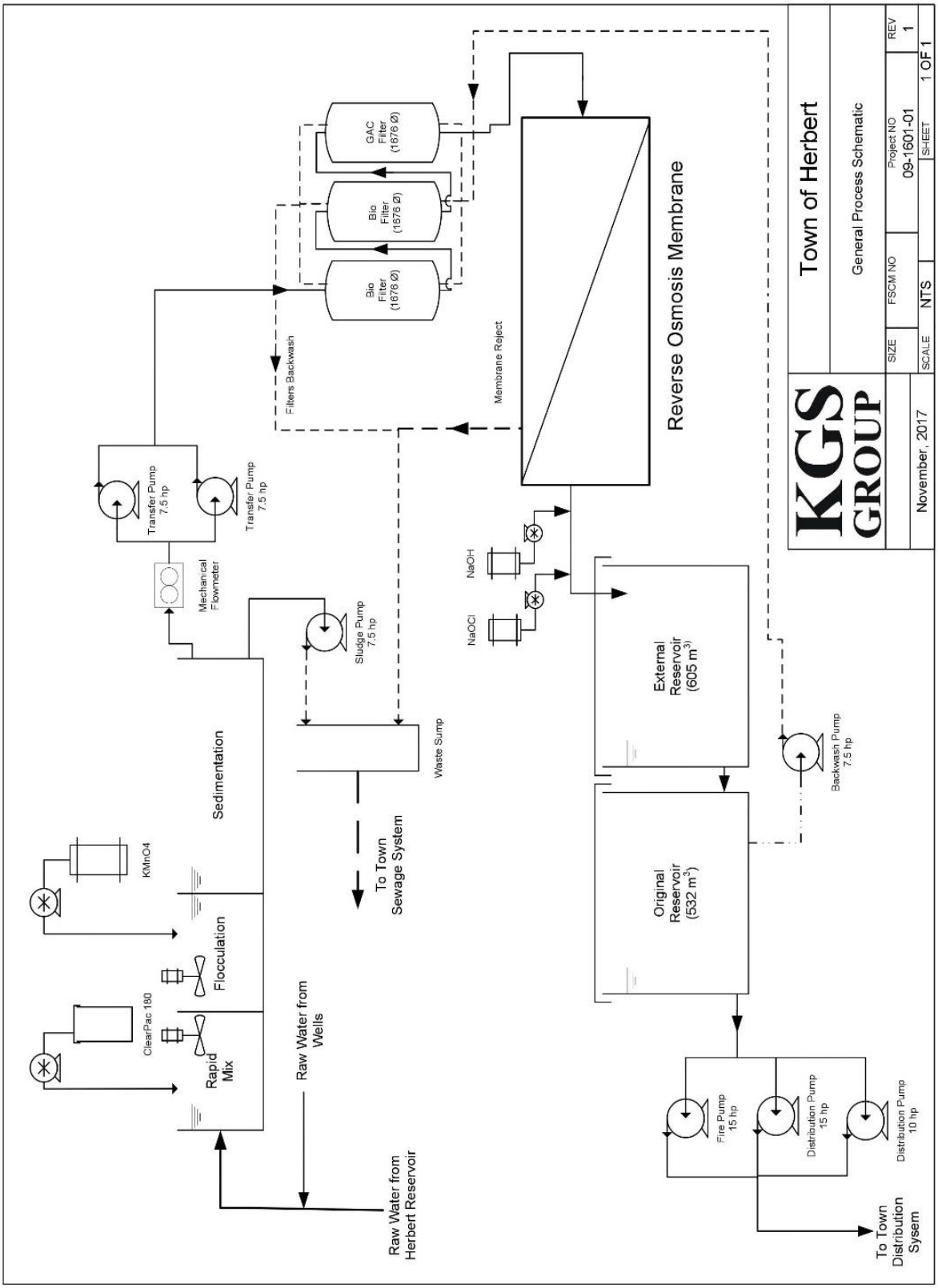


Figure 5. Drinking water treatment process for Herbert Town WTP.

80%. The membrane used in the system is thin-film membrane (TFM) manufactured by Osmonics model # AK8040F 400F. There was no information available on the level of hydrophobicity of the membrane sheets.

The plant is reported to often bypass the membrane unit due to the high rate of the fouling. Bypassing the membrane will increase the potential of THMs formation since there is no barrier after pre-treatment to remove DOC. Therefore, for such occasions, it is important to know THMFP of water after each pre-treatment method.

3.2. General Water Quality

General water quality parameters for both raw water supplies collected in August 2018 are summarized in *Table 6*.

Table 6. Raw water quality parameters for the Herbert WTP collected from the plant on Aug. 28, 2018

Parameter	Unit	GCDWQ* (Treated)	Surface Raw Water	Blended Raw Water
pH	-	7 – 10.5	8- 8.8	7.9 – 8.5
Total Alkalinity	mg/L $CaCO_3$	-	234	350.5
Total THMFP	µg/L	≤ 100	809.88 ± 60	865.89 ± 39
Total Hardness	mg/L $CaCO_3$	80 – 100	495	376
Calcium	mg/L	-	55.16	41.45
TDS	mg/L	≤ 500	1160	1243
Copper	mg/L	≤ 1	0.08	0.10
DOC	mg/L	-	22.7 ± 0.4	17.5 ± 0.7
BDOC	mg/L	-	7.5 ± 0.8	5.7 ± 0.3
Iron	mg/L	≤ 0.3	0.105	0.77
Manganese	mg/L	<0.12	0.06	0.01

* Guidelines for Canadian Drinking Water Quality (Health Canada, 2019b)

Both surface and blended raw water have high average concentrations of DOC, about 22.7 mg/L and 17.5 mg/L, respectively. The hardness and alkalinity of the blended water are 376 mg/L CaCO3 and 350.5 mg/L CaCO3.

3.3. Bench-scale Laboratory Experiments

In our experiments, unlike the plant process, the oxidation experiments were done before the coagulation and on the surface water with 120 minutes of contact time. The reason was to allow enough time for the oxidation processes to occur without interfering with the coagulation process. The contact time was determined based on the time it takes for the oxidized surface water to travel from the pumphouse to the plant. The water that enters the plant is a blend of the surface water and groundwater from the wells near the plant.

Laboratory bench-scale coagulation tests were conducted using the raw blended water with aluminum sulfate (alum), polyaluminum chloride (PACl), aluminum chlorohydrate (ACH) and ferric chloride. Based on the study by Sadrnourmohamadi et al. (2013) on the water with similar DOC, different coagulant doses form 20 mg/L to 120 mg/L were selected. The experiments were carried out at room temperature using the conventional method in a six paddle PB-700TM standard jar testers by Phipps & Bird (Richmond, USA). One litre 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.

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 $KMnO_4$ (Ma et al. 2001). Considering the high dugout water DOC (22.7 mg/L), 0.25, 0.5, 1, 1.5 and 2 mg/L of $KMnO_4$ were used in the oxidation experiments. The experiments were carried out with a Six-Beaker Jar Test Apparatus. Permanganate solution was added into 1-

litre beakers. Fast mixing was for 30 seconds at 300 rpm followed by slow mixing for 5 min at 35 rpm, and then the water was allowed to stand for 15 minutes. The residual Mn concentrations were measured by inductively coupled plasma (ICP) mass spectrometry. To avoid any interference of the oxidant in the BDOC and DOC measurements, before further analysis, the samples were quenched using sodium thiosulfate.

