EFFICIENT REMOVAL OF NATURAL ORGANIC MATTER FROM DRINKING WATER FOR REDUCING DISINFECTION BY-PRODUCTS

by

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ABSTRACT

Chlorine as a low-cost bactericide has been used for more than a century for the disinfection of drinking water. However, the contact between chlorine-based disinfectants and natural organic matter (NOM) leads to the production of hazardous disinfection by-products (DBPs).

Trihalomethanes (THMs) and haloacetic acids (HAAs) as two groups of regulated DBPs by U.S. EPA and Health Canada have been of concern in the last two decades for the water treatment facilities around the world, specifically small communities of Newfoundland. Enhanced coagulation (EC) and adsorption with activated carbon (AC) are two recommended methods by U.S. EPA for the removal of NOM. Although many studies have tested these methods in full scale and lab scale for the removal of dissolved organic carbon as the main precursor of THMs and HAAs, certain environmental factors in NL (e.g., seasonal variations) and treatment factors (i.e., fast mixing and settling time in EC, and aluminum coating in AC) have not been considered so far. This research aims to (i) examine the effect of five factors of pH, coagulant dosage, coagulant type, fast mixing speed, and settling time simultaneously on the removal of DBPs rather than DOC. (ii) establish prediction models for the removal of DOC and reduction of THMs and HAA5 based on NL water characteristics. (iii) decrease the power consumption of EC. (iv) to reduce the coagulant dosages (v) improve the mesoporosity of activated carbon for NOM removal by chemical activation using nitric acid and physical activation, (vi) enhance the removal of DOC and humic acids by surface charge modification through metal impregnation, (vii) study the efficient removal of NOM by combination of EC and AC (viii) study the variations of NOM characteristics in four communities of NL over two years. (ix) to figure out the most crucial factors affecting the production of HAA5 and THM4.

The results of this research on EC confirmed that optimization of EC parameters based on THMs and HAAs reduction, reduced the dosage of coagulant from 6.51-7.85 mg/mg DOC for DOC to 3.83-5.95 mg/mg DOC. Moreover, the energy consumption in the fast-mixing stage was reduced by 59.8%. The fly ash of pulp and paper company in corner brook was used to produce AC. Nitric acid at 10% concentration increased the Brunauer, Emmett and Teller (BET) surface area and pore width of the developed AC in comparison with chemical treatment with nitric acid at 5% concentration. Moreover, metal impregnation with 0.75% Fe and 1.00% Al enhanced the THM4 and HAA5 reduction by 33-44%. The investigation on the NOM characterization in four sources of drinking water in NL over two years revealed that very hydrophobic acid NOM and neutral hydrophilic are the main contributors to the production of HAA5 while very hydrophobic acids (VHAs) are the main precursors of THM4. The highest level of DOC was observed in summer and the highest contributor to the NOM content was VHAs in all seasons.

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List of Abbreviations and Symbols

α	Coefficient of Axial Points
β_0	Constant Coefficient
β_i	Linear Coefficient of Regression
AC	Activated Carbon
A	Isotherm Constant in Temkin Model
Ax	Nitric Acid (x% wt: wt)
Al	Aluminum Ion
Al-AC	Aluminum-Coated Activated Carbon
ANOVA	Analysis of Variances
AOC	Assimilable Organic Carbon
AOM	Advanced Oxidation Method
b	Temkin Sorption Heat Constant
BDCM	Bromodichloromethane
BET	Brunauer Emmett and Teller
BOM	Biodegradable Organic Matter
C	Carbon
$C_{(in)}$	Concentration of Pollutant in the Inlet of Column
$C_{(out)}$	Concentration of Pollutant in the Outlet of Column
C_e	Concentration of Adsorbate at Equilibrium
C_f	Final Concentration
C_i	Initial Concentration
CBPP	Croner Brook Pulp and Paper
CBPPL	Croner Brook Pulp and Paper Limited

CHI	Charged Hydrophilic
COD	Chemical Oxygen Demand
CREAIT	Core Research Equipment and Instrument Training Network
DBAA	Dibromoacetic Acids
DBCM	Dibromochloromethane
DBPs	Disinfection By-Products
DCAA	Dichloroacetic Acids
df	Degree of Freedom
DOC	Dissolved Organic Carbon
DPD	N-diethyl-p-phenylenediamine
E	Removal Efficiency
EC	Enhanced Coagulation
FA	Fulvic Acids
Fe	Ferric Ion
Fe-AC	Iron-Coated Activated Carbon
FTIR	Fourier Transform Infra-Red
H	Hydrogen
h	hour
HA	Humic Acids
HAA5	Five Regulated Haloacetic Acids
HAAs	Haloacetic Acids
HC	Health Canada
HM	Humic Material
HPSEC	High Performance Size Exclusion Chromatography

IARC	International Agency for Research on Cancer
IN	Iodine Number
IRIS	The Integrated Risk Information System
k	Number of Factors
K_f	Freundlich Constant
K_L	Langmuir Equilibrium Constant
k	Column Capacity Factor
MBAA	Monobromoacetic Acids
MBV	Methylene Blue Value
MCAA	Monochloroacetic Acids
MIEX	Magnetic Ion Exchange
MNP	Magnetic Nano Particle
MPAC	Impregnation of Commercial AC with Maghemite
MS	Mass Spectrometry
MTBE	Methyl Tert-Butyl Ether
MW	Molecular Weight
N	Nitrogen
N/A	Not Available
NHI	Neutral Hydrophilic
NL	Newfoundland and Labrador
NMR	Nuclear Magnetic Resonance
NOM	Natural Organic Matter
NRPOP	Northern Region Persistent Organic Pollution Control
NSERC	Natural Sciences and Engineering Research Council of Canada

NTP	U.S. National Toxicology Program
O	Oxygen
OFAT	One-Factor-at-a-Time
PFO	*Pseudo*-First Order
ppb	Part Per Billion
PSO	*Pseudo*-Second Order
PWS	Public Water Supply
qe	Equilibrium Adsorption Capacity
qm	Maximum Adsorption Capacity
qt	Adsorption at Time t
R^2	Coefficient of Determination
$R^2_{adjusted}$	Adjusted Coefficient of Determination
$R^2_{predicted}$	Predicted Coefficient of Determination
RDC	Research and Development Corporation
RSM	Response Surface Methodology
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
SHA	Slightly Hydrophobic Acids
SM	Supplementary Material
SUVA	Specific Ultraviolet Absorbance
TBM	Bromoform
TCAA	Trichloroacetic Acids
TCM	Chloroform
THM4	Four Regulated Trihalomethanes

THMs	Trihalomethanes
TOC	Total Organic Carbon
UV	Ultra-Violet Absorbance
V	Volume
$V_{(void)}$	Void Volume of Packed Resin
VE	Volume of sample treated by resin
VHA	Very Hydrophobic Acids
wt	Weight
WTP	Water Treatment Plant
X	The Effective Factor for the Response
Y	Predicted Value for the Response

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CHAPTER ONE

INTRODUCTION

1.1. Research Background

More than 90% of water treatment plants in Newfoundland use chlorination as a method of disinfection. It is reported that 441 water treatment plants out of 489 are equipped with chlorination systems including sodium hypochlorite, gas chlorination and calcium hypochlorite with 69%, 30%, and 1% shares, respectively (Department of Municipal Affairs and Environment, 2017). The reaction between chlorine-based disinfectants and natural organic matter (NOM) leads to the formation of disinfection byproducts (DBPs) (Liao *et al.,* 2018). Trihalomethanes (THMs) and haloacetic acids (HAAs) are the largest groups of DBPs by weight in drinking water (IARC, 2020), while many emerging DBPs are being reported on a regular basis. Due to the possible adverse health effects by DBPs, Health Canada has recommended the maximum acceptable concentration of 80 ppb (parts per billion) for five species of HAAs (HAA5) (i.e., monochloroacetic acids (MCAA), dichloroacetic acids (DCAA), trichloroacetic acids (TCAA), monobromoacetic acids (MBAA), and dibromoacetic acids (DBAA)) (Health Canada, 2020) and 100 ppb for four compounds of THMs (THM4) (i.e., chloroform [TCM], bromoform [TBM], bromodichloromethane [BDCM], dibromochloromethane [DBCM]) (Health Canada, 2020).

Chronic exposure to THMs and HAAs in drinking water through various pathways: ingestion, inhalation, and dermal contact increase the risk of adverse health effects. The International Agency for Research on Cancer (IARC) categorizes BDCM, DBCM, and bromoform in group 2B as hazardous compounds with possible increase of the risk of cancer (IARC, 1999). In addition, US National Toxicology Program (NTP) has identified six haloacetic acids as "reasonably anticipated to be a human carcinogen" including BCAA, BDCAA, CDBAA. DBAA, DCAA and TCAA (NTP, 2021).

Seventy-nine percent of the residents in Newfoundland and Labrador (NL) are serviced by the public water distribution system, where 15 % of the consumers were in contact with high levels of THM4 and HAA5 in their drinking water (Rahman *et al.,* 2020). Higher levels of THM4 and HAA5 were mostly reported by small communities with a population less than 500 (Chowdhury, 2018). The number of very small water distribution systems in Newfoundland is 386, which was 75.9% of the total 508 public water systems (MAE, 2016). The highest seasonal average of THMs and HAAs of public water distribution systems in four towns of New-Wes-Valley, Pouch Cove, Sunnyside, and Torbay in the last five years are presented in Table 1. 1.

Table 1. 1. Maximum seasonal average of trihalomethanes and haloacetic acids in the water distribution systems of selected communities in Newfoundland.

Location	Trihalomethanes [Maximum Seasonal Average (μgL^{-1})]					Haloacetic Acids [Maximum Seasonal Average (μgL^{-1})]				
	2016	2017	2018	2019	2020	2016	2017	2018	2019	2020
New-Wes-Valley	191.8	313.3	302.5	224.5	474.7	707.0	479.1	530.5	533.5	609.2
Pouch Cove	211.8	183.2	200.0	166.6	13.7	347.7	215.0	206.5	247.1	6.50
Sunnyside	105.0	48.7	40.7	47.8	350.5	200.6	50.6	45.9	42.3	300.8
Torbay	118.7	115.0	117.5	238.8	248.0	95.5	90.2	76.7	109.9	133.9

Adapted from: (Water Resources Management Division, 2021)

Moreover, rural areas and small communities, which are affected by a higher level of water contamination hazards, have had constraints of budget provision for applying new water treatment systems and skilled technicians (Minnes and Vodden, 2017). The U.S. EPA requires water treatment plants (WTP) to adjust the operating conditions to achieve a 15-50% of TOC reduction as this is the main precursor of DBPs formation (U.S.EPA, 1999).

Experimental studies and industrial applications of some water treatment methods such as enhanced coagulation (EC) (Sillanpää, *et al.,* 2018; Tafvizi and Husain, 2021) and activated carbon (Jiang *et al.,* 2017; Tafvizi *et al.,* 2021) have shown representative efficiencies in the reduction of DBPs. Moreover, these methods are recommended as the best available technologies by the U.S. EPA for the reduction of DBPs (U.S.EPA, 2020). The methods in use for water treatment in the province are many including conventional coagulation, flocculation, sedimentation, adsorption by activated carbon, membrane filtration and pH adjustment (Department of Environment and Conservation, 2011).

The levels of DBPs in some water distribution systems after enhanced coagulation have been much higher than the maximum acceptable concentration by Health Canada (Department of Environment and Conservation, 2011). High levels of dissolved organic carbon (DOC) (i.e., more than 5 mg/L) in the surface water of NL has been a challenge to WTP. The NOM content of 21.2 mg/L in tap water in some areas of NL was reported in 2019-2020 (Water Resources Management Division, 2020).

1.2. Statement of Problems

(1) Limited investigation on the seasonal changes of NOM in NL surface water resources

The unique properties of NOM in various water sources have been a challenge to WTP (Fabris *et al.,* 2008). NOM is derived from natural processes including the anthropogenic effects (Tubić *et al.,* 2013) and internal decomposition of organisms such as microorganism residues, animals, and plants (Schreiber *et al.,* 2005). Depending on the origin of NOM and different characteristics of the water basins, it contains various functional groups (Cheng *et al.,* 2005; Schreiber *et al.,* 2005; Zularisam *et al.,* 2006). Also, the quality of NOM changes seasonally due to oxidation-reduction processes as well as biological reactions in the surface water (Diem *et al.,* 2013; Sharp *et al.,* 2006). Studies to date have suggested the possible correlations among various types of NOM, their reactivity and DBPs formation (Chow *et al.,* 2008; Hua *et al.,* 2015; Hua and Reckhow, 2007). However, there is a lack of investigation on the seasonal changes of NOM in the surface water resources of Newfoundland, which affect the level of THMs and HAAs.

(2) Insufficient information on the optimization of enhanced coagulation for DBPs reduction

The versatility in the properties of NOM affects the water treatment processes. NOM compounds minimize the impact of disinfectants and result in a higher level of DBPs (Chow *et al.,* 2004; Liao *et al.,* 2018). The traditional water treatment precesses have not shown sufficient efficacy in the removal of NOM (Xia and Ni, 2015b) and the problem has been worsened by the seasonal alterations of NOM fractions in concentration and structure. Despite employing coagulation processes, the level of DBPs in some communities is higher than the maximum allowable level, which shows the necessity of an adjustment for the water treatment systems. Current water treatment systems should be improved in order to decrease the level of hazardous DBPs.

EC is one of the efficient methods for removing NOM, because it is an easy and low-cost process (Aryal *et al.,* 2011; Racar *et al.,* 2017; Song *et al.,* 2015). The WTP is required to alter their operational conditions by employing jar tests (EPA, 1999). Conventional jar tests are designed as one-factor-at-a-time (OFAT) experiments (Tshukudu et al., 2013). Despite the easiness of this strategy, a large number of experiments, and time consumption, when the prompt adjustment of operational conditions is needed, are the major drawbacks of this method. The response surface methodology (RSM) is a faster and more feasible method for the optimization of EC. Studies to date have been considered the concurrent effects of some factors on EC, such as coagulant dosage and pH (Racar *et al.,* 2017; Tshukudu *et al.,* 2013; Zainal-Abideen *et al.,* 2012), and the humic acid content and coagulant dosage (Watson *et al.,* 2016). However, a comprehensive study for investigating the individual and interaction effects of different factors such as fast mixing energy, and settling time on the coagulation for removing NOM and decreasing HAAs and THMs is necessary.

(3) Limited studies on the NOM removal by low-cost tailored activated carbon

Activated carbon is one of the most popular adsorbents for removing organic matter from water and is often used as the final step in a combined treatment system (Bhatnagar and Sillanpää, 2017; Cheng *et al.,* 2005; Lompe *et al.,* 2017; Shadbahr and Husain, 2019). A wide range of commercial activated carbons have been used for investigating the removal of NOM from water, but a limited number of studies on the tailoring of activated carbon from raw material for NOM removal are available. Previous studies on the development of activated carbon generated from fly ash of Croner Brook Pulp and Paper Company (CBPP) proved its ability in reducing the concentrations of NOM (Zhang *et al.,* 2017) by developing a microporous AC using physical activation through using water steam and carbon dioxide (Shadbahr and Husain, 2019). The produced AC can adsorb low molecular weight NOM. However, the humic acids with high molecular weight NOM are the significant contributors to THMs and HAAs, which can be removed efficiently by a mesopore structure *(Golea et al.,* 2017, 2020). Besides, the absorptivity of AC is highly dependent on the surface charge and surface functional groups (Tanthapanichakoon *et al.,* 2005), which has not been considered to date. NOM removal is dependent on the structure of the exterior layer of activated carbon (Amaral *et al.,* 2016). Also, the impregnation of iron to the commercial activated carbon showed satisfactory efficiency in NOM removal (Cheng *et al.,* 2005; Dastgheib *et al.,* 2004) while no study has shown the impregnation of aluminum on AC. Moreover, no studies so far have investigasted surface modification through metal impregnation of developed AC from the waste material of CBPP for NOM removal.

1.3. Objectives of the Study

The goal of this study is to improve the removal of natural organic matter from drinking water sources with cost-efficient methods. To acquire scientific data and to fill the technical gaps presented in section 1.2, the study was conducted an in-depth investigation of the characteristics of NOM in surface water of Newfoundland, and enhanced the efficacy of available technologies (i.e., enhanced coagulation and adsorption by activated carbon) in small communities for the removal of NOM. This research will be useful in managing the problem of high levels of THMs and HAAs in drinking water in NL. The major objectives of the thesis research are:

(1) To investigating the seasonal variation of NOM in water sources of drinking water in NL;

(2) To enhance the optimization conditions of the enhanced coagulation by decreasing chemical and power consumption based on DBPs removal;

(3) To improve the removal of NOM by developing low-cost activated carbon with enhanced adsorption capacity and modified surface charge by the metal coat of Al and Fe; and

(4) To improve the performance of enhanced coagulation and adsorption (i.e., solely and in combination) on the removal of NOM.

1.4. Research Contributions

The present study contributed to enhancing the removal of NOM and reduction of DBPs in drinking water systems, specifically in small water treatment systems in Newfoundland, Canada. In order to achieve the goal, water samples from a number of plants were analyzed for NOM characterization. The main fraction of NOM contributing to high levels of DOC was found to be VHA and NHI. VHA was the main precursors of THM4 while both VHA and NHI played a significant role in the formation of HAA5 in drinking water. The NOM characteristics were found to be seasonally variable. The EC was applied to the synthetic and real water matrices, which were optimized for the best performances. The optimized dosages of EC resulted in a significant reduction of coagulant dosages and energy supplies in the fast mixing. Activated carbon was developed using the industrial discarded materials, which were functionalized, and impregnated with aluminum and iron to enhance its performance for NOM removal. The activated carbon modified with aluminum/iron impregnation enhanced the removal of NOM, and decreased the levels of THM4 and HAA5 significantly in comparison to the non-modified AC. Moreover, the combination of two methods of optimized EC and modified AC improved the removal of both VHAs and NHIs, and can be beneficial for controlling high levels of DBPs and DOC during the water treatment processes.

1.5. Organization of Thesis

Chapter 2 presents a comprehensive literature review of NOM characteristics, seasonal variation of NOM, methods of removal of NOM, studies to date on the removal of NOM by enhanced coagulation and activated carbon. Chapter 3 presents a comprehensive study on the optimization of enhanced coagulation for the removal of DOC and decreasing THMs, and HAAs by employing the RSM for jar tests (i.e., task 2). Optimization and modeling were performed using two sets of experiments on two surface water samples and the results were validated using four natural water and two synthetic water samples. Analysis of variance (ANOVA) was used for recognizing the most crucial factors on the levels of DBPs during coagulation. Chapter 4 details objective 3 by developing a tailored activated carbon with improved pore structure and enhanced surface for NOM removal using low-cost material and applying metal coating (aluminum and iron ions). The adsorption capacity was optimized using a central composite design. The performance of AC was evaluated on synthetic and natural surface waters. Chapter 5 investigates the alterations of NOM (objective 1) over a 24-months sampling period in four surface water in Newfoundland. Also, the effectiveness of optimized conditions of enhanced coagulation and non-modified and metal-coated activated carbon on the removal of various NOM fractions (objective 4) are presented in this chapter.

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CHAPTER TWO

REMOVAL OF DISINFECTION BY-PRODUCTS IN SMALL WATER TREATMENT SYSTEMS (REVIEW ARTICLE)

This chapter has been converted to a journal manuscript, ready for submission. The present author is the first author of the paper, along with the co-authors, Dr. Tahir Husain, and Dr. Shakhawat Chowdhury. The present author designed and prepared the first draft of the manuscript and subsequently revised the manuscript based on the co-author's feedback and the peer-review process. Dr. Tahir Husain and Dr. Shakhawat Chowdhury reviewed the paper and assisted in revising the subsequent revisions.

2.1. Introduction

Natural Organic matters (NOM) refers to the mixture of naturally occurring organic compounds with different phenolic, hydroxylic, carboxylic and ketone functional groups (Cheng *et al.,* 2005; Leenheer and Croue, 2003). NOM influences environmental processes such as carbon cycling, fate and transport of water toxins (Maizel and Remucal, 2017). NOM compounds and their characteristics were reported to vary by originality, location, agricultural activities, temperature, seasonal changes, and chemical and biological reactions in the water basins (Fabrisa *et al.,*, 2008; Nkambule *et al.,*, 2012; Rigobelloa *et al.,* 2011). The studies in North America, Europe, and North Africa show a substantial increase in the NOM contents in surface waters during the last two decades (Evans *et al.,* 2005; Molot and Dillon, 2008; Rodríguez-Murillo *et al.,* 2015; Worrall and Burt, 2004) due possibly to global warming, acute rainfalls, and soil erosion (Nkambule *et al.,* 2012; O'Driscoll *et al.,* 2018). As a result, the accumulation of recalcitrant organic matter in the water not only has influenced the activities of the organisms (Imai *et al.,* 2002) but also brought challenges in drinking water management in terms of organoleptic characteristics of water such as odor, taste and color (Nkambule *et al.,* 2012; Tubić *et al.,* 2013). Beyond that, NOM decreases the lifespan of activated carbon by blocking the pores (Hong *et al.,* 2009), increases membrane fouling, and reduces the efficiency of coagulation (Song *et al.,* 2015). NOM elevates the chlorine demand for preventing bacterial growth in the pipeline, which eventually leads to the formation of a higher level of disinfection by-products (DBPs) (Chow *et al.,* 2004). Trihalomethanes (THMs) and Haloacetic acids (HAAs) are the largest groups of DBPs by weight in drinking water (IARC, 2020; Krasner *et al.,* 2016) that originate from natural organic matter and chlorination. To date, epidemiological studies on HAAs and THMs have found a correlation between these two groups of DBPs and increased risk of colorectal, and liver cancers (U.S. EPA-IRIS, 1999), as listed in Table 2.1, and birth defects (Evans *et al.,* 2020). A recent study in areas with excessive levels of total THMs and five regulated HAAs from 2008 to 2017 in Newfoundland showed an increased number of cancer cases (risk ratio = 1.8) in areas with elevated levels of DBPs (Rahman *et al.,* 2020).

To date, more than 600 DBPs have been recognized, from which four species of THMs (THM4), five species of HAAs (HAA5), bromate, and chlorite are regulated (Health Canada, 2020; U.S.EPA, 2019). The THM4 includes chloroform, bromoform, bromodichloromethane (BDCM), and chlorodibromomethane (CDBM). The HAA5 includes monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA) and monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA). Table 2.1 presents the carcinogenicity classification and possible adverse health effects of the regulated HAAs and THMs.