Hydrogen peroxide doses of 20, 40, 60, 80, 100 mg/L and UV fluence of 2000 mJ/cm^2 were applied in the H_2O_2/UV using the dugout water. UV irradiation was conducted using an annular reactor with a working volume of l litre, using a centrally mounted low-pressure UV lamp (Jelight Company, Inc., Irvine, USA). The samples were quenched using bovine liver catalase (lyophilized powder, ≥10 000 units 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 H_2O_2 within 10 min (Sarathy & Mohseni, 2009).

3.4. Analytical Methods

DOC concentration was determined using a SkalarHT Formacs TOC Analyzer (Skalar, GA). DOC is defined as the organic carbon concentration of sample water that has been filtered through a 0.45-µm membrane filter. DOC was determined by measuring total carbon and subtracting the measurement for total inorganic carbon through acidification of all forms of organic carbon.

THMFP measurements were conducted according to *Standard Methods 5710B* (APHA 2012). The chlorine demand was not determined before the THMFP test due to the small sample volumes of the coagulated or oxidized water (1 litre). 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) and using an Agilent 7890A GC System (Agilent Technologies, California, USA) equipped with a CombiPAL CTC Analytics auto-sampler and used electron capture detection.

3.5. BDOC Measurement Method Development

Following is a description of the method development with BOD seeds in a batch system that was then tested on the real raw water used in this study.

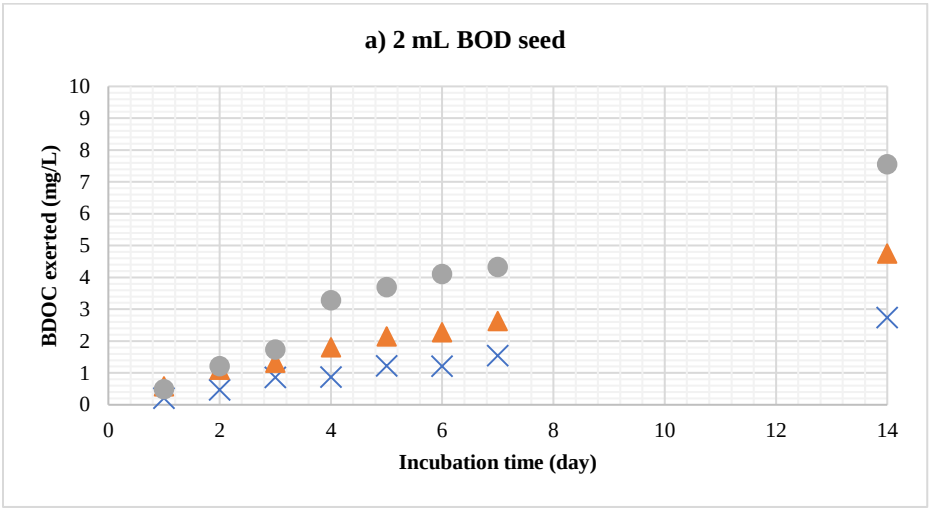
BDOC experiments were conducted on standard acetate solutions at concentrations of 3.5, 7, and 10 mg C/L. Acetate was chosen as a standard because of its easy and complete biodegradation. The final BDOC, for each standard solution, should be equal to $DOC_{initial}$. Therefore, accuracy was determined by comparing daily BDOC results with DOC_i of the standard acetate solutions. According to Equation 4, the recovery rate for a completely biodegradable acetate solution is 100%.

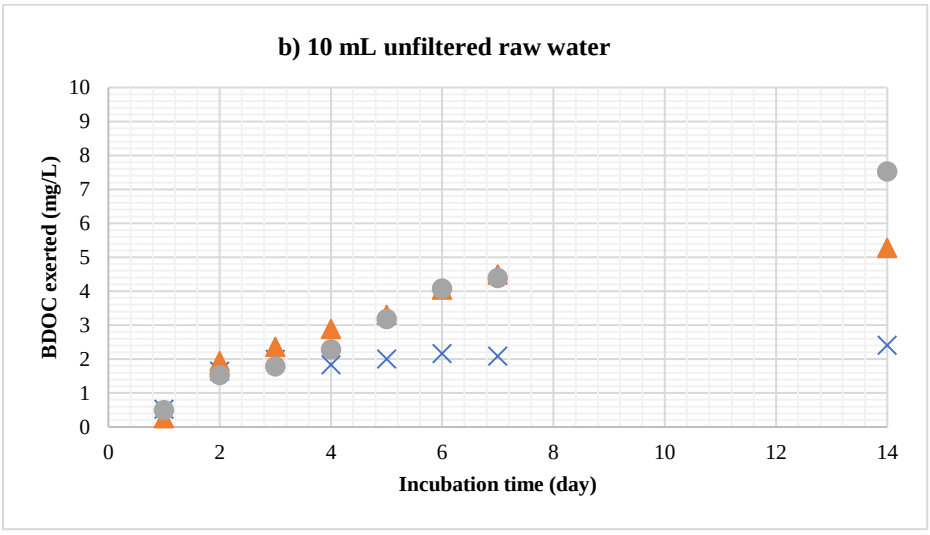
$$\text{Recovery (\%)} = (BDOC/DOC_{initial})*100 \quad \text{(Eq.4)}$$

The recovery rates close to 100% identify a successful and complete exertion of BDOC from the standard solution.

In the experiments, 2 and 10 ml of BOD seed solution (Bio-Systems Corporation, Illinois, USA) and 10 ml of unfiltered water samples (i.e. indigenous seed) were compared together in terms of BDOC values. Each inoculum was added to 230 ml of standard solution (20% of the bottle volume was left empty for headspace). The mixture was incubated at 20°C in an incubator (TS-606-G, WTW) for 28 days. The DOC was measured daily to follow the trend for BDOC exertion with respect to time.

Figure 6 is summarizing the results for each inoculum and each acetate concentration. For all acetate concentrations, samples inoculated with 10 mL of BOD seed reached the minimum DOC after 14 days providing highest BDOC recovery rates (BDOC values of 9.25, 6.52 and 3.32 mg/L, respectively for solutions of 10, 7 and 3.5 mg C/L). BDOC values remained relatively stable until the end of incubation.





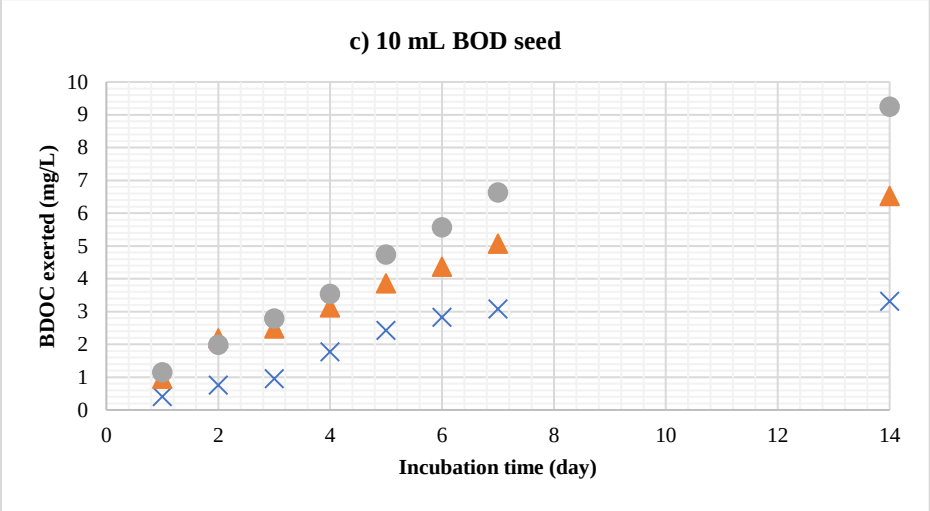


Figure 6. BDOC exertion at different acetate concentrations with inoculums of a) 2 mL BOD seed, b) 10 mL indigenous seed and c) 10 mL BOD seed.

According to *Table 7*, after 14 days, the average recovery rates of 10 mL BOD seed was 95%. In comparison, 10 mL of indigenous seed and 2 mL of BOD seed provided recovery rates of 78% and 70%, respectively, for 7 mg C/L solution and the same rate of 75% for 10 mg C/L solution.

Table 7. Recovery rates for each inoculum tested with respect to time.

DOC_i	Recovery (%)					
	2 mL BOD seed		10 mL indigenous seed		10 mL BOD seed	
Time	7 days	14 days	7 days	14 days	7 days	14 days
3.5 mg/L	44.55	78.86	60.05	69.14	88.69	95.34
7 mg/L	39.10	70.73	66.89	78.52	75.49	97.17
10 mg/L	43.41	75.86	44.00	75.53	66.54	92.83

The result indicated that a minimum of 14 days of incubation time was essential for all the samples. The 10 mL BOD seed inoculum was able to have the complete and highest BDOC recovery rate

within 14 days. However, samples inoculated with the other two inoculums underestimated the BDOC in 14 days and required longer incubation times.

Up to 25 days were needed for 2 mL BOD samples to reach recovery rates higher than 90%, while, with 10 mL indigenous seed, complete BDOC exertion was not observed during 28 days of incubation. This indicates that perhaps the number of bacteria in the raw water was insufficient to degrade even readily biodegradable substrates like acetate.

Overall, most accurate BDOC readings were achieved with 10 mL BOD seed inoculum. Following is a summary of the method used in this research that is a modification from the original method by Khan et al. (1998) with changing BOD seed type and volume added:

a) Filter the water sample through a 0.7 µm glass-fiber filter (GF/F, Whatman, Whatman International Ltd., Maidstone, England) previously rinsed with 300 mL of DI water.
b) Measure the DOC of the filtrate.
c) Dilute the sample with DI water to produce at least 230 mL of combined volume, and then place it in a washed container (BOD bottle) with at least 20% gas volume.
d) Shake the mixture to achieve saturation with dissolved oxygen.
e) After shaking, collect a 20-mL sample and measured for DOC, and record it as DOC_i.
f) Next, place the mixture in a washed BOD bottle.
g) Add 10 mL of air-saturated inoculum
h) Make sure the bottles are water sealed and then incubate them in the dark at 20 ± 0.5 °C for 14 days
i) Then, collect 20 mL of the supernatant and measure for DOC, and record as DOC_f.

j) A seed control (sample b) should be prepared in the same way except that the 10 mL seed is added to 230 mL of blank water with no sample, and the values were recorded as DOC_{bi} and DOC_{bf}.

The BDOC is then calculated using Equations 9 and 10:

$$BDOC\ (mg/L) = (DOC_i - DOC_f) - (DOC_{bi} - DOC_{bf}) \quad \text{(Eq.9)}$$

$$F = (mL\ of\ dilution\ water + mL\ of\ sample)/\ mL\ of\ sample \quad \text{(Eq.10)}$$

In our measurements, none of the samples were diluted; therefore, according to Equation 10, the dilution factor (F) was equal to one for all the samples.

This modified method was tested in the raw water of the Herbert WTP in triplicates with the DOC of 17.5 mg/L. In all cases, the BDOC results were close (standard deviations <0.6), with an average of 5.75 mg/L. Moreover, Joret et al. (1991) suggested that BDOC values represent 10–30% of the total dissolved organic carbon content of drinking waters. This rate for the raw water studied here was measured to be 32% and in the suggested range by Joret et al. (1991). This further approves the reliability and reproducibility of the modified method.

CHAPTER 4: PREMILANARY INVESTIGATION INTO THE CLAIMS OF THE IBROM PROCESS

4.1. Abstract

Membrane filtration is commonly applied to reduce dissolved organic carbon (DOC) to control trihalomethanes (THMs) formation; however, high levels of DOC can cause serious reverse osmosis membranes fouling. Integrated biological and reverse osmosis membrane (IBROM) process is a combination of biological filters and RO membranes. IBROM process claims to remove biodegradable dissolved organic carbon (BDOC), which apparently should result in reduced membrane fouling. However, the above claims have not been scientifically justified. 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 coagulation, oxidation and IBROM for treatment of dugout and groundwater blend (DOC= 17.5 mg/L). The BDOC of raw water was 5.7 mg/L (32% of DOC) with THM formation potential of 810 μg/L.

The results demonstrated that BDOC concentrations did not change significantly throughout the plant. Optimized lab-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 quite effectively removed by optimized coagulation and rather than the filters in the IBROM system.

Keywords:

Biodegradable dissolved organic carbon (BDOC), Integrated Biological and Reverse Osmosis membrane (IBROM), Membrane pre-treatment, Natural organic matter (NOM), Trihalomethanes (THMs)

4.2. Introduction

Many potable water sources in Canadian Prairies have exceptionally poor water quality due to the high concentrations of dissolved organic carbon (DOC) of up to 25 mg/L and hardness exceeding 300 mg/L $CaCO_3$ (Goss et al. 2017). Membrane filtration is commonly applied to reduce the DOC concentration and to control trihalomethanes (THMs) formation. However, water DOC should be below 2 mg/L prior to the treatment by reverse osmosis (RO) membranes in order to prevent frequent fouling issues (Badruzzaman et al., 2019). Therefore, nanofiltration RO membranes experience severe fouling when used to treat such extremely high DOC waters. One strategy to cope with the fouling of membranes is to reduce the concentration of membrane fouling compounds in the pre-treatment processes before membrane filtration.

4.2.1. Biodegradable DOC (BDOC) and Membrane Fouling

Membranes used for filtration of surface waters are mainly fouled by organic and microbial depositions. Membrane fouling can be effectively reduced by depleting biodegradable organic matter (BOM) in the source water (Bucs et al. 2018). Baker & Dudley (1998) reported biodegradable organic matter making up 56-66% of the composition of the fouling layer in the bio-fouled RO membranes that were taken out of a potable water treatment plant (WTP). The foulant accumulated on the membranes was primarily composed of the hydrophilic DOC fraction, which is typically more biodegradable. The easily biodegradable fraction of NOM can

cause biofouling by encouraging biofilm growth on the membrane surface (Al-Juboori & Yusaf 2012).

Biodegradable NOM is considered 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 (Huck, 1990). The BDOC parameter is often used as a measure of DOC biodegradability. Waters with a low concentration of BDOC are biologically stable, with low microbial regrowth and reduced or delayed biofouling of the membrane (Tubić et al., 2013; Al-Juboori and 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).