Table 2. 1. Carcinogenicity of Regulated trihalomethanes and haloacetic acids

Compound	Carcinogenicity	Adverse Health Effects	Ref
Chloroform	B2 (Probable human carcinogen)	kidney and liver tumors in animals	(U.S.EPA-IRIS, 1999)
Bromoform	B2 (Probable human carcinogen)	liver and kidney, central nervous system	(U.S.EPA-IRIS, 1993)
BDCM	B2 (Probable human carcinogen)	liver, kidney, and large intestine	(U.S.EPA-IRIS, 1987a)
CDBM	C (Possible human carcinogen)		(U.S.EPA-IRIS, 1987b)
MCAA	N/A		
DCAA	“reasonably anticipated to be a human carcinogen”		(NTP, 2021)
TCAA	reasonably anticipated to be a human carcinogen	liver	(NTP, 2021)
MBAA	N/A		
DBAA	“reasonably anticipated to be a human carcinogen”		(NTP, 2021)

The conventional water treatment systems have shown limited capacities in the removal of NOM (Xia and Ni, 2015b). Moreover, the problem has been worsened by alterations of NOM fractions in concentration and structure over the years. Therefore, it demands the water treatment plants be improved in terms of the operational conditions and treatment process (Baghoth *et al.,* 2011; Eikebrokk *et al.,* 2004; Kim and Yu, 2005; Liu *et al.,* 2016). This study aims to summarize the characteristics of NOM and DBPs, identify the low-cost treatment systems, and evaluate the improvement methods for small communities.

2.2. NOM Characteristics

Natural organic matter in water bodies (e.g., creeks, rivers, and lakes) might have been originated from three major groups of pedogenic (i.e., alloctonous), aquogenic (i.e., authocthonous) and anthropogenic activities (i.e., human activties). Pedogenic organic carbon is generated from the peripheral environment including the decay of dead plants by fungi and bacterial activities, and leach to the surface water by precipitation through porous media. Thus, the characteristics of fulvic acids in soil are observed in pedogenic organic matter. The organic matter that is produced in water bodies (e.g., lakes) and upstream water sources (e.g., rivers) by plankton decay and decomposition of freshwater habitats and their fecal matter belong to aquagenic organic matter. Organic matter that are generated as a result of human activities can be observed in substantial quantities in the surface and subterranean water bodies (Filella, 2009; Lozovik *et al.,* 2017).

The various origins of NOM cause structural and composition variation in NOM compounds (Maizel and Remucal, 2017; Rodríguez *et al.,* 2014). Pedogenic organic matter contains humic compounds (Michael-Kordatou *et al.,* 2015), which were generated by himification processes of dead plants. The aquogenic NOM contains algogenic organic matter depending on the stage of algal growth and peripheral conditions. It consists of biodegradable DOC, carbohydrates, amino acids and polysacharides and other compounds (Filella, 2009; Her *et al.,* 2004; Leenheer and Croue, 2003). NOM produced by anthropogenic activities and the wastewater pollutions can be formed by microbiological reactions from agricultural activities, residential and industrial wastewater. DOC derived from effluents contains soluble microbial products and personal care products mainly. Wastewater NOM produces carbonyl products e.g. formaldehyde and acetaldehydes containing potential health risks as emerging DBPs (Papageorgiou *et al.,* 2017).

The precise determination of molecular sizes of NOM compounds is very difficult due to the processes of aggregation and conformation of HM and spatial changes in the molecular structures of NOM. The molecular weight of NOM affects its reactivity and the formation of DBPs (Maizel and Remucal, 2017; Marais *et al.,* 2019). In most of the water samples, Fulvic acids (FA) are the dominant part (i.e., about 90% of HM). The results of various methods such as gel permeation, high-performance size exclusion chromatography and ultrafiltration membrane for the investigation of NOM in molecular scale revealed that the molecular weight (MW) of FA is in the range of 200-5000 Da with an average of 1kDa, while HA has a higher molecular weight (up to 100,000 Da) (Duan and Gregory, 2003; Maizel and Remucal, 2017; Rigobello *et al.,* 2011). A comparison of the structure and characteristics of humic acids, fulvic acids and humin is presented in Table 2. 2 and Figure 2. 1. Fulvic acids contain a higher number of carboxylic groups, while humic acids contain phenolic functional groups.

Table 2. 3 indicates the fractions of the most important functional groups in both fulvic acids and humic acids. Molecular weight and conjugated double bonds are correlated to color in NOM (more visibility at 400nm). An increase in the visibility and absorbance at the wavelength of 400nm is related to the length of conjugated bonds and high MW (Eikebrokk *et al.,* 2004). Studies showed that macromolecular structures of HAs consist of small structural units with the same properties that are connected by various bonds (Leenheer and Croue, 2003).

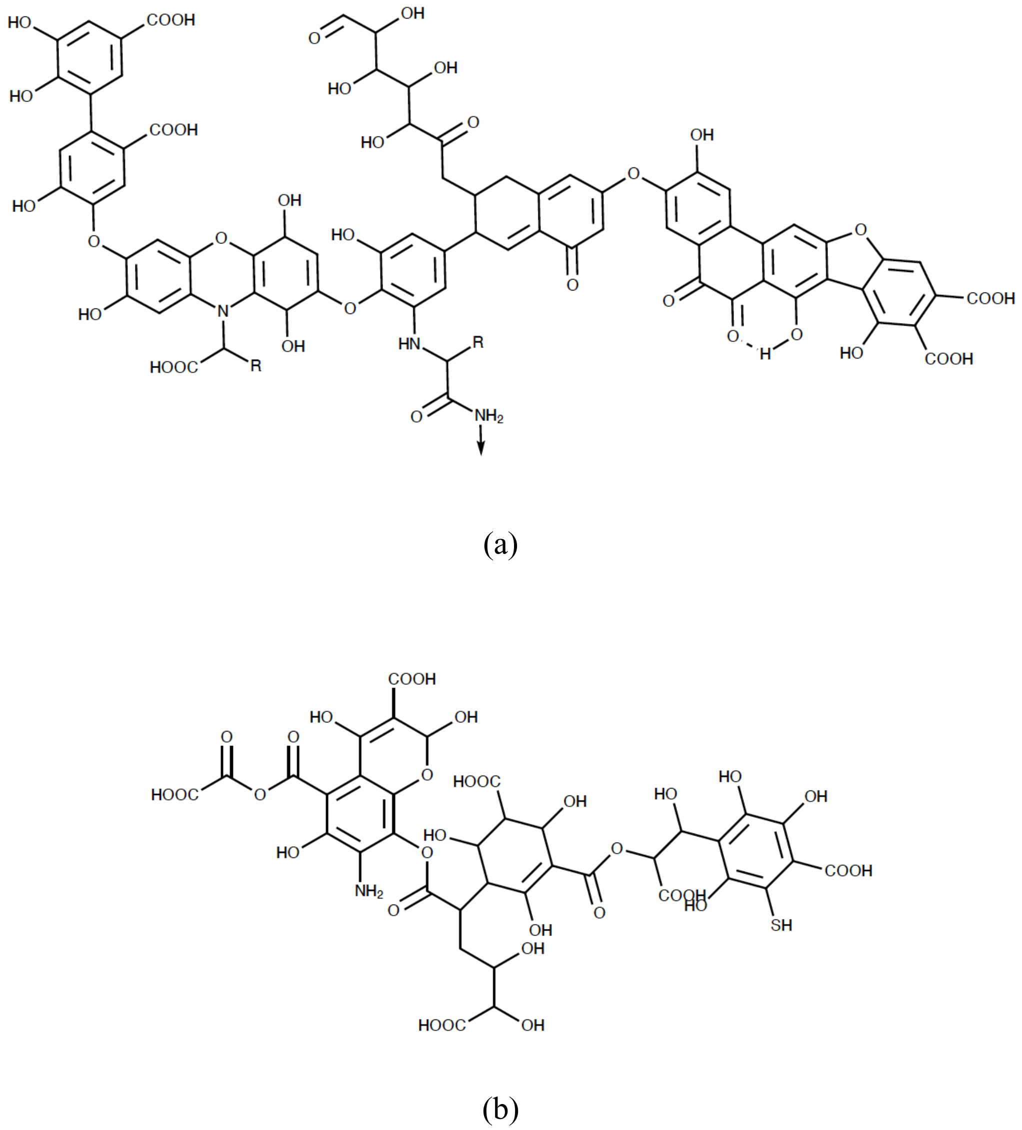


Figure 2. 1. Proposed models for humic acids (a) and fulvic acids (b) with their most significant functional groups

Redrawn by Chemdoodle® (v10.4) (Alvarez-Puebla *et al.,* 2006; Duan and Gregory, 2003; Ouni *et al.,* 2014)

Table 2. 2 Elemental distribution and physical characteristics of humic substances

Elements	Fulvic acids	Humic acids	Humin
Carbon (%)	45	55	55
Oxygen (%)	44-50	32.5	34
Hydrogen (%)	5	5	5.5
Nitrogen (%)	<1-3	3	4.6
Sulphur (%)	1	1.5	--
MW*	200-5000	10,000 - 100,000	100,000-10,000,000
Color	Yellow	Brown	Black

MW: Molecular Weight (Da). Adapted from (Baghoth *et al.,* 2012; Maizel and Remucal 2017; Ouni *et al.,* 2014; Pettit, 2011; Snoeyink and Jenkins 1980)

Table 2. 3. The functional groups in fulvic acids and humic acids (as a percentage of oxygen)

Functional groups	Fulvic acids	Humic acids
Carboxyl	58-65	14-45
Alcohol	11-16	13-15
Carbonyl	4-11	4-23
Phenol	9-19	10-38
Methoxyl	1-2	1-5

Adapted from (Snoeyink, and Jenkins, 1980; Chamoli, 2013)

2.3. NOM Characterization

NOM characterization is necessary for evaluating the efficiency of NOM removal in the water treatment processes and consequently to design and optimize the operation of treatment methods (Matilainen *et al.,* 2011). In water treatment plants, chemical oxygen demand (COD), DOC and UV254 are the general indicators for NOM content. However, these parameters indicate the overall contamination by organic matter and do not depict the characteristics of NOM (Tang *et al.,* 2015). These parameters are popular for the easy procedures of testing and availability in most water analysis laboratories. Therefore, these methods are still at the center of attention for researchers to define a relationship between those parameters and the chemical structure of NOM (Beauchamp *et al.,* 2019a; Beauchamp 2019b; Hua *et al.,* 2015; Marais *et al.,* 2019). Aromatic compounds and polarity of organic matter influence the treatability and the efficiency of NOM removal techniques (Nkambule *et al.,* 2012). Advanced analysis methods for NOM characterization including resin chromatography, high-performance size exclusion chromatography (HPSEC), pyrolysis gas chromatography, mass spectrometry, ultrafiltration, solvent extraction, electrophoresis and nuclear magnetic resonance spectroscopy, and infrared Fourier transforms have been developed. Table 2. 4 presents various methods of characterization of NOM and their applications. Conventional techniques for measuring NOM content are used in combination with descriptive methods for further comprehension of the properties of NOM, such as molecular weight, molecular size hydrophobicity and functional groups (Yan *et al.,* 2012; Zhang *et al.,* 2015). However, most of the advanced instrumental analyzers need highly skilled operators and sophisticated analyzing equipment.

Table 2. 4. NOM characterization techniques

Method	Application	References
DOC/TOC	the most famous method for evaluation of NOM content	(Filella, 2009; Leenheer and Croue, 2003; Matilainen *et al.,* 2011)
UV/SUVA	UV absorbance at 250-280 shows hydrophobic NOM content and DBPs formation potential. SUVA=UV/DOC (mg/L) SUV<2 shows high hydrophilic NOM SUV>4 shows high hydrophobic NOM	(Beauchamp *et al.,* 2019a; Beauchamp *et al.,* 2019b; Hua and Reckhow, 2007; Yan *et al.,* 2014)
Resin fractionation	fractionation of NOM based on hydrophobicity and polarity to 2 to six subgroups	(Baghoth, 2012; Chow, 2006; Croue *et al.,* 1993; Imai *et al.,* 2001; Leenheer and Croue, 2003)
SEC/HPSEC	NOM fractionation by molecular size HPSEC separates NOM components based on molecular weight	(Brezinski and Gorczyca, 2019; Hughes *et al.,* 2016; Kent *et al.,* 2014; Li *et al.,* 2013; Mahdavi *et al.,* 2017; Samios *et al.,* 2017)
NMR	NOM structure and functional groups	(Cao *et al.,* 2016; de Aquino *et al.,* 2019; H. C. Kim and Yu, 2005; Mao *et al.,* 2017; Matilainen *et al.,* 2011; Mazzei and Piccolo, 2015; Rodríguez *et al.,* 2014; D. Zhang *et al.,* 2017a)
FTIR/FTIR MS	Recognizing functional groups and quantifying the chemical structure of NOM	(Abdulla *et al.,* 2010; Her *et al.,* 2004; Landry and Tremblay, 2012; Pernet-Coudrier *et al.,* 2011)

DOC: dissolved organic carbon, TOC: total organic carbon, NOM: natural organic matter, UV: ultra-violet absorbance, SUVA: specific ultra-violet absorbance, SEC: size exclusion chromatography, HPSEC: high-performance size exclusion chromatography, MW: molecular weight, NMR: nuclear magnetic resonance, FTIR: Fourier transform infrared, MS: Mass spectrometry, C: carbon, H: hydrogen, N: nitrogen.

2.3.1. Low-Cost Characterization of NOM

DOC and TOC

The well-known methods for estimation of NOM content in water are total organic carbon (TOC) and dissolved organic carbon (DOC) analyses (Filella, 2009; J. Leenheer and Croue, 2003; Matilainen *et al.,* 2011). With removing particulate organic matter with a membrane of pore size of 0.45 um, DOC remains in the filtered water sample. In general, more than 90% of TOC belongs to DOC. TOC has been the most inclusive method for representing NOM content in the water that includes particulate organic matter and DOC. The level of DOC in all waters is reported to be in the range of 0.1 mg/L to 50 mg/L. Typically, the lowest concentration of DOC can be detected in groundwater aquifer, and the highest value was found in the bogs (Leenheer and Croue 2003). DOC is measured by oxidation methods including: the use of oxidizing material, burning of organic carbon in contact with a radiation source. Then an infra red detector measures the amount of produced carbon dioxide.

Ultra-violet Absorbance (UV)

UV absorbance data at wavelengths 250-280 nanometer such as 254 and 272 nm, have been recognized to be correlated to DBPs formation (Beauchamp *et al.,* 2019; Yan *et al.,* 2014). However, the coefficients of the parameters for the fitted models of DBPs based on UV absorbance need to be determined for the specific water source, and even the seasonal changes of NOM affect the coefficients within a single water source. Using multiple differential absorbance at wavelengths of 250 and 255 showed a stronger correlation with HAAs, especially DCAA and TCAA, while differential UV absorbance at 270 was a significant parameter in fitted models for predicting THMs (Beauchamp *et al.,* 2019). The results by Leenheer and Croue (2003) showed UV254 as an indicator of humic substances in water.

Studies to date have proved that single wavelength UV measurement is correlated to the NOM concentration and no reliable correlation was found with the reactivity of NOM. SUVA (i.e., the absorbance of UV at 254 nm divided by the concentration of DOC (mg/L) is reported to be an indicator of hydrophobic material content and DBPs formation in water (Golea *et al.,* 2017; Hua *et al.,* 2015; Pifer and Fairey, 2012; Qunshan Wei *et al.,* 2008). SUVA less than 2 represents a hydrophilic NOM content. In water samples with SUVA > 4, hydrophobic material, fulvic acids and humic acids including high molecular weight NOM are the dominant fractions (Ghernaout *et al.,* 2009). The investigations by Marais et al., (2019) revealed that UV absorbance and SUVA were strongly correlated to the aromaticity of NOM. However, a weak relationship between SUVA and the formation of THMs was obtained. As such, characterization of NOM fraction is of great importance while the main difficulty for NOM characterization is to find the most suitable fractionation procedure (Matilainen *et al.,* 2011).

NOM Fractionation

NOM compounds can be divided into three major groups: hydrophobic, hydrophilic and transphilic with acid, basic, and neutral subcategories depending on their absorptivity to ion-exchange resins during chromatography (Leenheer and Croue, 2003) as displayed in Figure 2.2. Various methods with some alterations to the original procedure, consisting of a series of adsorption to and desorption from resins at specific pH values (i.e., pH < 2 or pH > 8), are available to date (Kent *et al.,* 2014). The most frequently used technique for characterizing NOM is using various adsorbent columns with the collaboration of nonionic polymeric resins and ion-exchange resins. XAD resins are commonly used for the isolation of NOM based on hydrophobicity (Qin *et al.,* 2006).

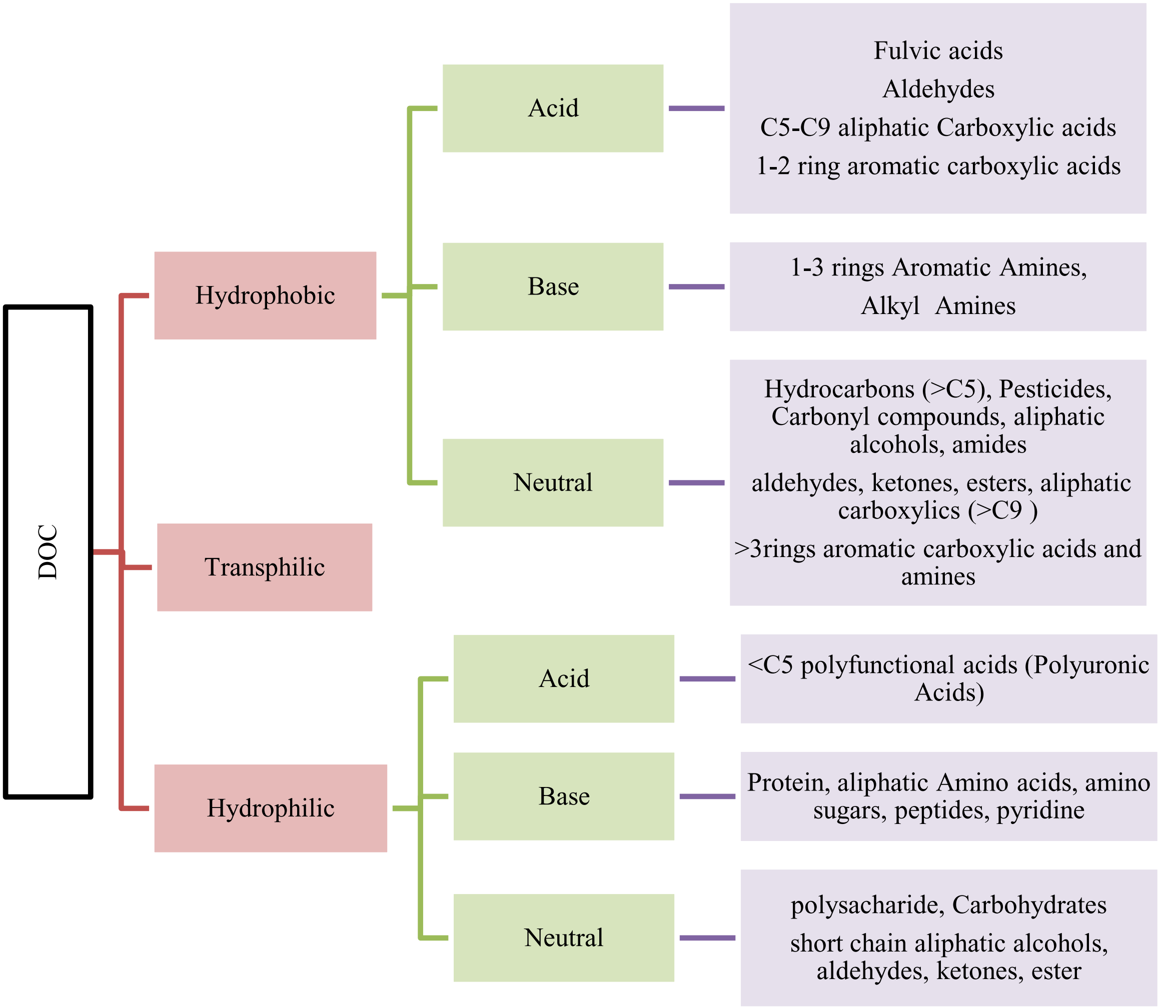


Figure 2. 2. Classification of Dissolved Organic Carbon (DOC) compiled from (Edzwald, 1993; Imai *et al.,* 2002; Leenheer and Croue, 2003; Świetlik *et al.,* 2004)

The method was first developed in 1981 by Malcolm et al., (1981) using synthetic resin at US Geological Survey. However, many researchers expanded the method following their needs in the experiments (Matilainen *et al.,* 2011). Leenheer used three different types of resins including Amberlite XAD-8, AG-MP-50, and Duolite A-7 to fractionate NOM into six groups of hydrophobic and hydrophilic NOM with subgroups of acid, base and neutral for each cluster based on polarity (Leenheer, 1981). Since then, some alterations have been applied to the technique to overcome its complications (Baghoth, 2012; Chow *et al.,* 2004; Imai *et al.,* 2001; Wang *et al.,* 2013a). Croue et al., (1992) first developed the fractionation procedure by employing XAD8 and XAD4 to isolate NOM fractions: hyrophobic, hydrophilic and transphilic (Croue *et al.,* 1993) fractions. This method was edited by Chow et al., (2004) based on the hydrophobicity strength of NOM fractions and their attachment to the resins: DAX8, XAD4 and IRA958. The method was widely employed for NOM characterization by other researchers (Drikas *et al.,* 2011; Fabris *et al.,* 2008; Hussain *et al.,* 2013; Kennedy *et al.,* 2005; Lin and Wang, 2011; S. Liu *et al.,* 2008). XAD8 was replaced by DAX8 due to the higher hydrophobic adsorption capacity of DAX8 (i.e., DAX8 >3 × XAD8 capacity in adsorption of humic acids) (Chow, 2006).

DAX-8 is a hydrophilic acrylic ester resin as presented in Table 2.5 and Figure 2.3 a. that has a low ion exchange capacity that adsorbs hydrophobic humic acids and fulvic acids with macromolecule structure (i.e., very hydrophobic acids) in its macroporous network. XAD-4 is a more hydrophobic resin composed of styrene-divinylbenzene network. XAD-4 has a larger surface area in comparison with DAX-8 and adsorb lower molecular size of hydrophobics (i.e., slightly hydrophobic acids/transphilic) (Malcolm and MacCarthy, 1992). The series of experiments in this research were characterized by Chow's method.

XAD fractionation is based on concentrating and separating a group of NOM compounds into the sorbent (resin) from the rest of the organic matter in the solute. The design of the adsorption columns is based on k'(Column capacity factor) of 50% (the mass of organic matter to the resin divided by the void volume of packed resin in the column) (Chow, 2006). Most of the NOM compounds showed affinity to DAX8 and the separation limit between hydrophobic and hydrophilic was not distinct. However, the separation of hydrophilic and hydrophobics are mathematically defined at 50% of matter retained on the resin. The hydrophobic content of solute consists of about 50% of the NOM concentration in water samples. (Leenheer, 1981).

$$V_E = V_{void}\,(1 + k') \tag{2.1}$$

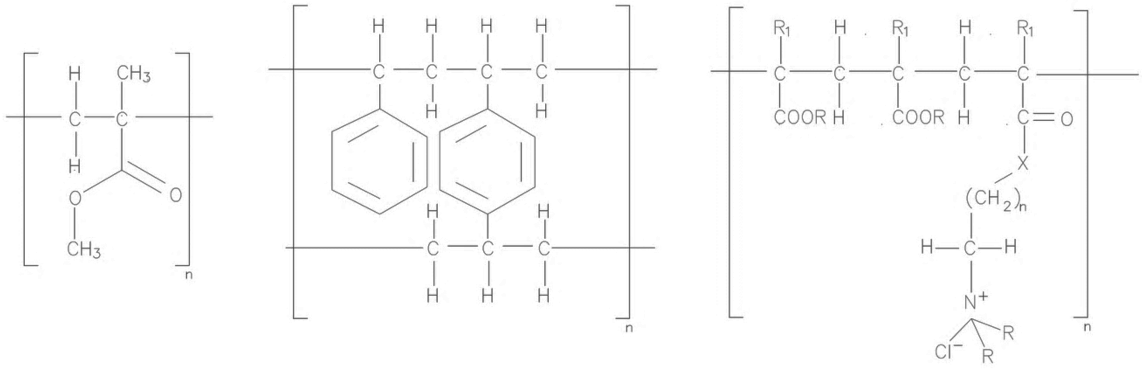
Where $V_E$is the volume of sample that can be treated by the resin to reach up to 50% breakthrough point. And k' is the column capacity factor. V_{void} is the void volume of packed resin in the column. The breakthrough happens at: $C_{out} = 0.5\, C_{in}$, where C is the concentration of adsorbate. Then Equation 2.1 turns to Equation 2.2 (Hughes et al., 2016; Leenheer, 1981):

$$V_{sample=0.5r} = 2V_{void}\,(1 + {k'}_{0.5r}) \tag{2.2}$$

In general, the fractionation techniques using XAD and DAX resins function are based on the polarity strength of NOM compounds in water. Hydrophilic NOM is soluble by establishing hydrogen bands with water, while the principal interacting force for the adsorption of hydrophobics (non-polar NOM) is Van der Waals at acidic pH to non-ionic resins with the aid of dissociation of NOM functional groups of carboxylic. The resins are strongly non-ionic to avoid ion-dipole bonds between the ions of solute with water. NOM compounds with the number of carbon per carboxylic more than 5 are adsorbed to XAD resins (Thurman and Malcolm, 1979). Ion exchange techniques are effective for the removal of charged hydrophilic NOM. IRA-958 is a strongly basic anion exchange resin with quaternary ammonium functional group and Cl^-. The removal of NOM compounds is presented in Equation 2.3 (Bolto *et al.,* 2004).

$$R - (N^{3e^-})^+ Cl^- + NOM^- \leftrightarrow R - (N^{3e^-})^+ NOM^- + Cl^- \qquad (2.3)$$

Where R is the resin, $(N^{3e^-})^+$ represents quaternary ammonium ion. In general, uncharged NOM compounds with no carboxylic functional groups that are not removed by ion exchange methods are less than 40% of DOC content in natural sources of water (Bolto *et al.,* 2004).



(a) (b) (c)

Figure 2. 3 The chemical structure of fractionation resin: (a) DAX-8 (polymethylmethacrylate), (b) XAD4 (styrene-divinylbenzene), (c) IRA958 (hypothetical structure of acrylic co-polymer quaternary ammonium).
Redrawn from (Moriarty *et al.,* 2013; Rohm and Haas, 2003; Sigma-Aldrich, 2020)

Table 2. 5. Characteristics of resins for NOM fractionation based on hydrophobicity in this research

Resin name	type	Porosity	Surface area	Column Capacity Factor	NOM type adsorbed	Ion exchange capacity	material	References
DAX8	Non-ionic	0.79cm^3/g	140-160m^2/g	K'<50	FA HA hydrophobic neutral	0.01 meq/g	Hydrophilic acrylic ester	(Malcolm and MacCarthy, 1992)(A. Chow, 2006)
XAD4	Extremely Non-ionic and hydrophobic	0.98 cm^3/g	725 m^2/g	K'<50	Transphilics	N/A	Styrene divinylbenzene	(Hughes *et al.,* 2016; Malcolm and MacCarthy, 1992) (Li *et al.,* 2002)
IRA958	Ion exchange resin	N/A	N/A	N/A	Charged hydrophilic	0.8 meq/ml 4.1 meq/g	Acrylic co polymer with quaternary ammonium	(Bolto *et al.,* 2004; Sigma-Aldrich, 2020)

2.4. NOM Treatability

DOC contains three broad groups based on biodegradability: non-biodegradable organic matter (NBOM), biodegradable organic matter (BOM) and assimilable organic carbon (AOC), which are 0.1% to 9% of TOC (Escobar *et al.,* 2001). The BOM induces biofilm formation in the drinking water distribution system and intensifies corrosion in pipeline as well as surface and suspended bacteria in watersheds. Also, it increases the level of disinfectant demand (Williams *et al.,* 2012). The BOM mostly includes non-humic substances. Humic material (HM) claims the majority of the aquatic NOM content (30% - 50%) (Rodríguez *et al.,* 2014), which are generated during the humification processes through chemical, biological, photochemical transformation, and polymerization of NOM radicals of plant litter (i.e., the primary source of HM) as well as animal residuals (Hayes and Clapp, 2001; Rodríguez *et al.,* 2014). HM are extracted from the surrounding soil of the watersheds by precipitation and groundwater inflow. HM are extremely resistant to further biological decomposition while non-humic substances, such as long-chain hydrocarbons, are biodegradable organic matter (Ghernaout *et al.,* 2009). Humic substances contain the same structure and functional groups but are significantly different in their molecular sizes (Rigobello *et al.,* 2011).

Humic substances are categorized into three subgroups regarding their solubility including humin, humic acids and fulvic acids. Humins are black macro molecular insoluble humic substances (Ouni *et al.,* 2014). Humic acids are soluble in alkali and are not soluble in strongly acidic environments ($pH < 1$) (Rigobello *et al.,* 2011). Brown to black HM with high molecular weight contains phenolic and aromatic carbon rings with two to three attached hydroxyl groups per ring and active carboxylic functional group (Ali and Mindari, 2016) as well as compounds with conjugated double bonds. Fulvic acids are soluble in both dilute base and strong acidic solutions (i.e., pH < 1). Aliphatic compounds with high nitrogen content such as sugars, carbohydrates, and amino acids belong to the hydrophilic category (Hua *et al.,* 2015).

2.5. Methods of Removal of Natural Organic Matter (NOM)

The distinctive characteristics of NOM in water sources in terms of functional groups, hydrophobicity and molecular weight (Ekström *et al.,* 2011; Fabris *et al.,* 2008; Liao *et al.,* 2018; Sharp *et al.,* 2006b), as well as the seasonal alterations of NOM fractions over time, impart complexity to the traditional water treatment systems in efficient NOM removal (Xia and Ni, 2015b). It is therefore necessary to adjust the conventional cost-effective treatment facilities to enhance their efficiencies in NOM removal and decrease the levels of hazardous DBPs. NOM compounds are not toxic but they have an inconsistent polymeric structure with a variety of functional groups that provides large adsorptive capacity. Therefore, NOM has a tendency to conglomerate with metal ions and trace toxic material that influences the toxicity parameters of water (Zhang *et al.,* 2015). Moreover, the reactions between NOM and chlorine-based disinfectants lead to the formation of DBPs and decrease the effectiveness of disinfectants in the distribution system (Liao *et al.,* 2018; Watson *et al.,* 2016).

The most widely used methods for NOM removal in the last decade are enhanced coagulation (Heiderscheidt *et al.,* 2016; Hussain *et al.,* 2013; Song *et al.,* 2015; Xie *et al.,* 2012) and magnetic ion exchange (MIEX) resin, a strongly basic anion exchange resin using chloride ions as exchanging agent removing up to 92% of NOM (Ates and Incetan, 2013; Chen *et al.,* 2018; Comstock and Boyer, 2014; Drikas *et al.,* 2011; Jutaporn *et al.,* 2019; Karpinska *et al.,* 2013; Wolska, 2015), biofiltration, which removes BOM using bilogical activities of biofilm on filtration media has resulted up to 24% DOC removal (Chen *et al.,* 2016; Fu *et al.,* 2017; Pharand *et al.,* 2015; Simon *et al.,* 2013). Advanced Oxidation processes using ozone, hydrogen peroxide, and UV radiation, produce highly reactive hydroxyl radicals, that react with NOM compounds and achieve TOC removal up to 31% (Agbaba *et al.,* 2016; Black and Bérubé, 2014; Lamsal *et al.,* 2011; Papageorgiou *et al.,* 2017; Wang *et al.,* 2013a), Activated Carbon (Božo, 2016; Chu *et al.,* 2015; Jiang *et al.,* 2017; Kristiana *et al.,* 2011b; Marc, 2013).

All the treatment methods for NOM removal that are used are categorized to three principle groups of chemical treatment, physical process, and biological methods as presented in Figure 2.4. Table 2.6 presents a comparison of the advantages and disadvantages of the most widely used methods of NOM removal. Also, a comparison of the cost efficiency of the methods shows that enhanced coagulation is the most inexpensive method for the removal of DOC. However, the expenses of activated carbon production and application are highly dependent on the carbon-rich material that is used for the production (Amaral *et al.,* 2016; Bhatnagar *et al.,* 2013).

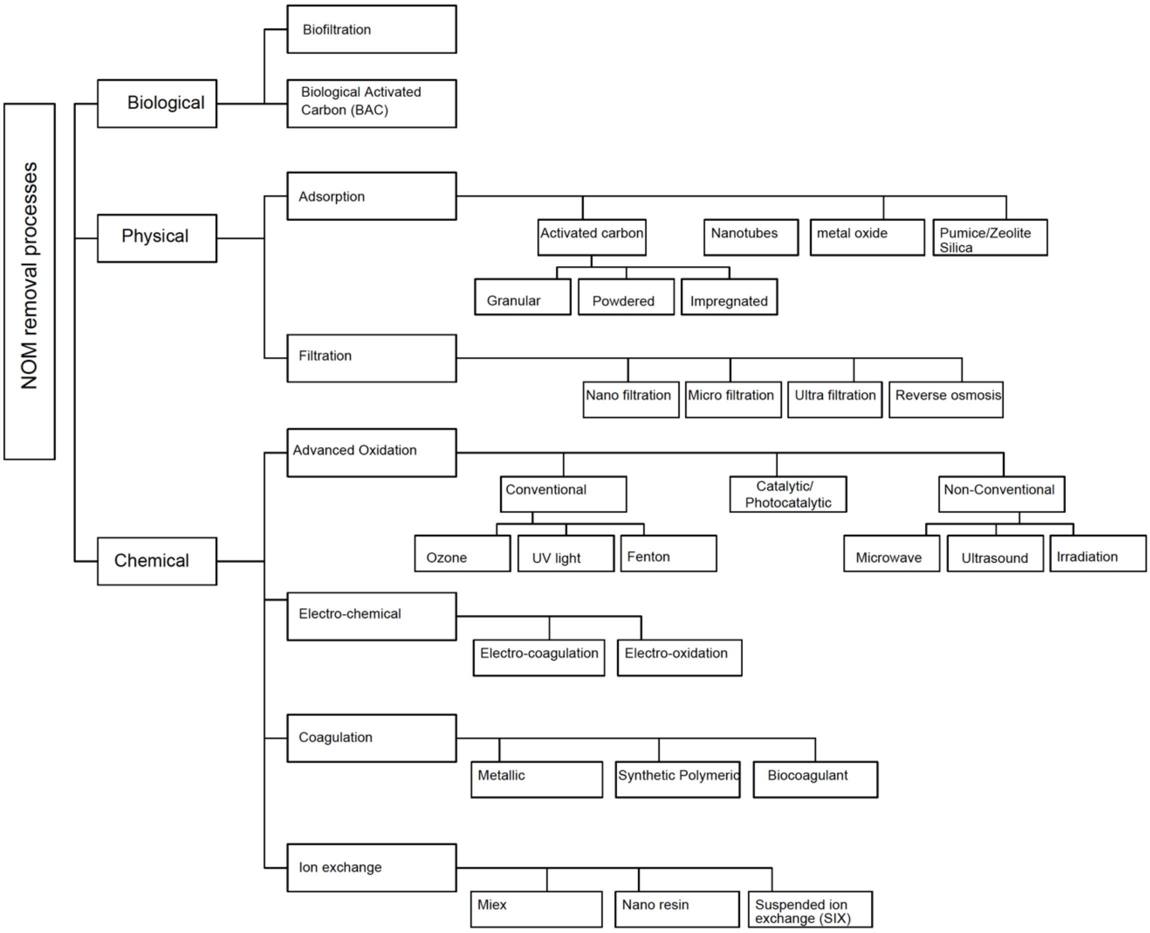


Figure 2.4. Methods of NOM removal
Compiled from Bhatnagar and Sillanpää (2017); Levchuk *et al.,* (2018); Särkkä *et al.,* (2015); Sillanpää *et al.,* (2018a); Zhang *et al.,* (2015)

Table 2. 6. A comparison on the methods of NOM removal

Treatment process	Advantage	Disadvantage	Cost-efficiency	Reference
Enhanced Coagulation	Conventional method, easy operation recommended method by EPA High removal percentage of DBPs, effective in the removal of hydrophobic and high MW NOM	higher dosage of coagulant for NOM removal Depending on DOC level the efficiency changes, low efficiency in removal of neutral hydrophilic NOM, sludge production	inexpensive operation	(Alfaro *et al.,* 2016; Beauchamp *et al.,* 2020; Department of Environment and Conservation, 2011; Jarvis *et al.,* 2008; Tafvizi and Husain, 2022)
Adsorption	Easy operation, simple design; recommended by EPA, Capable of the removal of heavy metals in water, ability to be regenerated	costly depending on the raw material, low, limited adsorption capacity,	Costly – inexpensive (i.e., Costs depend on the raw material)	(Bhatnagar and Sillanpää, 2017; Lompe *et al.,* 2017; Shadbahr and Husain, 2019; Tafvizi *et al.,* 2021b)
Advanced Oxidation	Fast reaction, possibility of adding to water treatment plants	sludge production, hydrogen peroxide residuals in water, energy intensive, not comparable with ferric salts coagulants	Expensive	(Särkkä *et al.,* 2015; Sillanpää *et al.,* 2018b)
Biological	removes biological degradable NOM	Requires extra nutrient, sludge production, sensitive process, requires large landscape	Costly	(Sillanpää, 2014)
Ion exchange	removes transphilics NOM, highly efficient	needs additional stages	Costly	(Sillanpää, 2014)

NOM: natural organic matter, MW: molecular weight, DOC: dissolved organic carbon, A study by Zhang *et al.,* (2017b) on the cost-efficiency of combined methods of NOM removal revealed that the combination of coagulation+filtration+adsorption and coagulation+sedimentation+filtration+membrane are the most cost-efficient methods compared to the combination of coagulation with ozone, biological activated carbon, membrane or some mixed methods in addition to coagulation. Further details are summarized below:

2.5.1. NOM removal by coagulation

Although coagulation has been mostly designed for turbidity and color removal in conventional water treatment plants, it is a preferred pretreatment method for NOM removal. Egyptians and Romans are the first nations that utilized coagulants, especially alum for water treatment and elimination of turbidity since 1500 BC (Teh *et al.,* 2016). However, EC is one of the most efficient, simple and cost-competitive techniques for removing DOC (Aryal *et al.,* 2011; Croue *et al.,* 1993; Racar *et al.,* 2017; Song *et al.,* 2015). The optimum concentration of the coagulant and its appropriate type for NOM removal may not be the same as that for turbidity removal (Hong *et al.,* 2009).

The coagulation-flocculation process comprises two steps: (1) fast mixing of coagulants with water and (2) flocculation through slow agitation to destabilize fine colloids by decreasing the electrical double layer around negatively charged NOM particles. The latter helps to develop clustered coarse flocs to precipitate during the settling time. The clear supernatant water flows to the outlet and the settled sludge, consisting of the coagulant hydroxides and sweeped NOM particles, is discarded (Sillanpää *et al.,* 2018a). Hydriphilic compounds in water depending on their functional groups contain N^+ or O^- (e.g., amine groups or hydroxyl groups) to carry a negative or positive charge. Co-ion particles (e.g., negatively charged NOM) adsorb each other by overcoming the repulsion forces between stabilized suspended particles by employing the van der waals forces between the colloids (Teh *et al.,* 2016). The stability of colloids in water is decreased by adding high dosages of coagulant resulting in the reduction in the double layer thickness and repulsive potential of colloidal particles. As a result, microparticles are produced and a collision between them by Brownian motion leads to the formation of larger flocs (Budd *et al.,* 2004; Edzwald, 1993; Zhan *et al.,* 2011). Destabilization of colloides depends on pH, dosage and type of coagulants. It is occurred by four mechanisms: double layer compression, bridging, charge neutralization and sweeping. Two last two methods are the most frequently reported mechanisms for NOM removal (Teh *et al.,* 2016). Polymer flocculants did not show considerable advancement in floc production and easier settlement in comparison to inorganic salt coagulants, especially $FeCl_3$ (Gkotsis, 2017; Jarvis *et al.,* 2008).

Enhanced coagulation is an extension to the conventional coagulation-flocculation process to maximize NOM removal. The process can be more feasible by using optimized coagulant dosage and elimination of NOM by charge neutralization rather than sweeping (Alfaro *et al.,* 2016). Studies to date showed that EC generally needs a higher dosage of coagulants (Duan and Gregory, 2003; Jarvis *et al.,* 2006). The optimum concentration of the coagulant and its appropriate type for NOM removal may be different from the operational conditions in turbidity removal (Hong *et al.,* 2009). The most popular are aluminum and iron salts including aluminum sulfate, sodium aluminate, aluminum chloride, and polyaluminum chlorides, ferric sulfate and ferric chloride (Budd *et al.,* 2004; Gkotsis *et al.,* 2017; Duan and Gregory, 2003; Jarvis., 2006). However, other coagulants such as high-performance aluminum chloride (Hussain *et al.,* 2013), tannin-based coagulants, PDADMAC (Heiderscheidt *et al.,* 2016) have also shown high efficiency in NOM removal.

Three valent ions of aluminum and iron produce complexes with positive charges that adsorb NOM particles with a negative charge. In natural water, pH ranges between 5-8 where almost all the colloidal particles have negative charges. Humic substances in pH values higher than 4 have negative charges due to the ionization of carboxylic functional groups (Duan and Gregory, 2003). Therefore, the optimum results for coagulation using ferric and alum salts occur in a slightly acidic condition (Qin, 2006). In high alkalinity water, adding those inorganic metal salt coagulants produces a significant amount of hydroxide ions, which leads to excessive sludge precipitation and waste of coagulants. Thus for NOM removal in the existing water treatment plants, the operator can increase the dose of coagulants or acidify it (Yan, 2006). Water acidification will increase the corrosivity, which can be compensated since it can reduce the dose of coagulants and consequently decreases the volume of sludge.

The NOM removal happens under the influences of neutralization, adsorption and sweeping by large hydroxide flocs for the colloidal particles (Rigobello *et al.,* 2011). The studies so far have shown that the effectiveness of coagulation in NOM removal depends on different factors including NOM characteristics, pH, coagulant type, dosage and water temperature (Božo, 2016; Jeong *et al.,* 2014; Kabsch-Korbutowicz, 2005) as well as SUVA level (Archer and Singer, 2006). In terms of characteristics, coagulation is more efficient for high molecular weight organic matter (Wang *et al.,* 2013b), and hydrophobic and aromatic compounds (Ghernaout *et al.,* 2009). Enhanced coagulation can remove up to 80% of hydrophobic materials and high molecular weight NOM, while the removal efficiency for hydrophilic and lower molecular weight compounds is not satisfactory (Hussain *et al.,* 2013; Archer and Singer, 2006). The overall efficiency of coagulation in DOC removal is in the range of 21% to 81%, which consequently decreases DBPs (Chulho, 2009; Hussain *et al.,* 2013; Liu *et al.,* 2005; Qin *et al.,* 2006; Umar *et al.,* 2016). Additional methods such as activated carbon, ion exchange, and membrane filtration are needed to remove low molecular weight and hydrophilic organic matter from water.

2.5.2. NOM removal by activated carbon

Adsorption by carbon-rich material has been one of the most well-known methods of water treatment for DOC removal as well as low concentrations of heavy metals (Bhatnagar *et al.,* 2013; Shadbahr and Husain, 2019) due to its easy operation and simple design (Lompe *et al.,* 2017). Past studies showed that carbon-based adsorbents had been used since the 1800s (Bhatnagar *et al.,* 2013). Activated carbon is mostly used in combination with other methods of water treatment because of its limited adsorption capacity and slow kinetics (Cheng *et al.,* 2005). The performance of AC has been widely studied for NOM removal. In particular, the adsorption of soluble NOM into the pores of AC and removal of biodegradable NOM lead to the formation of biofilm on the surface of activated carbon. However, clogging of the adsorbent as well as hydraulic headloss are two major obstacles of bioactivated carbon (Gibert *et al.,* 2013).