4.2.2. Chemical Coagulation

An effective DOC reduction via coagulation can directly influence downstream filtration processes and reduce membrane fouling. There have been many studies on the effectiveness of different coagulants for the removal of DOC and reduction of THMs; however, no study has looked carefully at the effects of coagulation on both DOC and BDOC in high DOC water (Sadrnourmohamadi et al. 2013).

4.2.3. Oxidation

The addition of a strong oxidant, such as hydrogen peroxide, ozone, or UV/H_2O_2 irradiation has been reported to protect the RO membranes from biological fouling by inhibiting bacteria's biological activity (Siddiqui et al. 2017).

Oxidation with potassium permanganate ($KMnO_4$). Experimental results have shown that potassium permanganate oxidation has a particularly useful role 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 (Xie et al. 2016). Galvín & Rodríguez (1998) reported that the use of permanganate as pre-treatment in low dosages of about 0.45 to 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 mentioned). To date, there is no literature reporting use and effect of $KMnO_4$ on drinking water sources with DOC higher than 6.8 mg/L (Godo-Pla et al. 2019; Ma et al. 2018). 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_2O_2) coupled with UV (H_2O_2/UV). H_2O_2/UV oxidation may cause partial oxidation of NOM, breaking its large molecular weight constituents into smaller and more biodegradable compounds such as aldehydes and carboxylic acids (Sarathy and Mohseni 2009). Up to 20 mg/L of H_2O_2 with UV fluence of 1500 mJ/cm^2 are typically applied in H_2O_2/UV commercial drinking water applications. The authors could not find any research reporting on the effectiveness of H_2O_2 /UV oxidation to control THMs in DOC water higher than 9.44 mg/L (Seo et al. 2019; Tubić et al. 2013). Sarathy & Mohseni (2009) have reported 15% mineralization of NOM for water with total organic carbon (TOC) equal to 2.18 mg/L during oxidation under these conditions. Toor and Mohseni (2007) reported 93% THMFP reduction (from 150 µg/L to 10 µg/L) by using 23 mg/L H_2O_2 and UV fluence of 2500 mJ/cm^2.

However, the DOC content of the raw water used in the above studies was very low compared to the DOC of raw drinking water sources in the Canadian Prairies.

4.2.4. Biological Filtration in the IBROM Process

Biological removal of DOC is an attractive addition or alternative to chemical removal, especially for systems supplied by waters with much organic carbon since they may sustain biological activity and promote DOC biodegradation. The biological pre-treatment studied in this paper is Integrated Biological and Reverse Osmosis Membrane or IBROM process. This relatively novel process is using two filters connected in series, using Filtralite media (Peterson et al. 2007). Filtralite media consists of lightweight expanded clay aggregates with high porosity and rough grain surfaces (Peterson et al. 2006). IBROM systems have been installed in 18 First Nations communities in 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 as one of the main nutrient sources. IBROM process claims that the removal of BDOC alone would result in less fouling on RO membranes (Peterson et al. 2006). The IBROM system installed in Yellow Quill WTP (Saskatchewan) reduced DOC by 1 mg/L only, resulting in RO membrane influent with high DOC concentrations of 8.9 mg (i.e., more than four times higher than the 2 mg/L concentration recommended for DOC of RO membrane influent). 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 six months or less is typically required to restore membrane performance (Ambrosi and Tessaro 2013).

The claims of IBROM systems removing BDOC and experiencing low membrane fouling have not been scientifically substantiated. There is no literature on the effectiveness of Filtralite filters on BDOC removal, and their reported DOC removal is very low - about 2 mg/L (Mitrouli et al. 2008).

4.2.5. DOC and THMs Formation Potential

THMs formation is affected not only by the concentration of DOC but also by the DOC characteristics. 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 is the main fraction in the formation of THM. On the other hand, Tubić et al. (2013) and Marhaba & Van (2000) report the hydrophilic fraction to have the highest specific THMFP. The 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 establish a relationship between the biodegradability of NOM and THMFP. Many studies have measured BDOC change during conventional treatment processes such as coagulation, primarily to control biofilm growth in the distribution system; however, they have not discussed how BDOC can affect THMFP (Umar et al. 2014).

4.2.6. Objectives

The goal of this research was to conduct some preliminary investigation into the claims of IBROM. The research was conducted using water collected from Herbert WTP (Saskatchewan) utilizing coagulation, oxidation, and IBROM for the treatment of a dugout and groundwater blend. The plant is experiencing serious levels of RO membrane fouling.

The first objective of this study is to evaluate the effectiveness of biological filtration (IBROM) and two other standard chemical membrane pre-treatment processes, coagulation, and oxidation, in terms of DOC and BDOC removal.

The second objective of this study is to investigate a potential correlation between the BDOC concentration and THMFP of the treated waters.

4.3. Materials and Methods

The research was conducted using water collected from Herbert WTP (Saskatchewan). The plant is utilizing coagulation, oxidation, and IBROM for the treatment of high DOC and TDS (total dissolved solids) dugout and groundwater blend.

4.3.1. General Raw Water Quality

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 8*. The oxidation experiments were conducted on the dugout water collected before water entering the treatment plant. This is an ideal oxidant addition location as it provides enough reaction time.

Table 8. Dugout and blended water quality parameters for Herbert WTP collected at the plant in Aug. 2018 (* Guidelines for Canadian Drinking Water Quality (Health Canada 2019b)).

Parameter	Unit	GCDWQ* (Treated water)	Dugout water	Blended water
pH	-	7 – 10.5	8- 8.8	7.9 – 8.5
Alkalinity	mg/L $CaCO_3$	-	234	350.5
THMFP	µg/L	≤ 100	809.8 ± 60	865.9 ± 39
Hardness	mg/L $CaCO_3$	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	5.7 ± 0.3
Iron	mg/L	≤ 0.3	0.105	0.77
Manganese	mg/L	<0.12	0.06	0.01

At the Herbert WTP the dugout water is blended with groundwater as it enters the WTP. Both dugout and blended raw water have high concentrations of DOC, at approximately 22.7 mg/L and 17.5 mg/L, respectively. The hardness and TDS of the blended water are 376 mg/L $CaCO_3$ and 1243 mg/L, very similar to the water qualities in the Canadian Prairies.

4.3.2. Biological Filtration

Evaluation of the effectiveness of the IBROM filtration process for removal of DOC and BDOC was conducted on-site at the Herbert WTP. *Figure 7* demonstrates the unit processes comprising IBROM located at the plant that are two granular filters containing Filtralite HC and NC 0.8–1.6 mm clay media and one granular activated carbon (GAC) filter followed by an RO membrane. Water samples were collected from before and after the IBROM filters to measure DOC and BDOC removal efficiency.