The cost-efficiency of adsorption methods is highly dependent on the accessibility and the price of the carbon-rich precursor materials (i.e., wood, oil, coal, and coconut shells) (Amaral *et al.,* 2016; Bhatnagar *et al.,* 2013). The industry of activated carbon has been burning thousands of tons of pricey materials such as wood and coal annually (Canales-Flores and Prieto-García, 2020). To address today's environmental issues and financial obstacles, novel techniques are required for the production of activated carbon from cost-effective materials. So far, studies have shown the triumph of AC production from agricultural waste, such as rice husk, eggshells, palm seeds shell, and silkworm excrement (Ali *et al.,* 2019; Canales-Flores and Prieto-García, 2020; Isoda *et al.,* 2014), waste coffee beans (Zięzio *et al.,* 2020) and industrial solid wastes (Ali *et al.,* 2019) and wastewater sludge (Zeng *et al.,* 2020).

The ability of AC in removing contaminants from water differs because of the pore structure including meso, micro, and macro as well as the functional groups on its surface (Bhatnagar *et al.,* 2013). NOM removal is possible by semi-micropore and mesopore activated carbon (Dastgheib *et al.,* 2004). A wide range of commercial activated carbons has been used for investigating the removal of NOM from water (Amaral *et al.,* 2016; Dastgheib *et al.,* 2004; Gibert *et al.,* 2013; Julcour-Lebigue *et al.,* 2012; Matsui *et al.,* 2011) A TOC removal up to 80% was achieved by modified activated carbon (Chu *et al.,* 2015). Also, a decrease of 95% of DBPs was observed by Kristiana *et al.,* (2011). The produced industrial activated carbons have shown capabilities in removing low molecular weight and preferentially aromatic compounds (Marc, 2013; Schreiber *et al.,* 2005) However, NOM removal is reported to be dependent on the structure of the exterior layer of activated carbon rather than the interior pore structure (Amaral *et al.,* 2016).

In order to modify the surface of activated carbon, impregnation by various metals such as aluminum, iron, copper, and silver (Bai *et al.,* 2016; Hu *et al.,* 2017; Mines *et* *al.,* 2018; Nicole, 2016; Shimabuku *et al.,* 2017; Valušová *et al.,* 2012) have been studied for the removal of toxic materials. Among all the metals, iron impregnation (Cheng *et al.,* 2005; Dastgheib *et al.,* 2004) and iron oxide (Lan *et al.,* 2015) for the removal of NOM precursors investigated and showed improvements in the removal TOC. The effective removal of DBPs precursors can be achieved by using a combination of AC and other methods, such as enhanced coagulation, MIEX resin, ultrafiltration (Altmann *et al.,* 2015; Kristiana *et al.,* 2011b; Margot *et al.,* 2013). The integrated treatment systems including AC and EC have enhanced the reduction of DBPs up to 95% and increased TOC removal by 70%. While another experiment showed an increase in the DOC removal of 8.5% (Watson *et al.,* 2015). The overall TOC removal in the whole system for two studies were between 70-95%. Also, the NOM fractions that are removed by coagulation are reported to be higher molecular weight, and the fractions that are adsorbed to the AC were found irrelevant to the eliminated NOM by coagulation (Altmann *et al.,* 2015).

2.6. Future Perspectives

The researchers have investigated the effective technologies to remove NOM from drinking water. However, further improvement is necessary to attain the goal of water treatment in many small systems. To provide serviced people with safe public water distribution system, future research is needed to consider the following issues:

- Epidemiological studies on the exposure of service people with individual compounds of THMs and HAAs are necessary to evaluate the chronic effects of each compound on human body at different ages, which can be achieved with long-term investigation on the correlation of water network and risks.

- Many rural communities have obligations in budget provision in order to provide activated carbon for their conventional water treatment system. Therefore, development of low-cost activated carbon for the removal of neutral hydrophilic and very hydrophobic acids is necessary to reduce DBPs formation
- The seasonal changes of NOM contribute to the performance of water treatment systems, and the types and quantity of the DBPs. Further investigation on the seasonal variation of NOM based on hydrophobicity is needed for water treatment systems.
- Many studies have investigated the effects of operational factors on coagulation and flocculation on the removal of DOC. However, these studies were not enough to produce adequate data to reach to a conclusion. Further study is necessary through multivariate optimization of enhanced coagulation in reducing NOM.

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CHAPTER THREE

ENHANCED COAGULATION FOR REMOVAL OF NATURAL ORGANIC MATTER AND DISINFECTION BYPRODUCTS: MULTIVARIATE OPTIMIZATION

A version of this chapter has been published in the Journal of Environmental Engineering Science in Feb 2022[1]. Hoda Tafvizi (the first author) along with the co-author, and corresponding author, Dr. Tahir Husain, designed the experiments. The first author conducted, and analyzed the experimental data for investigating the effect of five factors of pH, coagulant type, dosage, fast mixing energy and settling time on the removal of NOM and reduction of DBPS. The first author prepared the original draft of the manuscript and subsequently revised the paper based on the co-author's feedback, and the peer-review process. Dr. Tahir Husain assisted in reviewing and revising the paper.

3.1.Introduction

More than a century ago, chlorine was the first disinfectant used to eradicate waterborne diseases (Kristiana et al., 2011b). The chain of reactions between chlorine-based disinfectants and natural organic matter (NOM) decreases the effectiveness of chlorination in distribution systems and leads to the formation of hazardous disinfection byproducts (DBPs) (Liao *et al.,* 2018). Trihalomethanes (THMs) and haloacetic acids (HAAs) are two groups of DBPs that are regulated by the U.S. EPA and originate from

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[1] Tafvizi, H., and Husain, T. (2022). Enhanced Coagulation for Removal of Natural Organic Matter and Disinfection Byproducts: Multivariate Optimization. Environmental Engineering Science, 39(2), 155–167. https://doi.org/10.1089/ees.2020.0372

NOM. The U.S. EPA announced the maximum contaminant levels (MCL) of 80 and 60 ppb for four species of THMs (THM4) (i.e., chloroform, bromoform, bromodichloromethane, and dibromochloromethane) and five compounds of HAAs (HAA5) (i.e., monochloroacetic acids, dichloroacetic acids, trichloroacetic acids, monobromoacetic acids, and dibromoacetic acids), respectively (EPA, 1999). The International Agency for Research on Cancer (IARC) has classified chloroform and bromodichloromethane in Group 2B as possible human carcinogens with an increased risk of liver cancers (IARC, 1999).

Enhanced coagulation (EC) is one of the most efficient, simple, and low-cost methods for removing NOM from water (Racar *et al.,* 2017). The U.S. EPA requires conventional water treatment plants (WTP) to decrease the level of DBPs by considering a surrogate measurement of total organic carbon (TOC) removal because of its feasibility of testing. Accordingly, WTPs must reduce TOC level by 15–50% using EC based on the raw water's alkalinity and TOC, as mentioned in the supplementary information (SI) in Table S.1 (EPA, 1999).

However, in addition to the changes in the concentration and structure of NOM fractions over time, the unique properties of NOM in every water source, such as hydrophobicity, molecular weight, and structure (Liao *et al.,* 2018), expose EC WTPs to difficulties regarding DBPs (Sharp *et al.,* 2006a). In a study in Australia, EC in a full-scale WTP could remove DOC by 80–90%. However, the high levels of NOM content in water resources, as reported by the research, required additional materials (i.e., activated carbon) to decrease the level of DBPs (Kristiana *et al.,* 2011b) to the MCL. The level of DOC in two-thirds of surface waters of Newfoundland (NL), Canada, is more than 5 mg/L, with an average of 9 mg/L (Department of Environment and Conservation, 2011). A maximum of 14.4–21.2 mg/L DOC was observed in tap water in some areas of the province in 2019–2020 (Water Resources Management Division, 2020). Consequently, achieving the MCL for DBPs using the U.S. EPA suggestions and conventional jar tests has not been a success in some WTPs. Eight out of 16 treatment facilities in NL utilize EC as a part of their WTP for DOC removal. Meanwhile, 147 occurrences of THM4 level exceedance were observed among a total of 505 points of measurement in 2019–2020. In a case study, a DOC decrease of 65% in an EC full-scale WTP was not considered satisfactory for the reduction of DBPs to the MCL in NL (Department of Environment and Conservation, 2011). Therefore, it is necessary to conduct a comprehensive study to efficiently amend conventional WTPs in the province and reduce the levels of hazardous DBPs through predictive models specifically designed for NOM characteristics in NL by assessing the effective parameters in EC.

The U.S. EPA requires the WTPs to adjust the operational conditions of EC by employing jar tests (EPA, 1999). Conventional jar tests are one-factor-at-a-time (OFAT) experiments. Although this approach provides an easy trial-and-error setup (achieved by changing one factor while other factors remain fixed), it is not a recommended strategy as it requires a large number of experimental runs and is characterized by limitations when applying the optimal conditions for all variables. Considering the necessity of prompt adjustment of coagulation conditions by operators in WTPs, faster methods for optimizing EC conditions are required. The response surface methodology (RSM), as a more rapid and feasible statistical design of experiment (SDE), has been propitiously used in earlier studies to investigate the effect of multiple operational factors for coagulation and to minimize coagulant dosage. Table 3.1 summarizes the studies performed in the last 20 years to develop predictive polynomial equations and enhance operational conditions (i.e., minimized dosage and maximized DOC removal) in WTPs using synthetic and natural water samples. The optimization of dosage and pH in investigations on natural waters resulted in a coagulant dosage of 5.85 to 26.26 mg/mg DOC and a DOC removal of 34.3-75.0% by alum (Beauchamp *et al.,* 2020; Park *et al.,* 2000; Trinh and Kang, 2011). Up to 67% DOC could be removed by applying ferric chloride at an optimized dosage of 24.59 mg/mg DOC by considering the following factors: DOC, ferric chloride dosage, chlorine dosage, and disinfection time (Uyak and Toroz, 2006). One of the most famous approaches suggested by the U.S. EPA requires the water samples with specific characteristics to increase the coagulant dosage to the "point of diminishing return" (PODR), wherein the ratio of TOC removal and coagulant dosage (i.e., alum) is more than 0.3:10 during jar testing (EPA, 1999). To overcome the laboriousness of the EPA's suggested method, a recent study by Beauchamp *et al.,* (2020) on alum dosage and UV254 of raw water showed that a 180 mg alum cm/L dose of alum/UV254 reflected the PODR in EC. This presents a promising and faster technique for reducing DOC up to 75%. Nevertheless, most of the research studies to date have made an effort to reduce the surrogate parameters of DOC and UV254; however, the number of research studies on EC that have been performed by measuring THM4 and HAA5 is limited.

Table 3. 1. Summary of studies on the mathematical models of disinfection byproducts and organic carbon in enhanced coagulation.

References	Factors	Responses	Tested liquid	Developed Models	Design Method	Optimized results
Beauchamp et al., (2020)	pH, coagulant dosage, UV254	DOC, HAA6, UV254	natural water	N/A		CD:5.85 alum R: 75%
Racar et al., (2017)	pH, coagulant dosage	DOC turbidity, final pH	wastewater	$\text{DOC} = 166.35 - 89.18\text{pH} + 0.0998\ \text{Fe}^{3+} - 0.284\text{pHFe}^{3+} + 16.589\text{pH}^2 + 0.016(\text{Fe}^{3+})^2 + 0.0048\text{pH}^2\text{Fe}^{3+} + 188\text{pH}(\text{Fe}^{3+})^2 - 0.908\text{pH}^3 - 17.6(\text{Fe}^{3+})^3$	RSM	CD:1.56 ferric chloride R: 84.76%
Li et al., (2016)	pH, basicity, dosage	TOC, NH_4^+ $(PO_4)^{3-}$	effluent	$\text{TOC} = 52.376 - 3.24 \times \text{Dosage} - 1.228 \times \text{pH} - 53.895 \times \text{Basicity} + 0.046\text{Dosge}^2 + 0.083 \times \text{Dosage} \times \text{pH} + 1.416\text{Dosage} \times \text{Basicity} - 0.0813\text{pH}^2 + 1.581 \times \text{pH} \times \text{Basicity} + 13.46 \times \text{Basicity}^2$	uniform + RSM	CD: 2.74 PFC R: 73.2%
Alfaro et al., (2016)	pH, coagulant dosage, coagulation G, flocculation G, HPO/HPI, turbidity	DOC	synthetic water	Charge neutralization: $\text{DOC} = 2.35 + 0.24\text{pH} - 0.15\text{Dosage} + 0.29\text{Coagulation G} - 0.27\ \text{pH}^2 - 0.03\text{pH} \times \text{Dosage} - 0.02\text{pH} \times \text{Coagulation G} - 0.27\ \text{Dosage}^2 - 0.16\text{Dosage} \times \text{Coagulation G} + 0.09\text{Coagulation G}^2$ Sweeping: $\text{DOC} = 3.20 + 0.67\text{pH} - 0.03\text{Dosage} - 0.34\text{Coagulation G} - 0.07\text{Coagulation time} - 0.24\ \text{pH}^2 + 0.03\text{pH} \times \text{Dosage} + 0.07\text{pH} \times \text{Coagulation G} - 0.04\ \text{pH} \times \text{Coagulation time} - 0.02\ \text{Dosage}^2 + 0.18\text{Dosage} \times \text{Coagulation G} - 0.01\text{Dosage} \times \text{Coagulation G} - 0.11\text{Coagulation G}^2 + 0.03\ \text{Coagulation G} \times \text{time} - 0.004\ \text{Coagulation time}^2$	fraction factorial	CD: 14.98 alum R: 40.2 to 57.4% CD: 27.1 alum R: 54.8-69.8%
Trinh and Kang (2011)	coagulant type, coagulant dosage, pH	turbidity, DOC	natural water	$\text{DOC} = -26.24 + 271.59\text{PACl Dosage} + 15.96\ \text{pH} - 1305.28\ \text{PACl}^2 - 1.45\text{pH}^2 + 5.63\text{PACl Dosage} \times \text{pH}$	RSM, CCD	CD: 19.10 PACl R: 34.3%
Uyak and Toroz (2006)	DOC, UV_{254}, SUVA, alkalinity, Br^-, pH, temperature	THMs, DOC	lake water	$\text{TTHM} = 10^{1.414} \times (\text{DOC} - 2.1)^{0.199} \times (\text{Ferric} + 1.56)^{-0.066} \times \text{Cl}_2^{0.242} \times \text{Time}^{0.21}$	multilevel factorial	CD: 24.59 ferric chloride R: 34-67%
Park et al., (2000)	pH, coagulant dosage	DOC removal	natural water	$\text{DOC} = -950.867 + 292.11 \times \text{pH} + 4.65\text{Coagulant Dosage} - 23.611 \times \text{pH} \times \text{Coagulant Dosage} - 0.036744 \times \text{Coaguant Dosage}^2 - 0.15794\text{pH} \times \text{Coagulant Dosage}$	factorial	CD: 26.26 Alum R: 45.4%

*CD: Coagulant dosage is calculated in mg/mg DOC from the literature; R: Removal efficiency for DOC; N/A: Not available; PFC: Poly ferric chloride; PACl: Poly aluminum chloride

The results of the research studies obtained so far illustrate that the effectiveness of coagulation in NOM removal depends on various factors, such as NOM properties, pH, type of coagulants and their dosage, water temperature, UV254, and the level of specific ultraviolet absorbance (SUVA) (Agbaba *et al.,* 2016; Beauchamp *et al.,* 2020; Jeong *et al.,* 2014). In addition, other factors, such as fast mixing and settling time, are essential in the coagulation-flocculation–settling (CFS) process (Teh *et al.,* 2016). Rapid mixing is the second-highest power consumption unit in WTPs in the U.S.A, with an energy requirement of 0.008–0.022 $kWhm^{-3}$ from a power utilization total of 0.18–0.48 $kWhm^{-3}$ (Plappally and Lienhard, 2012). Due to the effect of mixing conditions on energy consumption and floc size (BinAhmed *et al.,* 2015; Vadasarukkai and Gagnon, 2017), the standard jar testing method of D2035-19 (ASTM, 2019) involves the optimization of stirring conditions as well as the parameters of coagulants and pH that the U.S. EPA mandated in 1999.

Thus far, no comprehensive study has attempted to assess the interacting effects of pH, dosage, coagulant type, fast-mixing speed, and settling time on the EC process in relation to the THM4 and HAA5 reduction. The empirical data from such a study would identify the most significant variables for reducing HAA5 and THM4 during EC, which in turn would assists in modifying the operational conditions, thereby reducing costs in WTPs, and decreasing the adverse health effects of DBPs on residents.

Addressing this research gap, the current study presents an investigation on the removal of NOM via EC to fulfill the following objectives: (1) identify and compare the optimal conditions for decreasing THM4, HAA5, and DOC by assessing the effect of five factors, namely: pH, coagulant type, dosage, and mixing speed in EC; (2)

improve optimal conditions required for EC in WTPs by decreasing power intensities and minimizing coagulant dosage; and (3) utilize the fractional factorial and central composite design (CCD) to decrease the number of jar testing experiments and subsequently develop predictive mathematical models for the reduction of DBPs and DOC in EC, with the aim of efficiently changing operational conditions in WTPs in NL.

3.2.Materials and Methods

3.2.1. Preparation and Procedures

Only reagent-grade chemicals were used in this study. The jar tests were performed using aluminum sulfate (Thermo Fisher Scientific, Canada) and anhydrous ferric chloride (VWR, Canada). Solutions of $FeCl_3$ and $Al_2(SO_4)_3$ at 1N concentration were prepared daily using ultrapure deionized water produced by a Barnstead Nanopure D11901 water system (Thermo Fisher Scientific, Canada), having an electrical resistance of 16 MΩ/Cm and a pH of 6.8, with a DOC of less than 0.1 mg/L. Sodium hydroxide and hydrochloric acid were supplied by VWR, Canada, for pH adjustment. Humic acids and polysaccharose for the preparation of synthetic water samples were supplied by Thermo Fisher Scientific, Canada.

The DOC and UV absorbance at 254 nm, as well as THM4 and HAA5, were measured before and after the EC procedure. UV absorbance was measured via a Genesys 10S UV/Vis spectrophotometer (Thermo Fisher Scientific, U.S.A.) while the pH was measured using a benchtop FE20 pH meter (Mettler Toledo, USA). The DOC test was performed on filtrates through a 0.45-µm nylon filter membrane (Whatman, England). The DOC was analyzed by a TOC-L PC-controlled analyzer (Shimadzu, Japan) equipped with an ASI-L autosampler using the high-temperature (680 °C) combustion catalytic oxidation method (ASTM D7573, 2013).

DBPs formation potential tests were conducted by dosing the samples with chlorine and holding for 72 h; this was achieved by adding 30% sodium hypochlorite solution, such that the residual free chlorine remained within 0.05 to 2.50 mg L^{-1} after contact time. The initial dosage of chlorine on the raw and treated samples was chosen based on the chlorine demand method D1291 – 17 (ASTM, 2017). The residual free chlorine was quenched using ammonium chloride at a concentration of 100 mg L^{-1} of sample before extraction of DBPs. THM4 and HAA5 samples were extracted in methyl tert-butyl ether (MTBE) according to the U.S. EPA methods.

3.2.2. Measurement of THM4 and HAA5

THM4 and HAA5 samples were extracted in methyl tert-butyl ether (MTBE) (J.T. Baker, U.S.A.) and analyzed according to the 551.1 (Hautman and Munch, 1997) and 552.2 (Pawlecki-Vonderheide et al., 1997) methods with an Agilent 6890 gas chromatograph-ECD. THM4 and HAA5 were examined in all raw and treated water samples. The results were analyzed using an internal standard (bromofluorobenzene) and surrogate (decafluorobiphenyl) for THM4. The internal standard and surrogate for testing the HAA5 were 1,2,3-trichloropropane and 2,3-dibromopropionic acid, respectively.

3.2.3. NOM Fractionation

The NOM in the water samples was characterized and fractionated based on its acidity and hydrophobicity. Four fractions of NOM, i.e., very hydrophobic acid (VHA), slightly hydrophobic acid (SHA), charged hydrophilic (CHI), and neutral hydrophilic (NHI), were detected based on their adsorption to the resins according to the rapid fractionation technique used in previous studies (Chow *et al.,* 2004; Vieira *et al.,* 2012). Resins, i.e., Supelite DAX-8, Amberlite XAD-4, and Amberlite IRA958, were purchased from Sigma Aldrich, Canada. Sodium hydroxide and hydrochloric acid of reagent grade were used for pH adjustment. Different fractions of NOM, i.e., VHA (separated by DAX-8), SHA (adsorbed to XAD-4), CHI (separated by IRA-958), and part of the NOM not absorbed by any of the resins (NHI), were analyzed for DOC. The preparation of the resins and the fractionation method utilized a modification of earlier techniques reported in Smith and Alqabany (2009) and Vieira *et al.,* (2012). The NOM fractions in the water samples were detected using the adsorption to the resins based on the method known as the rapid fractionation technique, initially suggested by Croue et al., (1993) and amended in subsequent studies (Chow *et al.,* 2004; Smith and Alqabany, 2009; Vieira *et al.,* 2012; Xing *et al.,* 2015). Figure 3.1 presents an abstract schematic of the method.

3.2.4. Coagulation-Flocculation Procedure

The coagulation-flocculation was performed using 600 mL round beakers and a PB-700 jar test device (Phipps and Bird, U.S.A.). Each test for coagulation and flocculation was carried out in a randomized order of the run list designed by Design-Expert software (Version 10.0.8.0). The speed and time of the process were set manually, and the samples were mixed for 1 min at a fast-mixing speed, followed by 20 min of mixing at 25 rpm for flocculation. This process was continued with settling at a designed settling time. The level of DOC, UV absorbance at a wavelength of 254 nm, THM4, and HAA5, after being in contact with chlorine for 72 h, were evaluated for all treated and untreated water samples.

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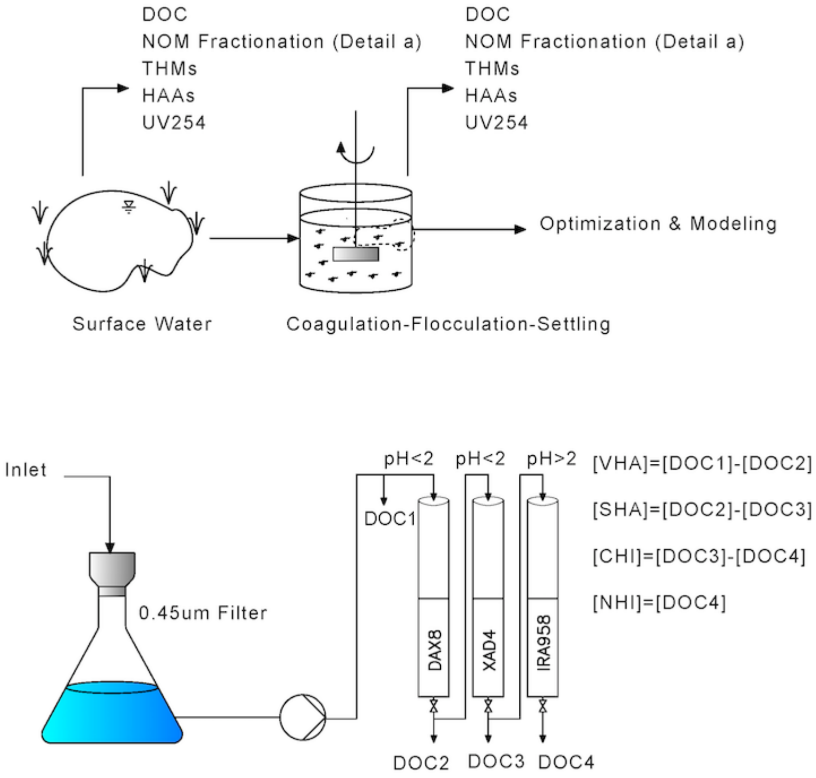
Figure 3.1 presents a schematic of the steps and experiments.

The reduction and removal efficiencies (R, %) of the parameters were calculated as follows:

$$R = \frac{C_i - C_f}{C_i} \times 100\%, \tag{3.1}$$

where C_i is the initial level (mg L^{-1}) of the targeted parameter in the untreated water and C_f is the final value of this parameter in the treated water.



Detail (a) NOM Fractionation by resin

Figure 3. 1. Schematic presentation of the experiments

3.2.5. Water sampling

Two surface water sources, where drinking water for Pouch Cove and Sunnyside (NL, Canada) towns originate from, hereafter referred to as Water 1 and Water 2, respectively, were explored in this study. The water samples were selected based on the DOC levels and NOM fractions throughout one year of sampling from August 2016 to August 2017. The samples were analyzed for pH, DOC, NOM fractionation, THM4, HAA5, and UV absorbance at a wavelength of 254 nm. Table 3.2 summarizes the characteristics of the water samples. The levels of HAA5 and THM4 were more than the MCLs mandated by Health Canada and the U.S. EPA. This is because, in this study, the method of DBPs formation potential within 72 h was chosen to understand the variations of the subjected parameters better. Four other water samples were used to validate the produced statistical models, and their characteristics are presented in Table S.3.5.

Table 3. 2. Raw water characterization.

Source	DOC (mg L^{-1})	HAA5 (ppb)	THM4 (ppb)	UV254 (cm^{-1})	SUVA254 (L mg^{-1} cm^{-1})	VHA (mg L^{-1})	SHA (mg L^{-1})	CHI (mg L^{-1})	NHI (mg L^{-1})
Water 1	9.351	327.690	2317.100	0.297	3.156	6.64	0.54	0.18	1.99
Water 2	5.220	545.760	1639.350	0.237	4.540	3.50	0.29	0.12	1.31

Specific UV absorbance at a wavelength of 254 nm (SUV254): 100x (UV254/DOC mg L^{-1}); VHA: Very hydrophobic acid; SHA: slightly hydrophobic acid; CHI: charged hydrophilic; NHI: neutral hydrophilic.

3.2.6. Statistical design of experiments

The SDE for the mathematical modeling and optimization includes the following steps: (i) recognition of factors and levels; (ii) designing of the run sheet via concurrent alteration of all independent variables; (iii) analysis of the results and establishment of the regression models; (iv) examination of the adequacy of the model and curvature in the linear analysis; (v) extension to RSM design (if necessary); (vi) validation of the model accuracy; and (vii) projection of the optimized condition.

3.2.7. Choice of factors and levels

The independent variables, i.e., pH (X_1), coagulant dosage (X_2), coagulant type (X_3; defined as Fe/(Fe + Al)), speed of fast mixing (X_4), and settling time (X_5) were selected for investigating the DOC removal, THM4 and HAA5 reduction, and UV absorbance at 254 nm. The coagulant type was considered a numerical factor to minimize the experimental runs for developing a time efficient method. Table 3.3 presents the actual and coded levels of the factors. The minimum and maximum values (–1 and +1) were selected based on the possibility of maintaining an extension to $-\alpha$ and $+\alpha$ in the RSM design.

Table 3. 3. *Actual and coded levels of the variables.*

Factor	Symbol	Coded and Real Factor Levels				
		(–α)	Lowest (–1)	Center Point (0)	Highest (+1)	(+α)
pH	X_1	4.5	5.5	6.5	7.5	8.5
Coagulant Dosage (mg/mg DOC)	X_2	0.48	3.83	7.18	10.53	13.83
Coagulant type Fe: (Fe + Al)	X_3	0.0	0.25	0.5	0.75	1.0
Fast mixing (rpm)	X_4	75.0	120.0	165.0	210.0	255.0
Settling time (min)	X_5	0.0	20.0	40.0	60.0	80.0

A preliminary study was conducted to determine the dosage of the coagulants and their ratios. The injection dose was estimated based on the initial experiments with 1–15 mg/mg DOC, corresponding to 0.015–0.75 mmol metal/mg DOC and a pH of 5.5–7.5 (Davis and Edwards, 2017), a fast-mixing speed of 120-210 rpm for 60 s (BinAhmed *et al.,* 2015), a settling time of 20–60 min (Jeong *et al.,* 2014; Rizzo *et al.,* 2005; Zhao *et al.,* 2013), and flocculation at 25 rpm (van Leeuwen et al., 2005) for 25 min.

3.2.8. Design procedure

The ability to point out clear effects with a small number of tests is crucial for choosing a test design. The number of runs in SDE can be reduced as long as the design's resolution remains satisfactory and the main effects and two-factor interactions are aliased with high-order interactions (Chen *et al.,* 2017). A half fractional factorial design 2^{5-1}, with a resolution V, provides the required criteria (Li *et al.,* 2009) and was chosen for two sets of experiments in this study. The total number of runs in the first stage was 19, including 16 fractional factorials and 3 center points to investigate the curvature and error. A CCD with 12 extra runs was used for the second stage of the experiment, where the curvature was observed in the results. Fifty runs were tested in triplicate. The experimental design procedure and a comparison with alternative methods, i.e., Box-Behnken design (BBD) and D-optimal, are presented in the SI in detail (section S.3.3).

To present a correlation between factors and responses in a linear model, a polynomial equation (Equation 3.2) can be used:

$$\mathrm{Y} = \mathrm{f(X)} = \beta_0 + \sum_{\mathrm{i}=1}^{\mathrm{k}} \beta_{\mathrm{i}} \mathrm{X}_{\mathrm{i}} + \sum_{\mathrm{i}=1}^{\mathrm{k}} \sum_{\mathrm{J}=\mathrm{i}+1}^{\mathrm{k}} \beta_{\mathrm{ij}} \mathrm{X}_{\mathrm{i}} \mathrm{X}_{\mathrm{j}} \; ; \; (k = 5) \qquad (3.2)$$

where Y is the predicted value for the responses, i.e., DOC removal, UV254, HAA5, and THM4; β_0 is the constant coefficient; β_i is the linear coefficient of regression; k is the number of factors (k = 5 in this study); and X is the effective factor for the response, Y. The RSM can fit a second-order quadratic model to the data according to Equation 3.3 below (Montgomery, 2013).

$$Y = f(X) = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j + \sum_{i=1}^{k} \beta_{ii} X_i^2 \,;\ (k = 5). \quad (3.3)$$

Estimation of the coefficients and similitude analysis were carried out via an analysis of variances (ANOVA) using the backward elimination of insignificant factors (p-value >0.10) with the Design-Expert (version 10.0.8.0). This software was also used for the contour maps and overlay plots of optimal conditions.

3.3. Results and Discussion

3.3.1. Experimental results

The experimental results for the responses of the DOC, HAA5, THM4, and UV254 for Water 1 and Water 2 are presented in the Appendix (Tables S.3.2 and S.3.3). The ANOVA results (Table S.3.4) showed a significant curvature term in the polynomial equations for Water 2. Consequently, the test extended to an RSM-CCD, and the results for 12 designed experiments of RSM are reported in Table S.3.3.

3.3.2. ANOVA and Fitted Models

A mathematical model was fitted to the data for each of the responses, thereby relating the response to a function of the effective variables. The confidence interval for the test was 90% in this study; therefore, for all the generated mathematical models the significant terms with p-value less than 0.10 were included in the regression. In this study, the data were appropriately fitted to the models, and an insignificant lack of fit, with a p-value >0.10, was obtained for each model, as presented in SI Section S.3.3

(Table S.3.4). The center points in the experimental design assessed the curvature. The p-values for the curvature term in all the dependent responses for Water 2 were <0.05. Thus, further investigation, with an extension to the RSM, was performed for Water 2. Three terms were used to examine the fitted models' precision at predicting new data: R^2_{adjusted}, and $R^2_{\text{predicted}}$. The models' ability to predict new points was assessed via $R^2_{\text{predicted}}$ and R^2_{adjusted}, where no substantial difference (difference >20%) was observed, indicating the goodness of fit of the developed quadratic and polynomial regression models. Further information on the produced models' prediction ability is presented in the SI in Section S.3.3.

The models' adequacy was assessed with prerequisite assumptions for the ANOVA, including the normality of residuals, independence of the runs overtime, and homogeneity of the residuals' variance. All the models were adequate, and the normality of the data was demonstrated for all of them; normal plots of the residuals are presented in Sections S.3.4 and S.3.5 of the SI.

The fitted regression models for four responses (DOC removal, UV254 reduction, THM4 reduction, and HAA5 reduction), in terms of the coded factors within the coded levels (–1,1) for Water 1 and Water 2, are as follows:

$$DOC_1 removal = 45.49 + 5.7pH - 4.18Dose - 9.7\frac{Fe}{Fe+Al} - 9.28\left(Dose \times \frac{Fe}{Fe+Al}\right), \quad (3.4)$$

$$DOC_2 removal = 37.32 + 4.02pH + 14.49Dose + 78.78\frac{Fe}{Fe+Al} - 14.3\left(Dose \times \frac{Fe}{Fe+Al}\right) - 6.08\,pH^2 - 54.84Dose^2, \quad (3.5)$$

$$UV254_1\, reduction = -43.25 - 7.5pH - 88.37Dose - 208.9\frac{Fe}{Fe+Al} - 171\,(Dose \times$$

$$\frac{Fe}{Fe+Al}), \tag{3.6}$$

$$UV254_2\ reduction = 25.87 + 5.27pH + 10.86Dose + 132.13\frac{Fe}{Fe+Al} - 12.9\ (Dose \times \frac{Fe}{Fe+Al}) \tag{3.7}$$

$$THMs_1\ reduction = 68.78 + 7.84pH - 1.29Dose + 6.89\frac{Fe}{Fe+Al} - 1.34\ Mixing\ speed + 1.35Settling\ time + 10.11\ (pH \times \frac{Fe}{Fe+Al}), \tag{3.8}$$

$$THMs_2\ reduction = 77.37 + 5.79pH + 23.34Dose + 9.11\frac{Fe}{Fe+Al} - 0.59\ Mixing\ speed - 2.27Settling\ time - 27.6\ \left(Dose \times \frac{Fe}{Fe+Al}\right) - 4.66(Dose \times Mixing\ speed) - 2.39pH^2 - 13.27Dose^2, \tag{3.9}$$

$$HAAs_1\ reduction = 57.40 + 7.58pH - 1.49Dose - 4.82\frac{Fe}{Fe+Al} - 1.13\ Mixing\ speed - 0.358\ Settling\ time + 1.78\ (pH \times Dose) + 8.29\ \left(pH \times \frac{Fe}{Fe+Al}\right) + 5.23\left(Dose \times \frac{Fe}{Fe+Al}\right) - 1.83(Dose \times Mixing\ speed) + 2.06(Mixing\ speed \times Settling\ time),\ \text{and} \tag{3.10}$$

$$HAAs_2\ reduction = 22.29 + 4.79pH + 4.74Dose + 144.73\frac{Fe}{Fe+Al} - 3.82\ Mixing\ speed - 3.54Settling\ time + 9.57\ (pH \times Dose) - 8.97Dose^2 - 104.61(\frac{Fe}{Fe+Al})^2, \tag{3.11}$$

where the actual levels of the variables are subjected to the following conditions: $5.5 \leq \text{pH} \leq 7.5$, $3.83 \leq \text{dose} \leq 10.53$ (mg/mg DOC), $0 \leq \text{Fe/Fe + Al} \leq 1$, $120 \leq$ mixing speed ≤ 210 (rpm), and $20 \leq$ settling time ≤ 60 (min). The subscripts 1 and 2 represent the models produced from the tests on Water 1 and Water 2, respectively.

3.3.3. Effect of factors on DOC removal and UV254

Equations 3.4 to 3.7 are used to predict DOC removal and UV254 reduction in

Water 1 and Water 2, respectively. The most effective model terms (p-value <0.05) with highest coefficients of the coded factors in order of importance are: type of coagulant (i.e., ratio of Fe/(Fe + Al)) > dose-coagulant interaction > pH > coagulant dosage in water 1 and $\frac{Fe}{Fe+Al} > Dose^2 > Dose \times \frac{Fe}{Fe+Al} \approx Dose > pH^2 > pH$ in water 2. Previous studies have demonstrated the quadratic effects of the pH and coagulant dosage and the significance of their interaction term in eliminating DOC in EC processes (see Table 3.1). A comparison between the produced models in this study with those in previous studies in terms of DOC removal and UV254 is presented in detail in Sections S.3.6 and S.3.7 of the SI.

3.3.4. Effect of factors on DBPs reduction

Equations 3.8 and 3.9 describe the fitted models for THM4 reduction in EC. The ANOVA results indicate that the most significant factors (according to their regression coefficients) are pH, Fe/(Fe + Al), dosage, mixing speed, and settling time. The order of importance of the factors is: $\left(pH \times \frac{Fe}{Fe+Al}\right) > pH > \frac{Fe}{Fe+Al} > Mixing\ speed \approx settling\ time \approx dose$ in Water 1 and $Dose \times \frac{Fe}{Fe+Al} > Dose > Dose^2 > \frac{Fe}{Fe+Al} > pH > Dose \times Mixing\ speed > pH^2 > Settling\ time > Mixing\ speed$ in water 2.

The results obtained from the interactions of dose-coagulant type and pH-coagulant type in two sets of experiments present two different coagulation mechanisms (i.e., charge neutralization and sweeping) are defined by the operational conditions. The regression coefficients for the pH and dosage for Water 1 indicate that the pH positively affects THM4 reduction, while the coagulant dosage negatively impacts it. A high pH and low dosage of ferric chloride increased THM4's removal. The observed results agree with the obtained models of DOC removal in this study (Section S.3.6). The contour graph for the interaction effect of pH × Fe/(Fe + Al) on THM4 reduction (Figures 3.2 (a)) indicates that aluminum sulfate at a pH <6 results in the lowest removal (<50.47%) of THM4 in Water 1. Charge neutralization is the predominant process for NOM removal at pH <6.0 owing to the dominance of polymeric Al species over amorphous Al $(OH)_3$ (i.e., the contributing compound to sweeping mechanism), which implies that the sweeping mode is more efficient in THM4 reduction than charge neutralization in both water samples.

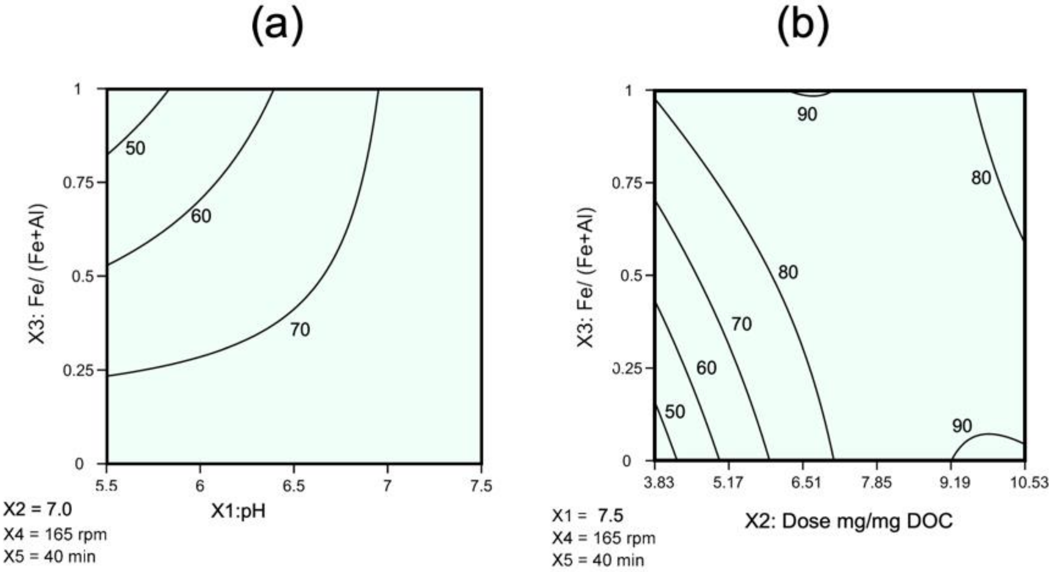


Figure 3. 2. Contour plot of the interaction effects for THM4 reduction (a) Water 1, and (b) Water 2

The negative regression coefficients of mixing speed reveal that the low mixing speeds (i.e., 120 rpm) contribute more effectively to THM4 reduction. Mixing steps are necessary for producing metal (Al and Fe) hydroxide particles resulting in the removal of THM4 precursors in sweeping mode. However, the high power of mixing (i.e., higher velocity gradient than 190 S^{-1} in this study and increased mixing time) contribute to the break of the produced amorphous $Al(OH)_3$ flocs that remove DOC in sweeping mode. The effect of the mixing speed on DOC removal was not statistically significant because the flocs were not critical for the regression models of DOC removal in this study as all undissolved flocs (i.e., >0.45 μm) were eliminated before testing by the TOC analyzer according to ASTM D7573 (2013). On the contrary, the presence of unsettled flocs with particle size >0.45 μm influenced THM4. THM4 samples were unfiltered in this study. A study by Abeynayaka *et al.,* (2012) on the performance of filtration systems after coagulation on DOC and THMs formation potential in full-scale and pilot-scale WTPs showed that the pore size in the filtration systems influences the removal of THM precursors. THMs level after sand filtration and ceramic microfiltration were 160 and 74 ppb, respectively. The results of Abeynayaka *et al.,* (2012) show consistency with the current study (i.e., unfiltered and pore size: 0.45 μm). However, an investigation on the relationship between floc size in coagulation and THM reduction is recommended as an extension to this study.

The settling time positively affected THM4 reduction in Water 1, albeit with less significance than dose, coagulant type, and pH, in which sweeping was the primary coagulation mechanism. With longer settling times, the flocs become larger, and there was an increase in the contact time between the small, precipitated flocs, which increased the NOM removal in unfiltered water samples. In contrast, neutralization was the dominant process for DOC removal in Water 2, where the regression coefficients of the settling time and mixing speed had the lowest values among all variables during THM4 formation. In general, the regression coefficients in the fitted model for reducing THM4 in Water 2 were consistent with the respective values in the DOC removal model (Equation 3.8). However, the settling time negatively affected THM4 reduction in Water 2. Previous studies by Vieira *et al.,* (2012) showed that the structure, molecular weight, and molecular size of NOM compounds influence the efficacy of treatment processes, and the type of DBPs produced. Their study showed that small to intermediate humic acid molecules were more prone to generating THM4 than larger molecules. Longer settling time increases the hydrolysis of large NOM molecules (such as NHI), leading to their disintegration into smaller molecules, as was proved in a previous study by Alfaro *et al.,* (2016) as well and observed in our results. NHIs are more prone to forming THM4 after EC and cannot be easily removed compared to hydrophobic compounds with higher molecular weights. Thus, as observed in this study, low mixing energy (i.e., stirring speed of 120 rpm that equals velocity gradient of 190 S^{-1}) and shorter settling time (i.e., 20 min) depending on the predominant mechanism of coagulation influenced the level of THM4. The results of this study are in agreement with observations by BinAhmed et al., (2015), where the largest and strongest flocs in EC were produced at a fast-mixing speed of 120 rpm for 60 s of mixing and contributed positively to the removal of THM4 precursors. Further, the study by Vadasarukkai and Gagnon (2017) showed that excessive energy consumption at the fast-mixing stage of EC does not contribute to the DOC removal for humic acids.

The regression models for reducing HAA5 (Equations 3.10 and 3.11) indicate that the variables of pH, dose, mixing speed, Fe/(Fe + Al), and settling time have a substantial effect on reducing HAA5 during EC. The order of importance of factors in Water 1 is: $pH \times \frac{Fe}{Fe+Al} > pH > Dose \times \frac{Fe}{Fe+Al} > Mixing\ speed \times Settling\ time > Dose \times Mixing\ speed \approx pH \times Dose > Dose > Mixing\ Speed > Settling\ time$; and that in Water 2 is: $\frac{Fe}{Fe+Al} > (\frac{Fe}{Fe+Al})^2 > pH \times Dose > Dose^2 > pH \approx Dose > Mixing\ Speed \approx Settling\ time.$

In terms of the pH, a higher pH positively affects the removal of HAA5 (see Figures 3.3 a, b). The highest levels of HAA5 reduction, i.e., 68 and 80% for Water 1 and Water 2, respectively, were obtained at higher pH levels.