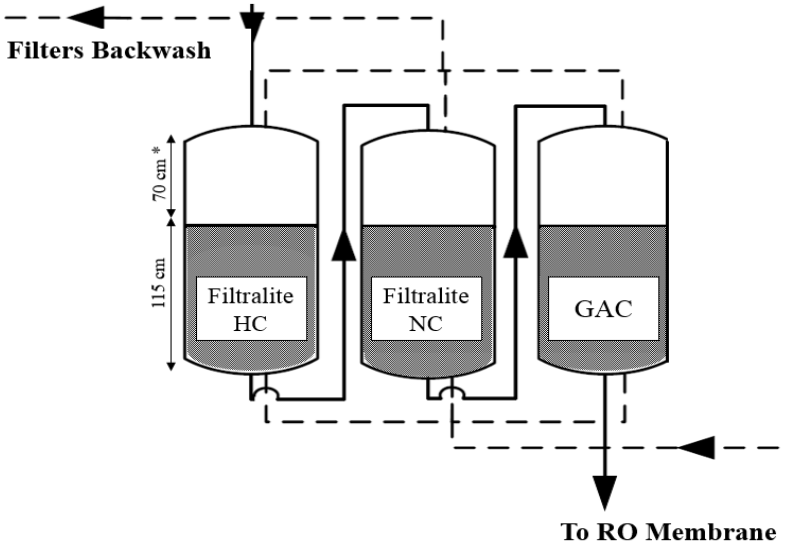


Figure 7. Schematic diagram of the on-site IBROM biofiltration set-up (*empty space for hydrostatic head development).

4.3.3. Bench-scale Coagulation and Oxidation Experiments

Laboratory bench-scale coagulation tests were conducted using the blended water with aluminum sulfate (alum), polyaluminum chloride (PACl), aluminum chlorohydrate (ACH) and ferric chloride. Based on the study by Sadrnourmohamadi et al. (2013) on water with similar DOC, different coagulant doses from 20 mg/L to 120 mg/L were selected. The experiments were carried out at room temperature using the conventional method in a six paddle PB-700TM standard jar testers by Phipps & Bird (Richmond, USA). One litre of water was coagulated for each coagulation dose; the rapid mix was at 100 rpm for 1 minutes followed by slow mixing at 30 rpm for 15 min. The samples were then allowed to settle for 30 minutes.

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 $KMnO_4$ (Ma et al. 2001). Considering the high dugout water DOC (22.7 mg/L), 0.25, 0.5, 1, 1.5 and 2 mg/L of $KMnO_4$ were used in the oxidation experiments. The experiments were carried out with a Six-Beaker Jar Test Apparatus. Permanganate solution was added into 1-litre beakers. Fast mixing was for 30 seconds at 300 rpm followed by slow mixing for 5 minutes at 35 rpm, and then the water was allowed to stand for 15 minutes. The residual Mn concentrations were measured by inductively coupled plasma (ICP) mass spectrometry. To avoid any interference of the oxidant in the BDOC and DOC measurements, before further analysis, the samples were quenched using sodium thiosulfate.

Hydrogen peroxide doses of 20, 40, 60, 80, 100 mg/L and UV fluence of 2000 mJ/cm^2 was applied in the H_2O_2/UV process. UV irradiation was conducted using an annular reactor with a working volume of l litre, using a centrally mounted low-pressure UV lamp (Jelight Company, Inc., Irvine, USA). The samples were quenched using bovine liver catalase (lyophilized powder, ≥10 000 units

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 H_2O_2 within 10 minutes (Sarathy & Mohseni, 2009).

DOC concentration was determined using a SkalarHT Formacs TOC Analyzer (Skalar, GA). DOC is defined as the organic carbon concentration of sample water that has been filtered through a 0.45-µm membrane filter. DOC was determined by measuring total carbon and subtracting the measurement for total inorganic carbon through acidification of all forms of organic carbon.

THMFP measurements were conducted according to *Standard Methods 5710B* (APHA 2012). The chlorine demand was not determined before the THMFP test due to the small sample volumes of the coagulated or oxidized water (1 litre). 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) and using an Agilent 7890A GC System (Agilent Technologies, California, USA) equipped with a CombiPAL CTC Analytics auto-sampler and used 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 water samples were filtered through 0.7 µm glass-fiber filter (GF/F, Whatman) and inoculated with 10 mL of biologically active BOD seeds (Bio-Systems Corporation, Illinois, USA) and incubated at 20 ◦C for 28 days. After the 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 real samples and the blank sample after the incubation period.

4.4. Results and Discussion

4.4.1. DOC, BDOC, and THMFP in Coagulation Experiments

Figure 8 shows the DOC removal by the four coagulants used in this study. For all coagulants, the removal of DOC increased with the increased coagulant dose as expected. PACl 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 pH of 7.2.

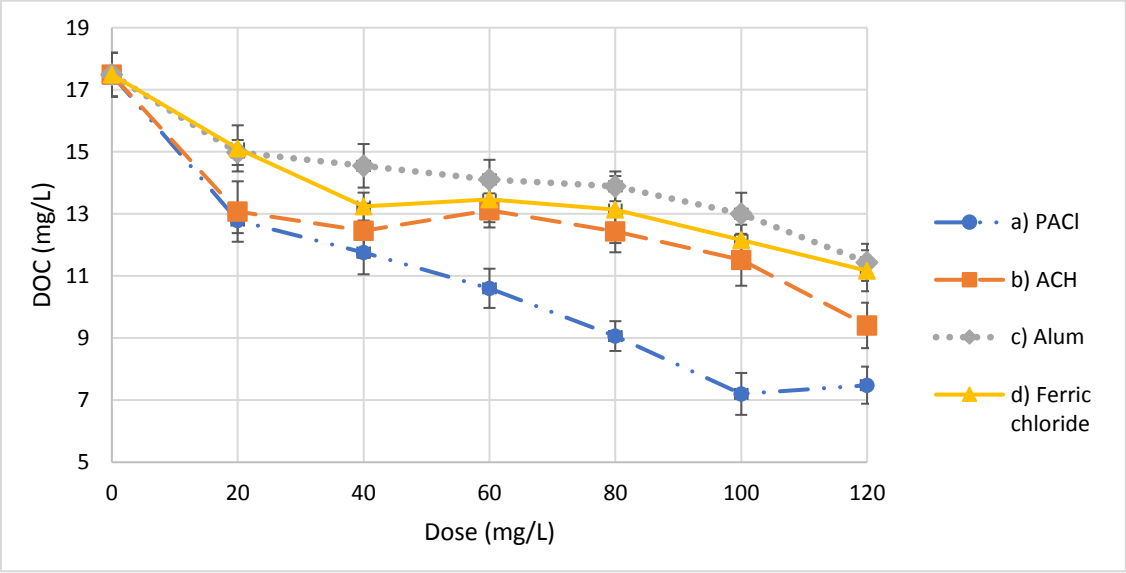


Figure 8. Removal of DOC for a) PACl, b) ACH, c) Alum and d) Ferric chloride at varying coagulant doses.

BDOC in the raw water was 5.75 mg/L (*Table 8*). *Figure 9* shows changes in DOC, BDOC, and THMFP in the coagulated waters. BDOC removal in coagulation ranged from 20-60% for different 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, 2019b). *Figure 9* demonstrates THMFP for all coagulants and dosages used in 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 highest average reduction in THMFP while having lower DOC removal compared to other coagulants.

The reduction of water THMFP in the coagulation is due to the reduction of total DOC. 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). Factors other than total DOC concentration play a role here. *Figure 9* shows that alum and ferric chloride were not as effective in removal of BDOC as PACl while they had highest reduction in THMFP. Our measurements indicated an inverse relationship between biodegradability and THMFP of the raw waters studied.

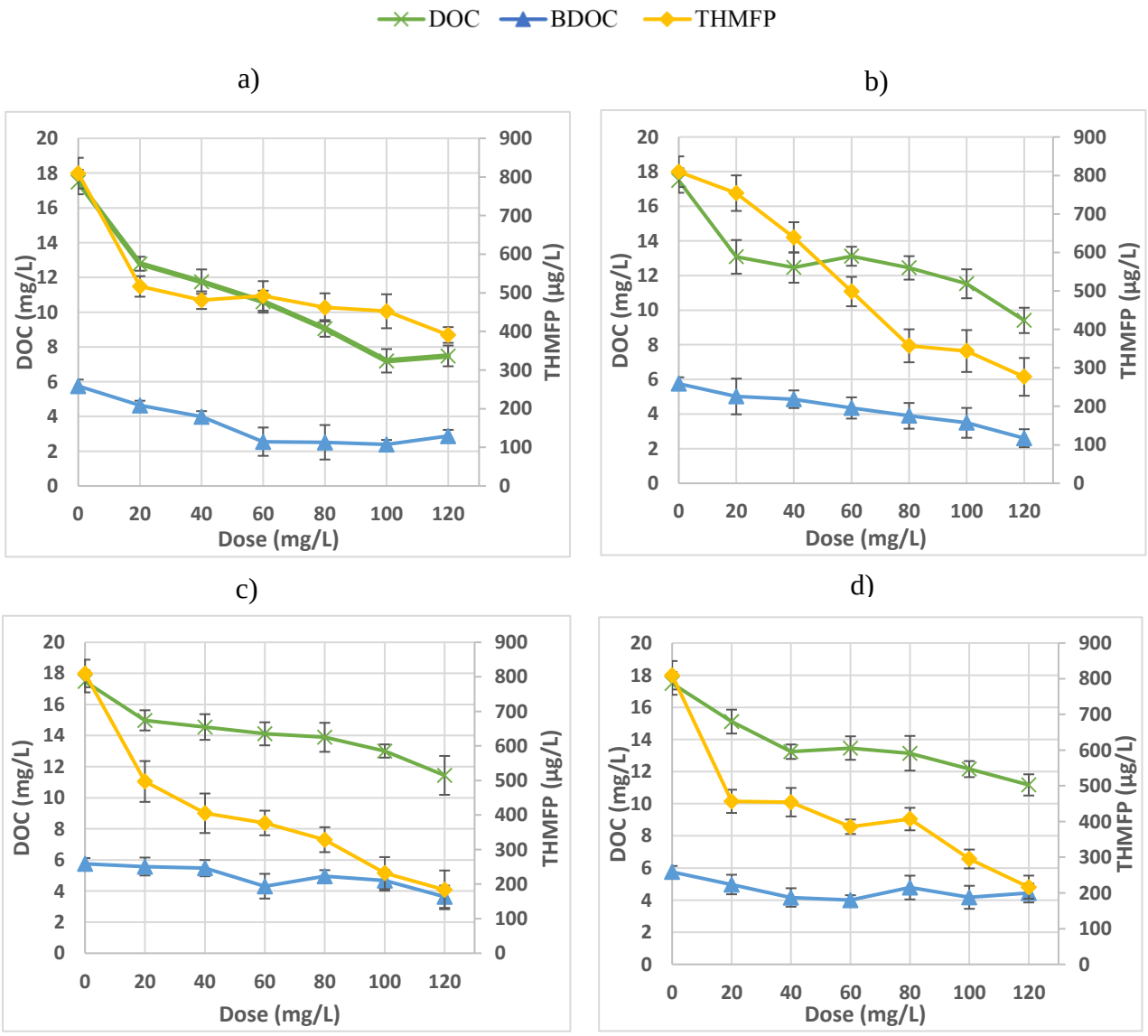
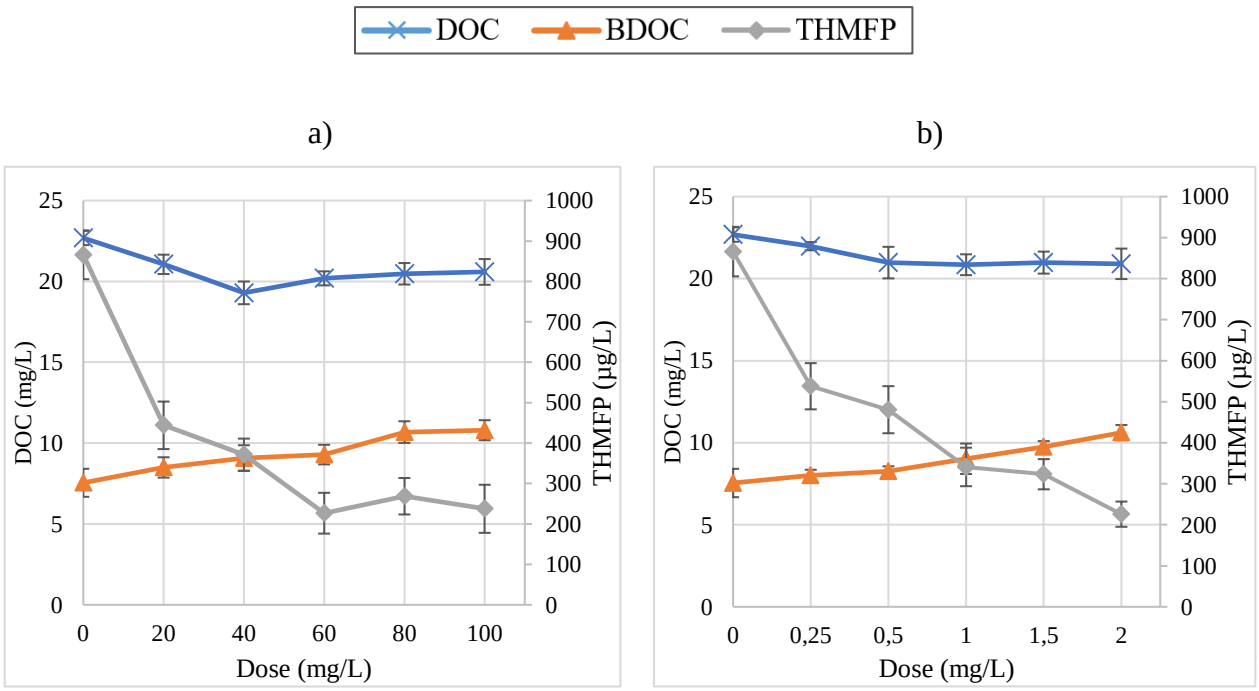


Figure 9. DOC, BDOC and THMFP for a): PACl, b): ACH, c): Alum and d): Ferric chloride at varying coagulant dose.

Overall, PACl showed greatest DOC removal according to lab-scale coagulations. DOC and BDOC in the optimally coagulated water (with 100 mg/L of PACl) were 7.5 mg/L and 2.4 mg/L, respectively. The DOC was still higher than recommended 2 mg/L, and therefore this water is likely to cause severe 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 case of waters with high DOC, coagulation alone is not capable of successfully lowering water DOC for RO membrane or making water biologically stable; however, it can reduce THMFP close to the MAC of 100 µg/L.

4.4.2. Oxidation Experiments with $KMnO_4$ and H_2O_2/UV

Figure 10 is showing DOC change in oxidation for different concentrations of $KMnO_4$ and H_2O_2/UV. None of the oxidants was able to effectively reduce DOC concentration. Oxidation with 0.5 mg/L of $KMnO_4$ had the maximum DOC removal of 8% (reducing DOC from initial 22.7 mg/L to 20.85 mg/L).