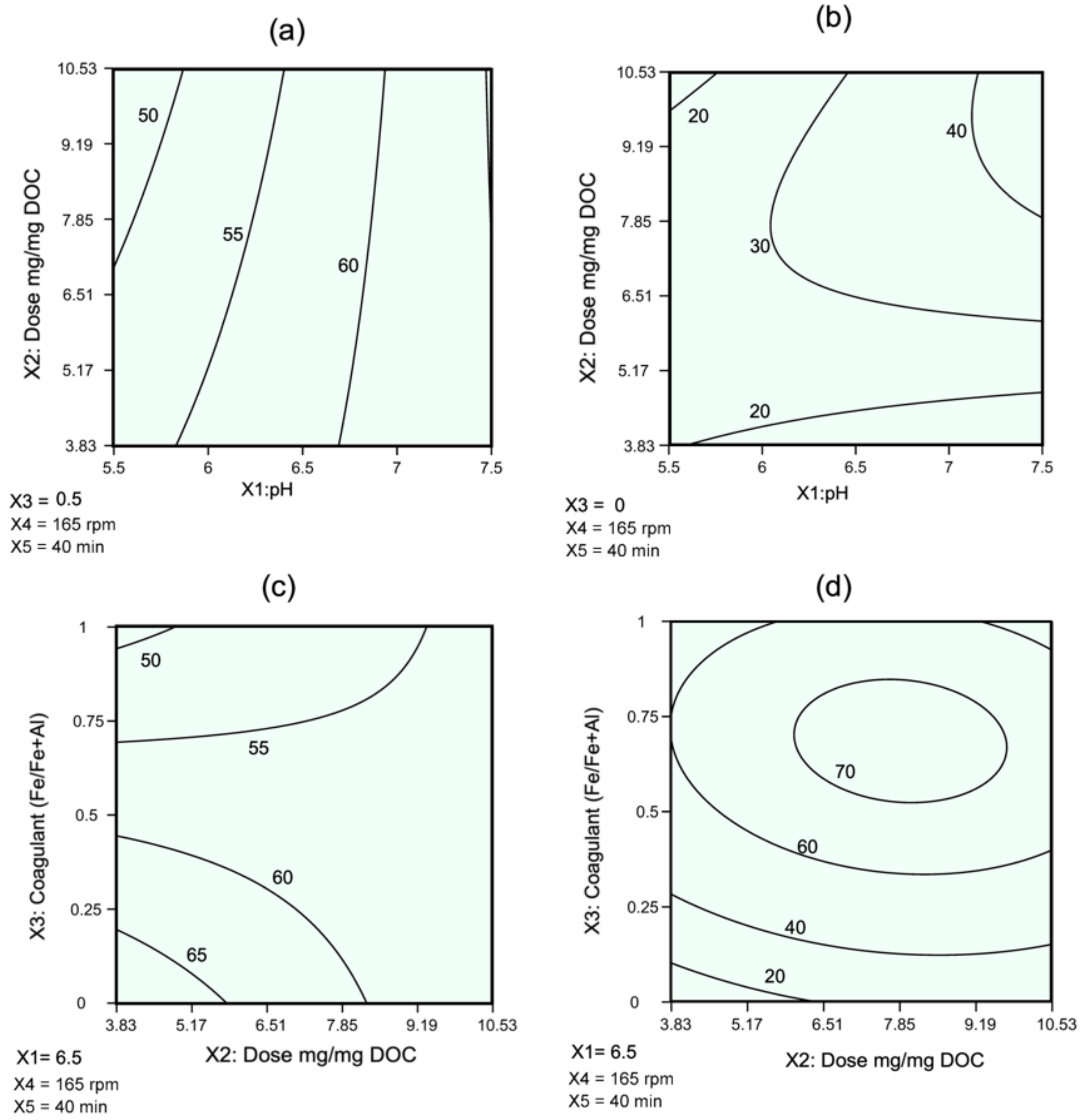


Figure 3. 3 Contour plot of the interaction effects for HAA5 reduction (a) Dose-pH in Water 1, (b) Dose-pH in Water 2, (c) Dose-Fe:(Fe + Al) in Water 1, and (d) Dose-Fe:(Fe + Al) in Water 1

A considerably steep increase in the removal of HAA5 occurred at a pH >7.5 and dose >9.20 (mg/mg DOC) in Water 2 (Figures 3. 3b, d). Observations by Lekkas and Nikolaou (2004) showed that the pH had a positive impact on the formation of HAA5. However, a review by Ged *et al.,* (2015) on 87 developed models for HAA5 and THM4 generation during the chlorination process in previous studies did not show any specific relationship between the production of HAA5 and pH. In terms of the dosage, a high dosage of coagulants increases the available amorphous metal hydroxide at a basic pH for entrapping NOM, which is consistent with the results of DOC removal in a study by Alfaro *et al.,* (2016) that is described in detail in the SI (Section S.3.6). The mixing speed and settling time negatively affected the decrease in HAA5 in Equations 3.10 and 3.11.

The interaction effect that the dose-coagulant type (Fe/Fe + Al) has on HAA5 reduction is presented in the contour plot (Figure 3.3c). For HAA5 removal in Water 1, the optimum dosage was <5.17, and the ratio for Fe/Fe + Al equals zero. Thus, a low dosage of aluminum sulfate at a high pH removes the HAA5 precursors in Water 1, which is consistent with the observed results of DOC removal in the sweeping process (see Section S.3.6). The contour plot of HAA5 reduction for the dose-coagulant type (Figures 3.3c, d) illustrates that higher pH values (pH >7.5), 0.75 < Fe/Fe + Al < 1.0, and 6.51 < dosage < 9.19 (mg/mg DOC) led to the maximum removal of HAA5. Similar results were obtained in the contour plots and fitted models of DOC removal. The developed models for HAA5 in both water samples revealed that the levels of pH, dose, coagulant type, fast-mixing speed, and settling time play a crucial role in DBPs removal in EC that have not been investigated thus far. The results of this study prove the necessity of investigation of EC contributing to THM4 and HAA5 production before filtration rather than relying only on the observations of DOC measurements.

3.3.5. Validation and optimization

EC is an economical process for the removal of DOC and DBPs. However, to prevent excessive consumption of coagulants and, consequently, to avoid producing a large amount of sludge, optimization is necessary. Moreover, taking into account the power intensiveness of the fast-mixing stage, a reduction in this unit's energy consumption can be financially beneficial for the WTPs. Therefore, undertaking a multivariate optimization of EC to minimize coagulant dosage and mixing speed and achieve higher DBP removal (i.e., maximization of HAA5 and THM4 reduction) is desirable. The optimal operational conditions for the individual responses were found through a desirability function using the Design-Expert software by employing the produced mathematical models. The results of optimization revealed that the minimization of DOC, THM4, and HAA5 occurs under different operational conditions, as visualized in the overlay plot (Figures 3. 4 a,b). The highest desirability for the maximum removal of THM4 and HAA5 occurs at coagulant doses as low as 3.83-5.95 mg/mg DOC, while the optimization based on DOC removal without considering fast-mixing energy and settling time results in coagulant doses of 6.51-7.85 mg/mg DOC. Thus, a reduction of 23.8 to 41.1% in coagulant dosage can be achieved by multivariate optimization of all five factors influencing DBP reduction compared to the optimization of only coagulant dosage, pH, and coagulant type for DOC removal.

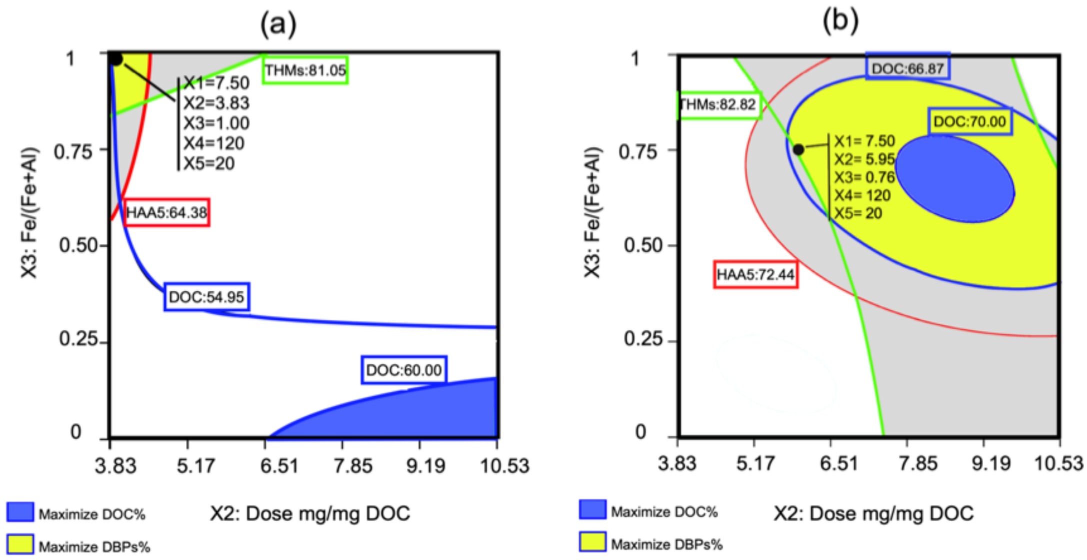


Figure 3. 4. Overlay plot for maximizing DOC, THM4 and HAA5 reduction (a) Water 1 and (b) Water 2

The predicted optimal conditions, i.e., not employed in model training, were validated on 6 water samples. The characteristics of Water 1, Water 2, and four other water samples, including two from natural sources in New-Wes-Valley, NL, and two synthetic water samples using humic acids and polysaccharides, are presented in the Table S.3.5. The generated mathematical models were used to predict the DOC, HAA5, and THM4 values which had a maximum removal of 67.31% for DOC, 78.14% for HAA5, and 84.00% for THM4 at pH = 7.50, dose = 5.95 mg/mg DOC, Fe/Fe + Al = 0.76, stirring rate = 120 rpm, and settling time = 20 min.

For Waters 3 to 6, a maximum DOC removal of 44.98-89.48% was achieved, and the THM4 reduction ranged from 68.38 to 94.00%. The highest error was observed in the results obtained from Waters 5 and 6, ranging from 33.18- 32.94% for DOC removal, 12.41-18.95% for THM4 reduction, and 13.63-41.75% for HAA5 reduction. In contrast, Waters 1, 2, 3, and 4 exhibited low error levels (<10%) in predicting DBPs reduction. The maximum removals of 91.00, 72.64, and 70.79% of THM4, HAA5, and DOC were obtained, respectively, in natural waters (Table S.3.6). The coagulant dosage obtained in previous studies using alum was 5.85 to 26.26 mg/mg DOC as presented in Table 3. 1. Our results present a minimum dosage of 3.83-5.95 mg/mg DOC for DBPs reduction, which is in a lower range compared with the reported investigations. The results obtained from Beauchamp et al., (2020) using alum at a concentration of 5.85 mg/mg DOC showed a maximum HAA6 and DOC reduction of 95 and 75%, respectively. However, the coagulant dosage for other coagulants (e.g., ferric chloride) was not evaluated in their research.

Figures 3. 4 a-c presents a schematic of the observed results of the reduction for DOC, HAA5, and THM4, contributing to the deviation of the hydrophobicity in the water samples from reference water (i.e., Water 2) and the error of the predictions. The hydrophobicity variations (i.e., VHA difference) and prediction error of the samples were calculated as follows:

$$VHA\ difference = \frac{\frac{VHA_{ref}\,(mg\,L^{-1})}{DOC_{ref}\,(mg\,L^{-1})} - \frac{VHA_{S}\,(mg\,L^{-1})}{DOC_{S}\,(mg\,L^{-1})}}{\frac{VHA_{ref}\,(mg\,L^{-1})}{DOC_{ref}\,(mg\,L^{-1})}} \times 100, \qquad (3.12)$$

$$error = \frac{R_p - R_a}{R_p} \times 100 \qquad (3.13)$$

where VHA_{ref} denotes the very hydrophobic acids' fraction of the reference water sample; DOC_{ref} is the DOC content of the reference water sample in modeling; VHA_s and DOC_s are the VHA and DOC content of the water samples used in validation, respectively, (i.e., Water 1 to Water 6); R_p is the predicted value for responses using the statistical model, and R_a is the natural value of the observed response under laboratory conditions.

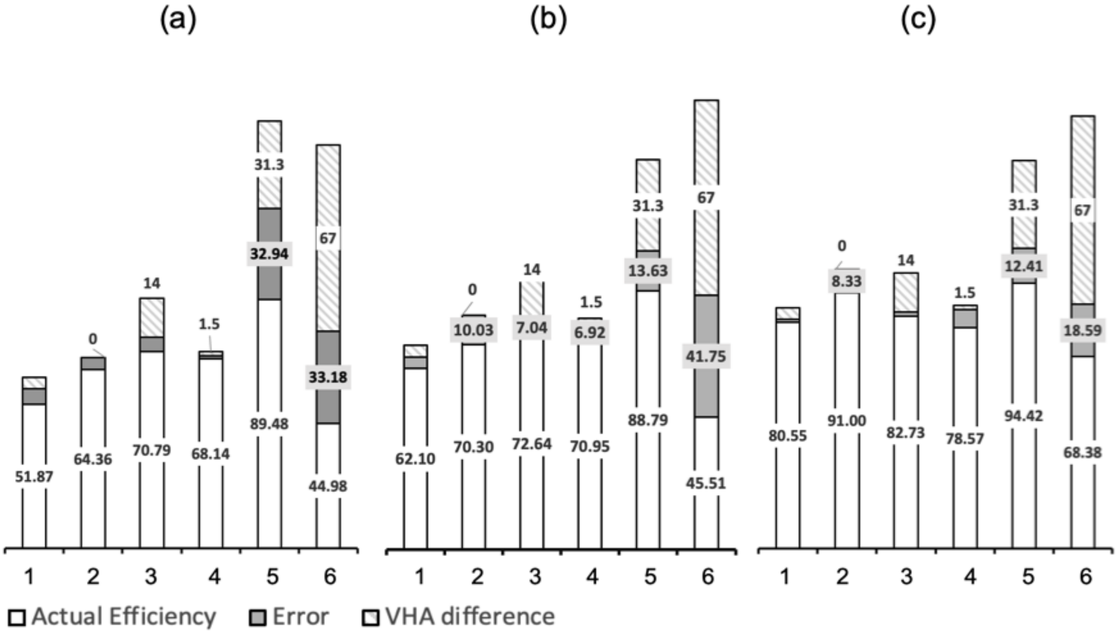


Figure 3. 5. A schematic of the correlation between measured responses, prediction error and VHA differences in (a) DOC removal, (b) HAA5 reduction, and (c) THM4 reduction

The natural values of the responses under laboratory conditions show that the actual DOC removal and DBP reduction were close to the values predicted by the mathematical models at optimal conditions for the samples with similar hydrophobicity to Water 2 (VHA difference: 0-14%). The highest prediction error levels are observed in all three models of DOC, THM4, and HAA5 in the synthetic water samples. VHA was the predominant fraction of NOM ranging from 67.05 to 81.16% in the natural water samples. In contrast, Water 5 was prepared using humic acids (VHA/DOC: 0.98), which possess extreme hydrophobic properties, and polysaccharose, i.e., a neutral hydrophilic NOM, was the main component of Water 6. Thus, the results of this study might be used for optimal operation of pilot-scale and full-scale WTPs with sources of water with similar hydrophobicity (VHA/DOC of 0.67-0.81) with anticipated error less than 10%. However, pilot-scale and full-scale WTP studies are suggested to advance this research further.

The results of this study are in agreement with the research by Alfaro *et al.,* (2016) in terms of the correlation of hydrophobicity and DOC removal in the EC process. Alfaro et al., (2016) found that DOC removal was correlated to NOM hydrophobicity and VHA/NHI fraction. The maximum DOC removal of 82.8 to 90.5% was achieved for a VHA/NHI: 100% with a coagulant dosage ranging from 21.92 to 40.51 mg/mg DOC in their study. The DOC removal for Water 5 with similar characteristics in our study shows the same removal efficiency with a lower coagulant concentration (Dose: 5.93 mg/mg DOC).

The optimal operating conditions in Table 3. 4 indicate that the lower settling time and fast-mixing speed (20 min and 120 rpm, respectively) contributed to the maximum removal efficiency of DBPs, which agrees with the observations in section 3.4.

Table 3. 4. Optimization results for the maximum removal of DOC, HAA5, and THM4.

Factor	Constraints	Predicted Values	
		Water 1	Water 2
pH	In range	7.50	7.50
Dose (mg/mg DOC)	Minimize	3.83	5.95
Coagulant (Fe:Fe + Al)	In range	1.00	0.76
Fast Mixing rate (rpm)	In range	120.00	120.00
Settling Time (min)	In range	20.00	20.00
DOC removal	Maximize	54.95	67.31
HAA5 removal	Maximize	64.65	78.14
THM4 removal	Maximize	81.43	84.00

An analysis of the velocity gradient and power reduction is presented in section S.3.9 of the SI. The velocity gradient in the current study was calculated as 190 s^{-1}, referring to the samples' volume and the G curve provided by the manufacturer of the jar testing device. The U.S. EPA suggests a velocity gradient of 300-1000 s^{-1} for proper mixing and a settling time of 30-60 min (EPA, 1999). The results obtained in the current study show that a reduction of fast mixing velocity gradient from 300 s^{-1} to 190 s^{-1} contributed to the reduction of THM4 and HAA5 and reduced the power consumption in fast mixing units by 59.88%, as estimated in section S.3.9 in SI. Excessive power consumption for mixing and a settling time >20 min could adversely affect the reduction of THM4 and HAA5.

Reductions in the coagulant dosage and fast mixing intensiveness can improve the cost efficiency of EC operations at WTPs. A hypothetical WTP with an average flow of 1 m^3s^{-1} has been used to evaluate the cost reduction due to power reduction and dosage optimization. The results are reported in Tables S.3.7 and S.3.8 in SI. As a result, optimization for DOC removal and DBPs reduction contribute to 7.81 and 5.95 mg/mg DOC of coagulant dosage, respectively. A dosage reduction from 7.81 to 5.95 mg/mg DOC at Fe/Fe+Al of 0.76 mol/mol contributes to a cost-cutoff of 194,920.25 CAD. The decrease in the velocity gradient of fast mixing unit contributes to a cost reduction of 4,198.00 CAD. Thus, the financial benefits from both adjustments equal a total saving of 198,478.25 CAD per annum in a typical WTP.

3.4. Summary

This study aimed to enhance the effectiveness and cost efficiency of EC for the reduction of DBPs in natural waters of Newfoundland via multivariate optimization and by using predictive statistical models. The principal results of the experiments in this study are as follows:

- Fractional factorial and CCD are effective methods for investigating the coagulation process, which reduces the number of jar test runs and assists the operators in saving time for operational conditions adjustment. Furthermore, multivariate optimization on DBPs removal reduces the coagulant dosage, energy consumption by fast mixing, and settling time.
- HAA5 and THM4 were affected by the following variables: pH, dose, coagulant type (Fe/Fe + Al), fast-mixing speed, and settling time.
- The optimal operational conditions for maximizing DBPs reduction and decreasing coagulant dosage were as follows: a pH of 7.5, dosage of 3.83–5.95 mg/mg DOC, Fe/Fe + Al of 0.75–1.00, fast-mixing velocity gradient of 190 s^{-1}, and a settling time of 20 min.
- The models of THM4 and HAA5 reduction established acceptable predictability (error <10%) under the optimized operation conditions in water samples with a VHA/DOC ratio of 0.67 to 0.81 (with similar hydrophobicity levels to Water 1 and Water 2).

This study showed that the models used thus far for the reduction of THM4 and HAA5 have not considered crucial parameters, such as the settling time and fast-mixing speed during EC. These factors contribute to improvements in the efficiency of the EC process for water treatment systems by: (1) decreasing the level of DBPs and NOM; (2) decreasing the possible health risks for residents as a result of lowering the DBPs level; (3) minimizing the chemical consumption during EC and energy consumption at the fast-mixing stage, thereby benefiting the environment; and (4) aiding in lowering the operating costs of WTPs.

The results of this research can be utilized for the optimization of operational conditions needed for EC in WTPs with water sources containing hydrophobic NOM (VHA/DOC = 0.67–0.81). The generation of an inclusive model for DBPs reduction of all water samples in CFS processes requires further studies to include variations in VHA/DOC levels (e.g., VHA/DOC: 0.2–0.4 and 0.4–0.6).

3.5.References

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CHAPTER FOUR

LOW COST ACTIVATED CARBON FOR REMOVAL OF NOM AND DBPS: OPTIMIZATION AND COMPARISON

This chapter has been published in *Water Journal* in August 2021[2] coauthored by Hoda Tafvizi (first author), Dr. Shakhawat Chowdhury, and Dr. Tahir Husain (a corresponding author). The first author designed, conducted and analyzed the experimental data. The first author prepared the original draft of the manuscript and subsequently revised the manuscript based on the co-authors' feedback, and the peer-review process. Dr. Shakhawat Chowdhury assisted in, reviewing, revising and a part of data analysis in the paper. Dr. Tahir Husain supervised and helped with reviewing the paper.

4.1. Introduction

Chronic exposure to disinfection byproducts (e.g., trihalomethanes (THMs) and halo acetic acids (HAAs)) in drinking water through ingestion, inhalation, and dermal contact increases the risk of adverse health effects. The International Agency for Research on Cancer (IARC) categorizes certain types of THMs and HAAs in Group 2B with the possible increase of the risk for liver cancers (Chowdhury *et al.,* 2019; Rahman *et al.,* 2020). The U.S. EPA suggests the maximum allowable levels of 80 ppb (parts per billion) for four THMs (THM4) (i.e., chloroform, bromoform, bromodichloromethane, dibromochloromethane) and 60 ppb for five HAAs (HAA5)

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(i.e., monochloroacetic acids, dichloroacetic acids, trichloroacetic acids, monobromoacetic acids, dibromoacetic acids) (U.S.EPA, 2002). The formation of disinfection byproducts (DBPs) occurs continuously in the municipal water as long as natural organic matter (NOM) is in contact with chlorine-based disinfectants (Chowdhury *et al.,* 2019). An increased level of NOM in the last two decades (Evans *et al.,* 2005; Molot and Dillon, 2008; Rodríguez-Murillo *et al.,* 2015; Worrall and Burt, 2004) due to global warming, acute raining, soil erosion (Nkambule *et al.,* 2012; O'Driscoll *et al.,* 2018), and water contamination has led to reduced or worsened effectiveness of water treatment processes by decreasing the lifespan of activated carbon pores (Hong *et al.,* 2009). Of the residents in Newfoundland and Labrador (NL), 79% are serviced by the public water distribution system, where 15 % of the consumers are in contact with high levels of THM4 and HAA5 in their drinking water (Rahman *et al.,* 2020). The average of the dissolved organic carbon (DOC), a surrogate indicator of NOM content, in two-thirds of the surface waters of NL is more than 5 mg/L, with an average of 9 mg/L in some areas of the province. Figure 4.1 displays a contour plot of the variation of DOC in surface water samples in NL. To reduce DBPs in compliance with regulations and to overcome the challenges in municipal water systems, water treatment facilities are looking for new and affordable advanced treatment methods.