40 mg/L of H_2O_2/UV showed maximum removal of 15% (reducing DOC from initial 22.7 mg/L

Figure 10. Change in DOC, BDOC and THMFP in oxidation with a) H_2O_2/UV and b) $KMnO_4$

to 19.3 mg/L). These results demonstrate that oxidation is not able to remove a significant amount of water DOC, which has previously been reported in the literature (Wan et al., 2019; Xie et al., 2016; Liu et al., 2012).

However, oxidation with $KMnO_4$ and H_2O_2/UV significantly reduced the THMFP of the water (*Figure 10*). THMFP reduced from an initial concentration of 865.9 down to 225.8 µg/L (74% reduction) at a dose of 2 mg/L $KMnO_4$. In the case of H_2O_2/UV, THMFP reduced to 237.5 µg/L (72% reduction) with 100 mg/L of H_2O_2.

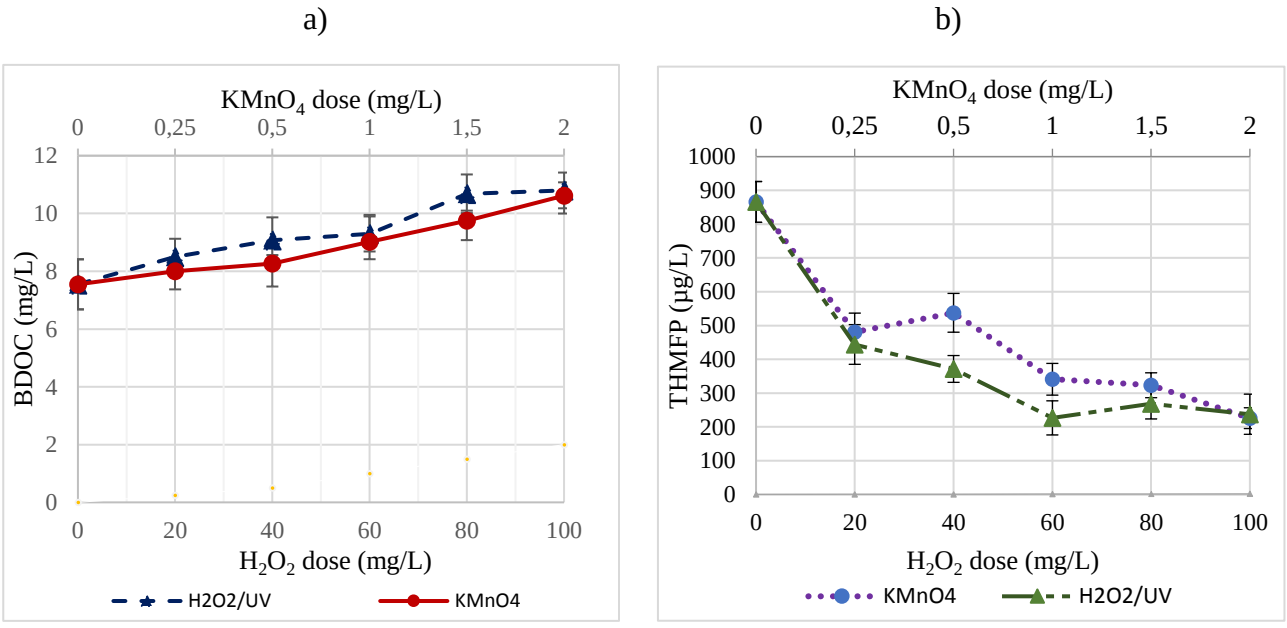


Figure 11. Change of a) BDOC and b) THMFP compared in oxidation with $KMnO_4$ and H_2O_2/UV.

According to *Figure 10*, while the reduction in THMFP of water treated with H_2O_2/UV averaged 64%, the corresponding reduction in DOC was only 10%. The same was observed in $KMnO_4$ with 7% and 56% 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 11*, a). The original BDOC content of the water was 7.54 mg/L. Oxidation with 2 mg/L of $KMnO_4$ resulted in the highest increase of BDOC by 28% and to 10.6 mg/L. 100 mg/L of H_2O_2 with 2500 mJ/cm^2 UV fluence increased BDOC to the maximum of 10.8 mg/L. This confirms the trend observed between BDOC and THMFP in coagulation. Higher BDOC water showed lower THMFP.

It appears that oxidation of NOM whether by $KMnO_4$ or H_2O_2/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, 2015a). Therefore, the concentration of hydrophobic NOM is reduced after oxidation. Speculating that oxidants mainly react with hydrophobic NOM, it can be stated that after pre-oxidation there would be lower concentrations of hydrophobic NOM left in the water, and therefore, when chlorine (a strong oxidant) is added, the level of THMs formed is reduced heavily.

H_2O_2/UV appeared to be more effective in terms of control of THMs than permanganate. Although the DOC change was very similar for both oxidants tested (*Figure 10*), the water oxidized with H_2O_2/UV always contained more BDOC. Also, water oxidized with H_2O_2/UV had lower THMFP compared to water oxidized with $KMnO_4$ (*Figure 11*, b).

An important note to consider is the residual concentration of Mn in the water oxidised with $KMnO_4$. The MAC of Mn in the Canadian Drinking Water Guidelines is 0.12 mg/L with AO < 0.02. According to *Table 9* , Mn concentration for all the $KMnO_4$ doses except 0.25 mg/L, are

higher than this MAC and therefore care should be taken when introducing Mn to the water in order to meet the guidelines on Mn acceptable concentration.

Table 9. Residual Concentration of Mn after oxidation with $KMnO_4$

$KMnO_4$ dose (mg/L)	0.25	0.5	1	1.5	2
Mn (mg/L)	0.045	0.102	0.220	0.302	0.469

4.4.3. BDOC Change Attributed to Biological Filtration

Table 10 is summarizing the DOC and BDOC before and after 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.

Table 10. DOC and BDOC concentration change along the treatment train of the Herbert WTP.

Water Quality	Dugout	Blended	Clarifier	IBROM Filters (Filtralite)
DOC (mg/L)	22.7 ±0.4	17.5 ± 0.7	15.4 ± 0.6	13.68 ± 0.9
BDOC (mg/L)	7.54 ± 0.8	5.75 ± 0.3	5.56 ± 0.7	5.96 ± 0.4

Table 10 indicates that the two Filtralite filters have 11% DOC removal. (DOC decrease from 15.4 mg/L to 13.68 mg/L). There was a minimal increase of BDOC in IBROM effluent at the Herbert WTP (7%). The results indicate that the IBROM process installed at the Herbert WTP is not effective in the removal of BDOC nor DOC.

4.5. Conclusions

Removal of DOC, BDOC, and THMFP from the high DOC and TDS water by IBROM, chemical coagulation, and oxidation were evaluated. A blend of dugout and groundwater collected from Herbert WTP (Saskatchewan) was used. The blended raw water had a DOC of 17.5 mg/L and TDS of 1243 mg/L. The following conclusions can be made from this study:

1. Biological filters constituting the IBROM system operating at Herbert WTP were found to be ineffective in removing water BDOC or DOC. Actually, a small increase in water BDOC was measured in the biological filters' effluent.
2. Laboratory-optimized coagulation was found quite successful in reducing water DOC and BDOC. Maximum DOC and BDOC reductions by coagulation were observed with 100 mg/L of PACl and down to 7.5 mg/L and 2.4 mg/L, respectively.
3. Alum and ferric chloride showed the greatest reduction in THMFP from 809.8 µg/L down to 183.5 µg/L and 216.2 µg/L, respectively, with a total DOC reduction of 34% and 36%. Removal of DOC and formation of THMs varied for different coagulants.
4. Oxidation resulted in a decrease in THMFP and an increase in water BDOC. H_2O_2/UV oxidation reduced the DOC by only 15% while increasing the formation of BDOC up to 30%. Oxidation with $KMnO_4$ and H_2O_2/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.

Overall, the IBROM system studied here was ineffective in removal of BDOC. 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.

Chapter 5: SUMMARY AND CONCLUSION

High concentrations of NOM in Canadian Prairies cause problems such as being higher than MAC for THMs in the treated water and frequent membrane fouling issues that result in membrane replacement and, consequently, high operational costs. With such water sources, pre-treatment is an essential requirement before the membrane filtration process in order to reduce the DOC concentration of water before entering the membrane.

Moreover, while most of the pre-treatment efforts in the WTPs are focused on reducing DOC and THMFP, high biodegradability of water, indicated by BDOC concentrations, can cause bacterial growth in the distribution system. The results of this research in oxidation and coagulation were used to find if BDOC concentration can affect THMFP, independent of DOC.

This thesis has investigated the change of DOC, THMFP, and BDOC after the following methods of pre-treatment for membrane filtration, coagulation bench-scale experiments conducted using alum, polyaluminum chloride (PACl), aluminum chlorohydrate (ACH), and ferric chloride; and oxidation bench-scale experiments conducted using $KMnO_4$ and H_2O_2/UV. Additionally, BDOC change was measured in the biofiltration unit in the IBROM process that is the only pre-treatment unit in the IBROM process. These biological filters contain a novel media named Filtralite. The measurement of BDOC was done on-site of a real-IBROM plant located in Herbert, Saskatchewan, Canada.

The result indicated that no BDOC removal was observed in the biological filters of the IBROM process at the Herbert WTP. In fact, a small increase in BDOC was measured after the two biofilters. This indicates that contrary to the IBROM process claims, this process is not able to render the water biologically stable and may cause membrane fouling by not removing DOC/BDOC from the water before membrane treatment.

Coagulation was effective in reducing DOC and BDOC concentrations, and consequently reducing THMFP of the treated water. The DOC and BDOC of raw water were 17.5 mg/L and 5.7 mg/L and were reduced to a minimum of 7.5 mg/L and 2.4 mg/L, respectively, with 100 mg/L of PACl.

PACl, with the maximum reduction of DOC (57%), however, did not have the maximum reduction in THMFP. Alum and ferric chloride showed the greatest 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 BDOC was higher when the water was treated with alum and ferric chloride, compared to treatment with PACl, suggesting that there is an inverse relationship between BDOC and THMFP.

The same trend was observed with oxidation. Oxidation degraded the large hydrophobic NOM into smaller hydrophilic NOM that is less prone to form THMs and is more biodegradable than the other fractions. It appears that by applying pre-oxidation before chlorine addition, concentration of the hydrophobic fraction of NOM, that is the main fraction reacting by chlorine, is reduced. Since there is less hydrophobic NOM to react with chlorine, the THMFP is reduced consequently. H_2O_2/UV and $KMnO_4$ oxidation reduced the DOC by 15% and 8% and increased BDOC by 30% and 28%, respectively. THMFP was significantly reduced from the initial THMFP of 865.9 µg/L down to 237.5 µg/L with H_2O_2/UV oxidation and down to 225.8 µg/L with $KMnO_4$ oxidation, respectively.

The results of the study show that coagulation can be useful in reducing DOC, BDOC, and THMFP of the water to a considerable extent. In order to reduce potential membrane fouling, further treatment is necessary to reduce DOC down to 2 mg/L. In the case of oxidation, THMFP was reduced substantially, rendering oxidation as the most effective pre-treatment method to control THMs concentrations. However, it resulted in increased BDOC concentration. Therefore, it is imperative to have a unit of biological treatment to remove BDOC from the water before reaching the membrane.

Overall, the result of this study showed that the biological filters in the IBROM process were ineffective in removal of BDOC. Moreover, coagulated and oxidized water samples with higher 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 membrane filtration.

Chapter 6: ENGINEERING SIGNIFICANCE OF RESEARCH

The engineering significance of this study lies in the suggestions that it can provide to the water treatment plants.

Canadian Prairies and First Nations Communities suffer from poor-quality water. It has been reported that in Manitoba, almost 70% of potable water treatment plants that use surface water sources are not in compliance with THMs regulations set by the province. The main objective of this research was to study the effectiveness of removal of THMs precursors by chemical coagulation, oxidation, and biofiltration in the IBROM process. The removal of DOC is the main challenge to the effectiveness of this treatment process. The results of this research can be applied to water treatment plants that are facing frequent membrane fouling issues.

The results of this study showed that oxidation and coagulation can significantly reduce THMFP and DOC levels, respectively. Therefore, the application of these processes before the membrane filtration can effectively reduce the costly membrane replacements.

With regard to the IBROM process, the results of this study suggest that the application of biofiltration alone is not enough for the removal of DOC and BDOC before the membrane filtration. Hence, each water treatment plant should analyze their raw water quality before upgrading to any new system. Though membranes are useful for NOM removal, if proper pre-treatments are not utilized, they can be fouled quickly and out of use in a short time.

Moreover, another significant result of this study is that when the BDOC concentration of water is high, the THMFP is lower. Though this can be an advantage health-wise, a high concentration of BDOC is reported to cause microbial growth on the surface of membranes and distribution system. This study suggests using an oxidation process followed by biological filtration; THMFP can be effectively reduced by oxidation, and BDOC formed during this process can be removed with a biofiltration unit.

Chapter 7: RECOMMENDATIONS AND FUTURE RESEARCH

Based on the laboratory and plant investigation, the following recommendations are made:

- Pre-oxidation should be used in the treatment process to reduce THMs concentrations
- Coagulation can reduce both THMs and DOC concentrations. An oxidation unit followed by coagulation can help maximize the DOC and THMs reduction.
- BDOC showed a tendency to increase after oxidation; therefore, a biofiltration unit is necessary in order to remove BDOC before membrane filtration.

Future research should investigate the biodegradability of each fraction of NOM (HPO/HPI acid, base, and neutral) to find out which part of the NOM is the most biodegradable and which fraction is most prone to form THMs.

Future research can also include an investigation of the application of pre-oxidation and coagulation together. It has been suggested by literature that oxidation can improve NOM removal by coagulation.

Experiments should be done on a full and bench-scale column of Filtralite media. In order to make sure that the filters are biologically active, there should be an introduction of air, and the bacterial growth inside the filters should be maintained.

A future project could study flux decline or morphology change of the membrane surface in a bench-scale treatment chain of oxidation/ coagulation/ RO membrane, coagulation/ oxidation / RO

membrane, or oxidation/ Filtralite biofilters/ RO membrane. This can directly provide insight into the actual effect of these pre-treatment processes on the membrane fouling reduction.

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