In recent years, the most famous technologies for the removal of NOM from water are enhanced coagulation (EC) (Sillanpää *et al.,* 2018a), electrochemical methods (Särkkä *et al.,* 2015), advanced oxidation method (AOM) (Sillanpää *et al.,* 2018b), membrane (Lidén and Persson, 2016), and adsorption (Bhatnagar and Sillanpää, 2017). Adsorption by carbon-based adsorbents has been used since the 18th century (Bhatnagar *et al.,* 2013). This is one of the most favorable and promising methods in water treatment for the removal of DOC and hazardous contaminants in low concentrations owing to the convenient operation, low maintenance, (Lompe *et al.,* 2017) high efficiency, and simple design (Bhatnagar and Sillanpää, 2017; Shadbahr and Husain, 2019). However, the cost-efficiency of adsorption methods is highly dependent on the accessibility and the price of the carbon-rich precursor materials, i.e., wood, oil, coal, and coconut shells (Amaral *et al.,* 2016; Bhatnagar *et al.,* 2013). Industrial activated carbon for the removal of odor, hazardous materials, and water treatment has burnt thousands of tons of wood, coal, and oil per year (Canales-Flores and Prieto-García, 2020). Considering the financial and environmental obstacles, new technologies are available for producing activated carbon from inexpensive carbon-rich materials, such as agricultural waste (e.g., barley husk, rice husk, eggshells, palm seed shell, silkworm excrement) (Ali *et al.,* 2019; Canales-Flores and Prieto-García, 2020; ElShafei *et al.,* 2014; Isoda *et al.,* 2014), sewage sludge (Zeng *et al.,* 2020), used coffee grounds (Zięzio *et al.,* 2020), and industrial solid wastes (Ali *et al.,* 2019). The Corner Brook Pulp and Paper Limited (CBPPL) is the principal manufacturer of standard newsprint in western Newfoundland, Canada, with an average newsprint production of 700 tones per day. The boiler and bottom ash of the factory have been recognized as accessible local sources of high carbon content material for the development of porous activated carbon that is capable of resolving the waste management impediments (i.e., thousands of tons of fly ash disposal to landfill yearly) and water treatment issues in the province (Husain and Taghizadehgan, 2019; Shadbahr and Husain, 2019; Zhang *et al.,* 2017a) Investigations to date have proved the capability of AC derived from the fly ash of CBPPL in removing low to moderate levels of DOC (Husain and Taghizadehgan, 2019; Zhang *et al.,* 2017b) and arsenic (Shadbahr and Husain, 2019).

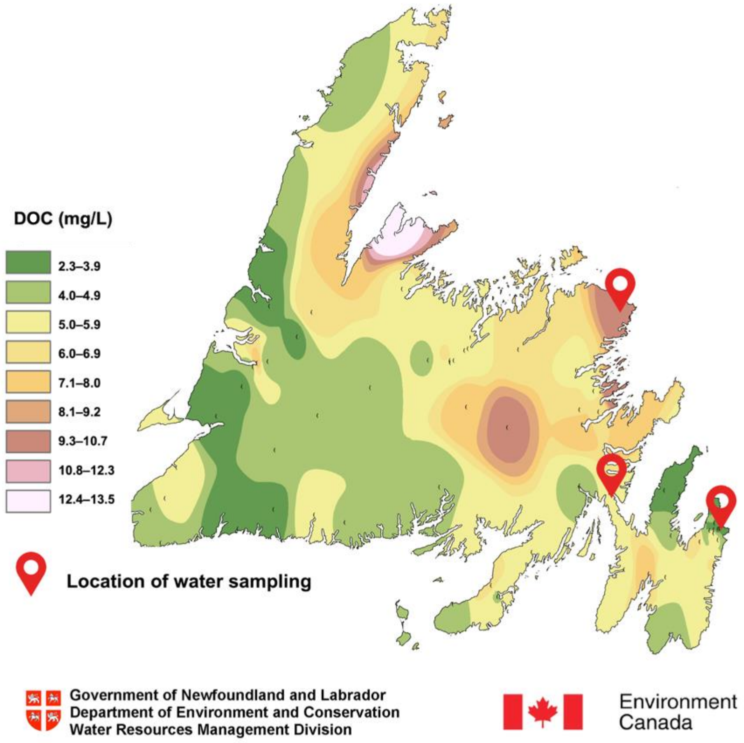


Figure 4. 1. Contour map of dissolved organic carbon (DOC) in surface water of Newfoundland and Labrador (NL) and the locations of water sampling in this study [adapted from (Department of Environment and Conservation, 2011)].

Using a mixture of steam and CO_2 at 850 °C, the developed AC showed a microporous structure (Shadbahr and Husain, 2019), which can be beneficial for the removal of small- to moderate-sized NOM molecules. The high molecular weight NOM that are the main precursors for the halogenated DBPs (i.e., THMs and HAAs) can be better eliminated by a mesopore structure (Golea *et al.,* 2020; Golea *et al.,* 2017). However, the absorptivity of AC is highly dependent on the surface charge and surface functional groups (Tanthapanichakoon *et al.,* 2005), which has not been considered thus far. To overcome the inefficacy of pore size distribution in removing certain toxic chemicals, surface modification of AC by optimization of the oxidizing agent (i.e., acid mixture) (Shawabkeh *et al.,* 2015) and developing more O-functional groups on the surface of AC, as well as alterations of surface charge by metal ions, were suggested to increase the affinity of high molecular weight NOM. Previous studies on the pore structure of AC have shown the positive effect of oxidization by nitric acid on increased mesopore volume of AC. A study by El-Hindawy in 2003 showed that the oxidation of corncob using nitric acid with a ratio of $50cm^3$: 5g of HNO_3:carbon for 1 h at 60 °C increased the mesoporosity of surface pores (El-Hendawy, 2003). In another research, HNO_3 at 5.2 N was used for 3 h at boiling point, and the oxidization of ash in the waste material (i.e., refuse-derived oil) resulted in the dissolution of ash to nitric acid, hence the mesopore volume was increased (Nagano *et al.,* 2000).

Studies on metal impregnation of AC using iron oxide (Kim *et al.,* 2013; Lompe *et al.,* 2017) and ferric chloride following high-temperature treatment have, thus far, shown improvements in the removal of NOM (Dastgheib *et al.,* 2004), arsenic (Shadbahr and Husain, 2019), bisphenol (Arampatzidou *et al.,* 2018), and aluminum (Mahdavi *et al.,* 2018). Aluminum-coated AC has also been used for the removal of arsenate (Sawood *et al.,* 2021) and dye (Kazeem *et al.,* 2018). Aluminum sulfate (alum) and ferric chloride are promising and cost-efficient coagulants with high capabilities in removing DOC and humic acids (HA) in water treatment plants during coagulation–flocculation and sedimentation processes (Tafvizi and Husain, 2021). However, coagulation is not effective in removing low molecular weight and hydrophilic NOM (Chow *et al.,* 2009), while coagulation in combination with AC has resulted in enhanced removal of DOC and HA (Kristiana *et al.,* 2011a; Xing *et al.,* 2019). Besides, the combination of the two processes reduces the requirement of coagulant doses for water treatment (Szlachta and Adamski, 2009). Many studies have compared the capability of ferric chloride and aluminum sulfate on the removal of NOM as coagulants. However, to the best of the authors' knowledge, no study has made an attempt to consider ferric chloride as a coating agent without high-temperature (i.e., T > 200 °C) activation for NOM removal. Besides, studies thus far have not used Al impregnated AC for NOM removal. Moreover, no comprehensive study has been carried out to compare the efficiencies of aluminum sulfate and ferric chloride coated AC on NOM removal without employing high temperature chemical activation. The objectives of this study are to: enhance the pore structure of AC produced from pulp and paper waste materials for NOM removal; maximize adsorption capacity by a central composite statistical design of experiment and consider the factors of pH, time, and dosage; optimize metal (i.e., Al and Fe) coating on AC considering the levels of metal leaching, dye removal, iodine number, and surface area; and increase the removal of HA as the main precursor of THM4 and HAA5 using metal-coated AC.

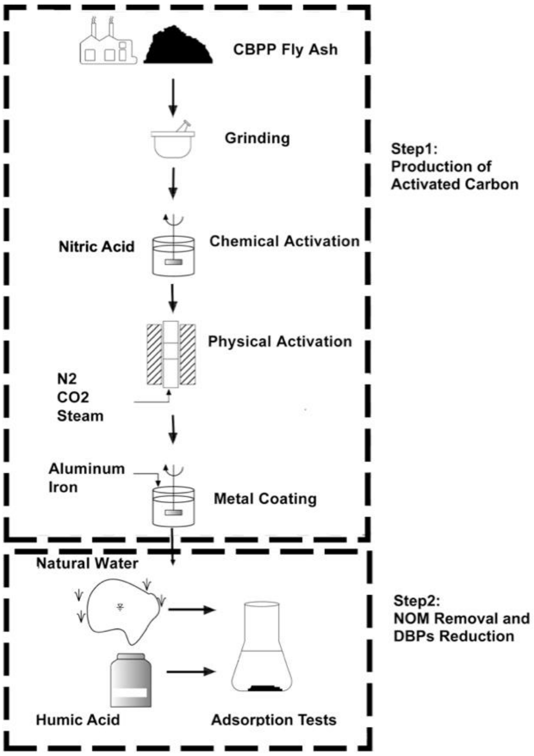
4.2.Materials and Methods

4.2.1. Production of activated carbon

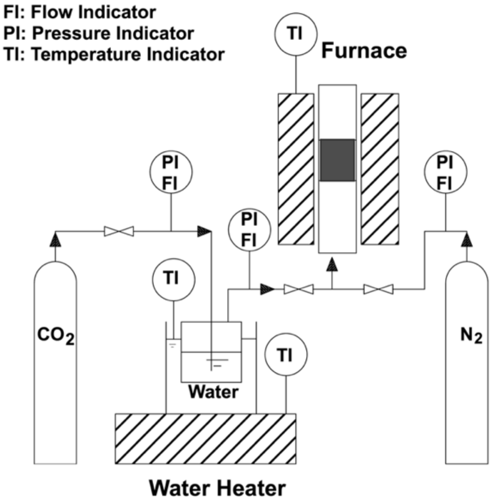
The carbonaceous waste (i.e., fly ash) of CBPPL at Corner Brook, NL, was chosen as the source of AC because of its abundance. The fly ash was first crushed and sieved by a No. 50 mesh to remove the particles larger than 300 microns. Then the sieved fly ash was washed with hot water at 80 °C and was filtered through a 0.45 µm nylon filter. The process was followed by drying the fly ash slurry in an oven overnight at 110 °C. The ground fly ash before washing with nitric acid is named CBPP-R in this paper. The suggested process by Shawabkeh *et al.,* 2015 for chemical activation and wash with nitric acid was followed with some modifications. The fly ash was immersed in nitric acid at the concentrations of 0% wt/wt, 5%, and 10% for hydrolysis and removing metals. The fly ash was in contact with acid in the ratio of 1 g to 10 mL, and the mixture was heated and stirred magnetically for four hours at boiling temperature of 110 °C. Then the fly ash was rinsed with double deionized water (DDIW) several times to reach a stable pH (i.e., delta pH < 0.5). After that, the sample was dried overnight (i.e., more than 12 h) in an oven at 110 °C until the weight was stabilized. The samples after drying are called CBPP-A0, CBPP-A5, and CBPP-A10, respectively. The washed samples were tested for elemental analysis, methylene blue adsorption, iodine number, and BET surface area.

Carbonization and activation are the important steps for increasing pore volume and surface area of AC. Previous studies have shown that increasing temperature during carbonization increases pore volume and surface area of AC and decreases the yield (Shadbahr and Husain, 2019; Zhang *et al.,* 2017a). The past study on CBPP waste management showed that increasing temperature under N_2 flow at the rate of 500 cm^3

min^{-1} at 15 °C per min to reach 850 °C and continuing carbonization for 1 h at the target temperature followed by 2 h of activation at 850 °C using a mixture of CO_2 and steam resulted in a reasonable yield (i.e., less than 50%) and high surface area (SA) (i.e., SA of 1146 g m^{-2}) (Shadbahr and Husain, 2019). However, the CBPP activation resulted in a microporous structure, which is not favorable for removing high molecular weight NOM. The method for physical activation suggested by Tanthapanichakoon *et al.,* (2005) and modified by Shadbahr *et al.,* (2019) was followed to produce AC in this study. Figures 4.2a, and 4.2b illustrate a schematic diagram of the steps of experiments in this study. The first step includes the production of AC (i.e., fly ash, grinding, chemical activation, physical activation, and metal coating), and the second step was performed to evaluate the performance of the metal-coated AC in NOM removal using natural water samples and humic acid solutions.



(**a**)



(**b**)

Figure 4. 2. Schematic of (a) the steps of production of activated carbons and evaluation of their performances in NOM and DBPs removal, (b) physical activation.

4.2.2. Metal impregnation on AC

The preparation of AC was followed by the metal coating of AC with iron 3 valent capacity and aluminum ions using ferric chloride and aluminum sulfate. The dried AC was added to 50 mL of prepared solutions of metal ions with different concentrations at an AC: metal ion ratio of 0.25, 0.50, 0.75, 1.00, 3.25, 5.50, 7.75, and 10.00% wt: wt. The mixture of AC and metal ions was shaken at 150 rpm on a shaker for 72 h at 25 °C to allow metal ions to penetrate the pores and the surface of the AC. Then the mixture was filtered by a 0.45 µm nylon filter and was dried in an oven at 110 °C for hydrolysis. The coated AC with iron (Fe-AC) and aluminum (Al-AC) were washed with DDIW several times to remove excess metal ions from the surface. The process was completed by drying the AC in an oven at 110 °C until the moisture was removed, and the weight of the AC was stabilized.

4.2.3. Reagents, materials, and instruments

Only analytical grade chemicals, including nitric acid (HNO_3) at the concentrations 5 and 10 wt/wt, were purchased from VWR, Canada, for oxidizing the carbon. The stock solutions of ferric chloride anhydrous ($FeCl_3$) and aluminum sulfate ($Al_2(SO_4)_3 \cdot 18\ H_2O$) were prepared daily as sources of Fe and Al for metal-coated AC and coagulation. Hydrochloric acid (HCl) 37% wt/wt, iodine solution (0.1 N), and sodium thiosulfate ($Na_2S_2O_3$) (0.1 N) were also purchased. Methylene blue (1500 ppm) was used for "single-point isotherm" indicating maximum adsorption of adsorbent within 30 min at 25 °C (Raposo *et al.,* 2009). NaClO at 30% wt/wt was used for chlorination. Methyl tert-butyl ether (MTBE) purchased from J.T. Baker, USA, was used for extraction of THM4 and HAA5 following the methods: EPA 551.1 (Hautman and Munch, 1997) and EPA 552.2 (Pawlecki-Vonderheide *et al.,* 1997) with an Agilent

6890 gas chromatograph equipped with ECD. UV absorbance was measured using a Genesys 10S UV/Vis's spectrophotometer (Thermo Fisher Scientific, USA). pH was measured using a benchtop FE20 pH meter (Mettler Toledo, USA). Carbon dioxide and nitrogen were of 99.99% purity and were purchased from Praxair Canada Inc. for AC generation.

4.2.4. Optimization

To find the most efficient operational conditions for the highest adsorption capacity, an optimization was carried out through the following steps: choosing the factors and levels; statistical design of experiment and developing a run sheet; analysis of the results and recognition of effective factors; developing the regression models through analysis of variances (ANOVA); evaluation of model accuracy; and projection of the optimized condition. The independent variables, i.e., time (A), AC dosage (B), and pH (C), were selected for investigating the DOC removal and equilibrium adsorption (qe). The AC dose was estimated based on the preliminary experiments (Zhang, *et al.,* 2017b). Table 4.1 demonstrates the factors and corresponding levels for the experiment.

Table 4. 1. The factors and their levels.

Factors	Symbol	Levels				
		(–α)	Lowest (–1)	Center (0)	Highest (+1)	(+α)
Contact Time (h)	A	0.50	5.26	12.25	19.23	24.00
Dosage (g/L)	B	0.05	0.14	0.27	0.40	0.50
pH	C	4.00	5.20	7.00	8.80	10.00

To acquire the lowest number of runs corresponding to clear effects, a response surface methodology (RSM) and central composite design (CCD) were chosen. The CCD design for 3 factors and 17 runs (13 runs and 4 center points) provides a resolution V design where the main and two-factor interactions are aliased with high order interactions (Montgomery, 2013). The experiments were performed in triplicate. A second-order quadratic model can correlate the factors to the responses (i.e., DOC removal and qe) using Equation (4.1).

$$\mathrm{Y} = \mathrm{f(X)} = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{J=i+1}^{k} \beta_{ij} X_i X_j + \sum_{i=1}^{k} \beta_{ii} X_i^2\,;\ (k = 3) \tag{4.1}$$

Similitude analysis and estimation of the coefficients in the quadratic model were performed using ANOVA via a backward elimination of insignificant factors (*p*-value > 0.10) with the Design-Expert, Stat-Ease, Inc., Minneapolis, USA, version 10.0.8.0 (2017). This software was also used for the generation of contour plots.

4.2.5. Characterization of AC and methods

The methods that were used for characterization of AC were: ASTM method D3838-05 for pH value, ASTM method D2867-09 for moisture content, ASTM method D2866-11 for ash content, single point isotherm within 30 min at 25 °C (Raposo *et al.,* 2009) for methylene blue adsorption, ASTM method D4607-1 for iodine value, pH of zero potential, and particle size using a Zetasizer Nano ZS (Malvern); Brunauer, Emmett, and Teller (BET) using a Micrometric Tristar II 3020 for nitrogen adsorption–desorption at 77K for measuring specific surface area and pore volume; ASTM method D8371-20 for metal content (Al and Fe) in AC using incineration; strong acid digestion, and ICP-OES for elemental analysis; scanning electron microscopy (SEM) using TERRA instruments for the investigation of surface microstructure and surface metal analysis.

4.2.6. Water sample analysis

Raw water samples were collected from three lakes that were the sources of small drinking water systems (i.e., serving less than 3000 people (Chowdhury, 2013)) in NL, Canada. The selected water samples were collected from August 2016 to July 2019 for evaluating the efficiency of AC in the removal of moderate to high levels of DOC and a VHA: DOC fraction of NOM (i.e., 0.67 to 0.81). Synthetic water samples containing model compounds of very hydrophobic acids and neutral hydrophilic fractions were prepared using HA and polysucrose with different mixing ratios as reported in Table 4.2. The stock solutions were prepared at a concentration of 1 g of the target chemical into 250 mL DDIW and stirring at 200 rpm overnight. The procedure was followed by passing the stock solution through a 0.45 μm nylon filter and slowly increasing the volume to 1 L before analysis by a DOC analyzer according to ASTM D7573 (2013). All raw and treated water samples were analyzed for pH, UV absorbance at the wavelength of 254 nm, DOC, and NOM fractionation based on hydrophobicity as described in (Tafvizi and Husain, 2021). DBPs (i.e., regulated THM4 and HAA5) were measured according to the formation potential content within 72 h after chlorination to minimize the noise/signal ratio of subjected parameters. The levels of free chlorine after 72 h were measured following N-diethyl-p-phenylenediamine (DPD) colorimetric method. The free chlorine levels were in the range of 0.05–0.20 mg/L.

Table 4. 2. Characteristics of water samples.

Sources	DOC (MgL^{-1})	UV254 (Cm^{-1})	THM4 (ppb)	HAA5 (ppb)	VHA (%)	SHA (%)	CHI (%)	NHI (%)
Natural	5.22–10.31	0.237–0.557	1639.35–2485.10	327.69–2157.70	67.05–81.20	5.56–7.41	1.92–3.11	8.21–25.09
Synthetic	9.05–9.42	1.063	1088.17	2213.49	100.00	0.00	0.00	0.00

DOC: dissolved organic carbon, UV254: ultraviolet absorbance at wavelength 254 nm, THM4: four regulated trihalomethanes, HAA5: five regulated haloacetic acids, VHA: very hydrophobic acids, SHA: slightly hydrophobic acids, CHI: charged hydrophilic, NHI: neutral hydrophilic.

4.2.7. NOM characterization

The water samples were characterized for NOM content by measuring DOC according to ASTM D7573 method (ASTM D7573, 2013), and NOM fractionation was performed based on hydrophobicity and acidity. NOM fractions were identified by adsorption into resins in four categories (i.e., very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilic (CHI), and neutral hydrophilic (NHI)) following the "rapid fractionation technique" [53,54] with modification in previous research (Tafvizi and Husain, 2021). NOM removal was evaluated using the modified AC with metal coating using iron and aluminum (i.e., Fe-AC and Al-AC) and non-modified AC. The NOM removal and DBPs reduction were calculated as:

$$R = \frac{C_i - C_f}{C_i} \times 100 \quad (4.2)$$

where C_i and C_f and are the initial and final concentrations of the water samples. The NOM removal was evaluated using natural water samples. The adsorbents were shaken in 200 mL of water samples at a concentration of 150 mg/L for 15 to 1440 min at the ambient temperature of 22 ± 2 °C. The process was followed by filtration of the mixture through 0.45 µm membrane. Then, the NOM removal was measured for all the metal-coated AC and raw AC. The metal-coated AC with Fe and Al showed the highest NOM removal efficiencies, which were selected for the equilibrium adsorption isotherms and kinetic studies.

4.2.8. Equilibrium adsorption isotherms

The adsorption of DOC in humic acid solution and natural water samples were investigated on the selected metal-coated ACs in synthesized and natural water samples. The synthetic water samples containing humic acids at a concentration of 10 mg/L and natural water samples were used for this step. Selected adsorbents at a concentration of

0.02 to 1 g/L were in contact with 200 mL of water samples on a shaker at a rotation speed of 150 rpm for 24 h to reach the equilibrium. Then the samples were passed through a 0.45 μm membrane filter and were tested for DOC content. The nonlinear form of Langmuir, Freundlich, and Temkin was used for the analyses using MATLAB (MATLAB R2020b, 2020). The amount of adsorbed DOC at time t, qt (mg/g) was calculated using the following

equation:

$$qt = \frac{C_i - C_f}{W} \times V, \qquad (4.2)$$

where C_i and C_f and the initial and final concentrations of DOC (mg/L) in the water samples, W (g) is the weight of tested adsorbent in the mixture, V (L) is the volume of the synthetic or natural water sample.

4.2.9. Adsorption kinetic models

To investigate the sorption kinetic models, AC and the optimized metal-coated ACs were added to the humic acid solution and natural water samples at a dosage of 0.15 g/L. The mixtures were shaken on a shaker for 5 to 1440 min. Then, the mixtures were filtered through a 0.45 μm filter and were tested for DOC and UV254. *Pseudo*-first order, *pseudo*-second order, and Evolich models were fitted to the data to figure out the best kinetic models.

4.3.Results and Discussion

4.3.1. Characterization of adsorbents

4.3.1.1. Effect of nitric acid on fly ash and activated carbon

To evaluate the effect of nitric acid on the pore structure of adsorbents before physical and thermal activation, elemental analysis was performed on CBPP-A0, CBPP-A5, and CBPP-A10. The effects were also investigated through measurement of

IN, MBV, BET surface area, mesopore, and micropore volumes of adsorbents after physical activation. The results of elemental analysis are presented in Table 4.3. The data from the treatment with nitric acid at concentrations of 5 and 10% show a decrease in the levels of iron, aluminum, copper, and calcium. The increase in the concentration of nitric acid shows 0.97 to 23.60 (mol × 10^{-6}) improvement in the removal of metals from the fly ash. However, the doubled intensity of acid washing (i.e., from 5 to 10%) did not have the same effects in the removal of all elements (i.e., zinc and copper). The magnitude of metal removal depends on the type of metal (i.e., reduction potential) and strength of the acid. Nitric acid solution with 0–10% concentration is categorized as very diluted with the capability of dissolving most reactive metals (i.e., reduction potential < −0.4 V) (Kurushkin, 2015). The results show that the chemical treatment of fly ash with nitric acid is a crucial step before activation. The highest level of metal removal (mol× 10^{-6}) from the adsorbent precursor (i.e., CBPP before activation) belongs to calcium that poses the lowest reduction potential value among the listed metals in Table 3 (Swift and Butler, 1972) and the highest concentration of metal in the fly ash. An increase in the concentration of nitric acid from 5 to 10% does not affect the reactivity of the nitric acid (Kurushkin, 2015). However, an increase in the available oxidant in the acid solution has resulted in an obvious improvement in the removal of calcium, magnesium, and aluminum from the fly ash. The measured pH for three different types of nitric acid-washed fly ash (i.e., CBPP A0, CBPP-A5, and CBPP A10) after several rinses with DDIW are 11.05, 3.45, and 3.24. The ash and moisture contents for CBPP-A0 are 13.88 ± 27 and 1.72 ± 0.10, respectively. The values for CBPP-A5 are 3.92 ± 0.05 and 0.47 ± 0.05, respectively. The ash and moisture content for CBPP-A10 are 3.62 ± 0.05 and 0.43 ± 0.05, respectively.

Table 4. 3. The effect of nitric acid on elemental analysis.

Element	Metal Content (ppm)			Metal Removal (mol × 10^{-6})			
	CBPP-A0 [1]	CBPP-A5 [1]	CBPP-A10	A0	A5	A10	Diff.
Iron	784	175.19	121	0.00	10.90	11.87	0.97
Aluminum	947	281.31	201	0.00	24.75	27.73	2.98
Magnesium	511	185.33	86	0.00	13.40	17.49	4.09
Zinc	11.72	9.07	6.75	0.00	<1	<1	NA
Copper	7.28	<2	<2	0.00	<1	<1	NA
Calcium	2656	1481	535	0.00	29.31	52.92	23.60

[1] Data retrieved from previous studies (Shadbahr and Husain, 2019; Zhang *et al.,* 2017a). A0: nitric acid (0% wt: wt), A5: nitric acid (5% wt: wt), A10: nitric acid (10% wt: wt), CBPP: Corner Brook pulp and paper fly ash, Diff.: metal removal (mol× 10^{-6}) = A10 – A5.

To increase the absorption properties of acid-washed fly ash, 10 g of the samples (CBPP-A0, CBPP-A5, and CBPP-A10) were placed in the tube furnace (Carbolite Gero, Germany). The furnace was programmed to increase the temperature at a rate of 15 °C/min using nitrogen gas, with a rate of 500 cm^3/min, to reach 850 °C for carbonization. Then, the nitrogen flow was switched to a mixture of CO_2 gas (purity > 99.99%) and water vapor, with a flow of 500 cm^3/min, for two hours at 850 °C, to perform the activation process and to increase the porosity, which was described in the previous research (Husain and Taghizadehgan, 2019; Shadbahr and Husain, 2019). The importance of the surface area and the characteristics of the porous structure of activated carbon are inevitable for the evaluation of adsorbents, which can be measured by BET sorption. Methylene blue dye and iodine can be used as easy methods for the estimation of the surface area and the porous structure of AC. MBV can express estimation of the mesoporous volume and IN shows the microporous structure of AC (Nunes and Guerreiro, 2011). The results of IN and MBV for activated samples are presented in Figure 4. 3. An increase in the concentration of nitric acid has increased both MBV and IN. MBV for the activated carbon that was cleaned by 5 and 10% nitric acid are 214 and 265 mg/g, while the related IN adsorption were 1023 and 1212 mg/g, respectively. Thus, a 23.77 and 18.47% increase for MBV and IN, respectively, were obtained by increasing the concentration of nitric acid from 5 to 10%. Thus, an increase in the concentration of nitric acid (i.e., from 5 to 10%) resulted in better development of mesopore structure rather than micropores. The results agree with earlier findings. El-Hindawy found that nitric acid increased the mesoporous structure of activated corncob of the surface pores (El-Hendawy, 2003). Another study on oil waste also showed that treatment with HNO_3, even in moderate concentrations (i.e., at 5.2 N), improved the mesoporosity of adsorbent (Nagano et al., 2000). As a result, AC-A10 was selected for further investigations and metal coating.

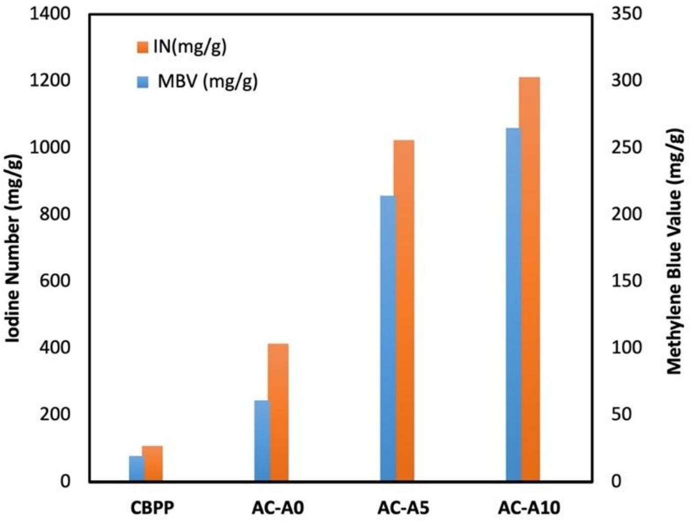
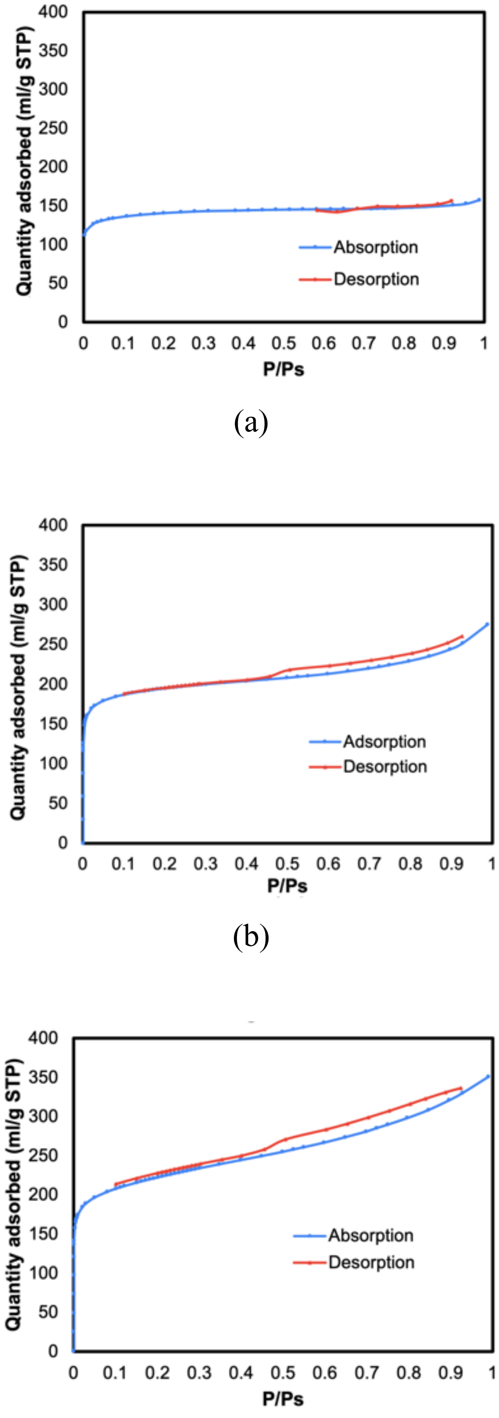


Figure 4. 3. The effect of nitric acid on methylene blue value and iodine number after activation.

The BET surface area and pore size distribution are ruling characteristics that show the ability of the medium to remove the adsorbates (Auta and Hameed, 2012). N_2 adsorption isotherms of AC-A0, AC-A5, and AC-A10 are presented in Figure 4. 4a–c. BET surface areas of 455.79, 726.83, and 808.29 m^2/g were obtained for AC-A0, AC-A5, and AC-A10 accordingly. The pore volumes of 0.11, 0.18, and 0.21 cm^3/g have resulted, respectively. An increase in the concentration of nitric acid solution increased the pore volume and BET surface area. The pore width analysis for AC-A5 showed an average pore width of 9.2 nm, while the pore width for AC-A10 was 10.5 nm. Thus, nitric acid positively contributed to the development of a more porous surface structure and wider pores. The N_2 adsorption–desorption isotherm for AC-A0 in Figure 4. 4a belongs to type I isotherms, indicating a microporous structure. An increase in the concentration of nitric acid in Figures 4. 4b,c demonstrates the change of isotherm to type II with an increase in the amount of macropores and a mixture of monolayer and multilayer adsorptions (Thommes *et al.,* 2015). The results in gas adsorption agree with soaring values of MBV with an increase in nitric acid concentrations, which confirms the positive effect of nitric acid in increasing the mesopores and macropores in AC-A10.



(a)

(b)

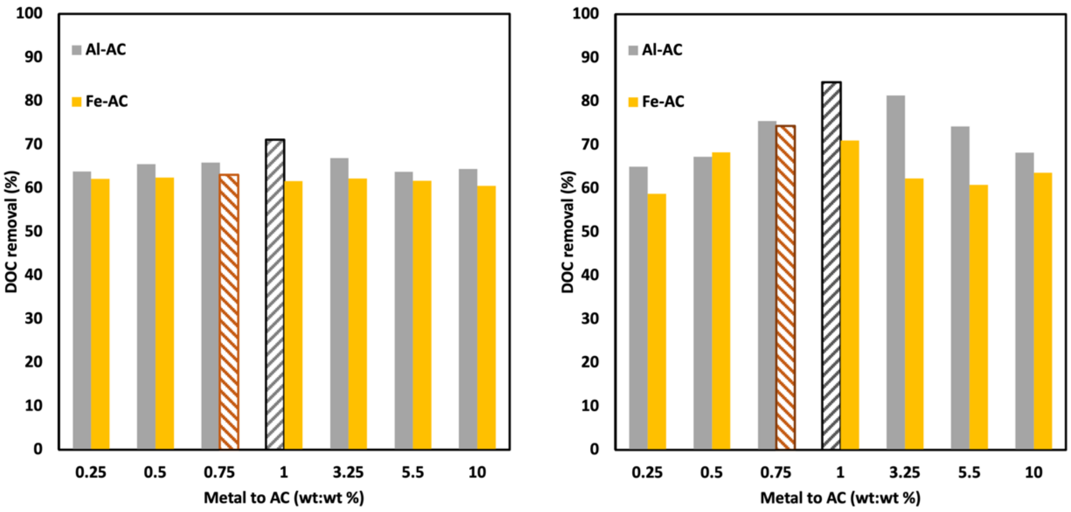
(c)

Figure 4. 4. N_2 adsorption isotherm: (a) AC-A0, (b) AC-A5, (c) AC-A10.

4.3.1.2.Metal coating on activated carbon

Optimization and Metal Leach

Adsorption tests were performed in triplicate testing using natural water (i.e., water samples 1 and 2) to determine the best dosage of metal impregnation on the fly ash-based AC-A10 using ferric chloride and aluminum sulfate. Thus, AC-A10, Fe-AC, and Al-AC with impregnation rates of 0.25 to 10.00% (wt: wt) of AC to metal ions were mixed with water sample 1 at a dosage of 0.15 g/L. Adsorbents were in contact with water for 24 h to employ the highest adsorption capacity of developed AC, as was resulted in the optimization step. The performance of AC-A10 and modified AC (i.e., metal-coated) in DOC removal are presented in Figures 4. 5a, b. The highest NOM removal by Al-AC of 71.09 and 84.40% was obtained by metal: AC ratio of 1% in water samples 1 and 2, respectively. The best performance of Fe-AC has resulted in a metal: AC ratio of 0.75% with 63.07 and 74.32% in water samples 1 and 2, respectively. The adsorption results on both water samples revealed that modified AC with iron and aluminum had an increased DOC removal with increasing metal to AC ratio up to 0.75% and 1.00% iron and aluminum, respectively. A decrease in NOM removal was observed with higher impregnation rates. However, the deviations in the removal of DOC in water sample 1 by Fe-AC were not as obvious as the results obtained in water sample 2. Generally, Al-AC showed a higher NOM removal in comparison to the iron-coated ACs in both water samples. Thus, the best modified AC with metals is Al-AC 1% and Fe-AC 0.75%.



(a) (b)

Figure 4. 5. DOC removal by metal-coated activated carbons: (a) water sample 1, (b) water sample 2.

The results of ICP-OES on raw and treated water samples by Al-AC and Fe-AC with metal: AC ratio of 0.25 to 5.5% are presented in Table 4.4. The results of the treated water samples show that the highest concentrations of Al and Fe are 100 ± 10 and 70 ± 10 ppb, respectively. The maximum allowable concentration of aluminum and iron in treated waters according to “secondary drinking water regulation” are 200 and 300 ppb, respectively (U.S. EPA, 2018). Thus, even with high levels of metal coating on the activated carbon (i.e., 10%), the metal leaching from developed AC in this study was not observed. Further, the concentrations of Al, Fe, and Ca in treated water samples were decreased. The results of Fe and Al concentration show that Fe concentration has dropped to 0.05 mg/L in the treated water sample by 1.00% Al-AC (i.e., removal = 68%) in comparison with the removal efficiency of 56% by 0.75% Fe-AC. Therefore, the produced adsorbents in this research are safe for water treatment.

Table 4. 4. Metal leaching by modified activated carbon during water treatment

Water Sample	Metal Content (mg/L)								
	Fe	Al	Mg	Ca	Zn	Cu	As	Mn	Hg
Raw Water	0.16	0.13	6.66	2.41	0.017	<0.01	<0.02	0.009	<0.1
0.25% Al-AC [1]	0.06	0.05	6.60	2.28	0.015	0.03	<0.02	0.036	<0.1
0.50% Al-AC [1]	0.06	0.06	6.65	2.30	0.016	<0.01	<0.02	0.023	<0.2
0.75% Al-AC [1]	0.06	0.08	6.59	2.31	0.016	0.05	<0.02	0.011	<0.1
1.00% Al-AC [1]	0.05	0.08	6.66	2.36	0.018	0.01	<0.02	0.011	<0.1
3.25% Al-AC [1]	0.06	0.09	6.57	2.30	0.016	<0.01	<0.02	0.009	<0.1
5.50% Al-AC [1]	0.06	0.10	6.54	2.31	0.018	0.04	<0.02	0.008	<0.1
0.25% Fe-AC [1]	0.06	0.04	6.63	2.48	0.017	<0.01	<0.02	0.053	<0.1
0.50% Fe-AC [1]	0.07	0.04	6.81	2.42	0.016	<0.01	<0.02	0.044	<0.1
0.75% Fe-AC [1]	0.07	0.04	6.63	2.34	0.012	<0.01	<0.02	0.037	<0.1
1.00% Fe-AC [1]	0.07	0.05	6.56	2.33	0.013	0.03	<0.02	0.024	<0.1
3.25% Fe-AC [1]	0.07	0.04	6.62	2.30	0.012	0.06	<0.02	0.009	<0.1
5.50% Fe-AC [1]	0.06	0.05	6.56	2.34	0.013	0.04	<0.02	0.023	<0.1

[1] Treated water samples with modified activated carbon. Al-AC: aluminum coated activated carbon, Fe-AC: iron coated activated carbon.

Characterization of Metal Coated Activated Carbon

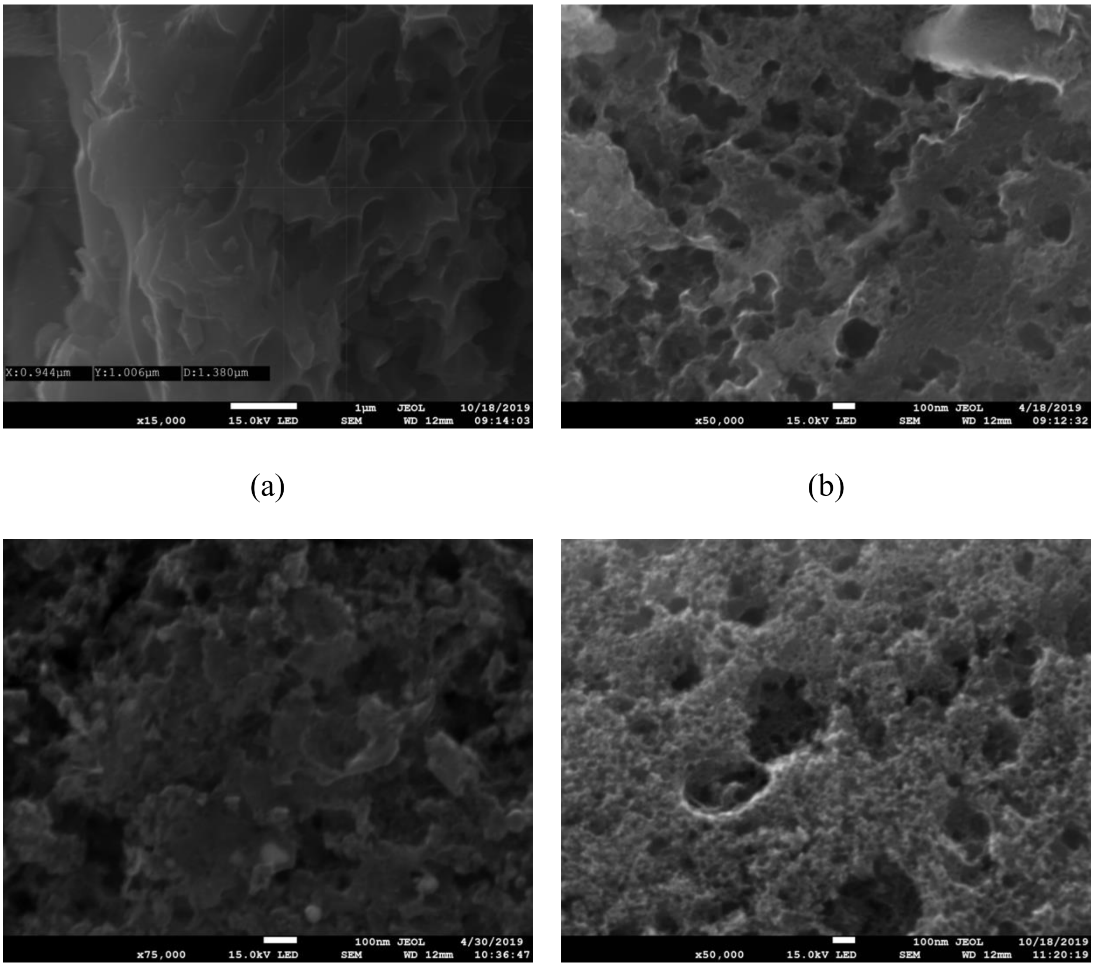
The BET surface area, micropore volume, Langmuir surface area, MBV, IN, zero potential pH, and particle size by Zetasizer for AC-A10, 0.75% Fe-AC, and 1.00% Al-AC are presented in Table 4.5. The results from the N_2 adsorption isotherm show that the metal coating of AC decreases surface area and micro pore volume (i.e., AC-A10 > 1.00Al-AC > 0.75% Fe-AC). The results of DOC adsorption by Al-AC and Fe-AC showed higher NOM removal by Al-AC compared to Fe-AC. The results agree with the lower surface area and Langmuir surface area of 0.75% Fe-AC in comparison to Al-AC. In addition, the iodine numbers of 931 and 925 mg/g for Fe-AC and 1.00 Al-AC demonstrate a more microporous structure for 0.75 Fe-AC. The iodine adsorption showed a significant decrease by metal coating on AC, which shows that a small portion of micro pores (i.e., 4.7 to 10.8% of Langmuir surface area) have been blocked by metal oxides.

Table 4. 5. Metal leaching by modified activated carbon during water treatment.

Sample	Surface Area (BET) (m^2/g)	Micropore Volume (cm^3/g)	Langmuir Surface Area (m^2/g)	MBV (mg/g)	IN (mg/g)	pH_{pzc}	Size (d.nm) *
AC-A10	808.29	0.21	995.65	265	1212	5.98	2039
1.00% Al-AC	783.29	0.18	948.92	234	925	6.61	1976
0.75% Fe-AC	709.89	0.19	888.09	226	931	6.43	2620

AC: activated carbon, BET: Brunauer, Emmett, and Teller, IN: iodine number, MBV: methylene blue value, pHpzc: pH of zero potential charges, Al-AC: aluminum coated activated carbon, Fe-AC: iron coated activated carbon, * size (d. m): measured particle size by Zetasizer.

The SEM results for CBPP-A10, AC-A10, 1.00% Al-AC, and 0.75% Fe-AC are presented in Figure 4. 6a–d. The captured images demonstrate a high share of macropores and mesopores in a high surface area (808.29 m^2/g) of AC with 10% nitric acid (Figure 4. 6b). Metal coatings on AC have decreased the porous structure of the surface of AC (Figure 4. 6c,d).



(a) (b)

(c) (d)

Figure 4. 6. Scanning electron microscopy images for (a) CBPP A-10, (b) AC-A10, (c) 1% Al-AC, (d) 0.75% Fe-AC.

The captured images agree with the results for BET surface areas. The images demonstrate an uneven morphological structure in metal-coated AC with aluminum and iron. The surface of CBPP-A10 and AC-A10 are smoother with wider pores.

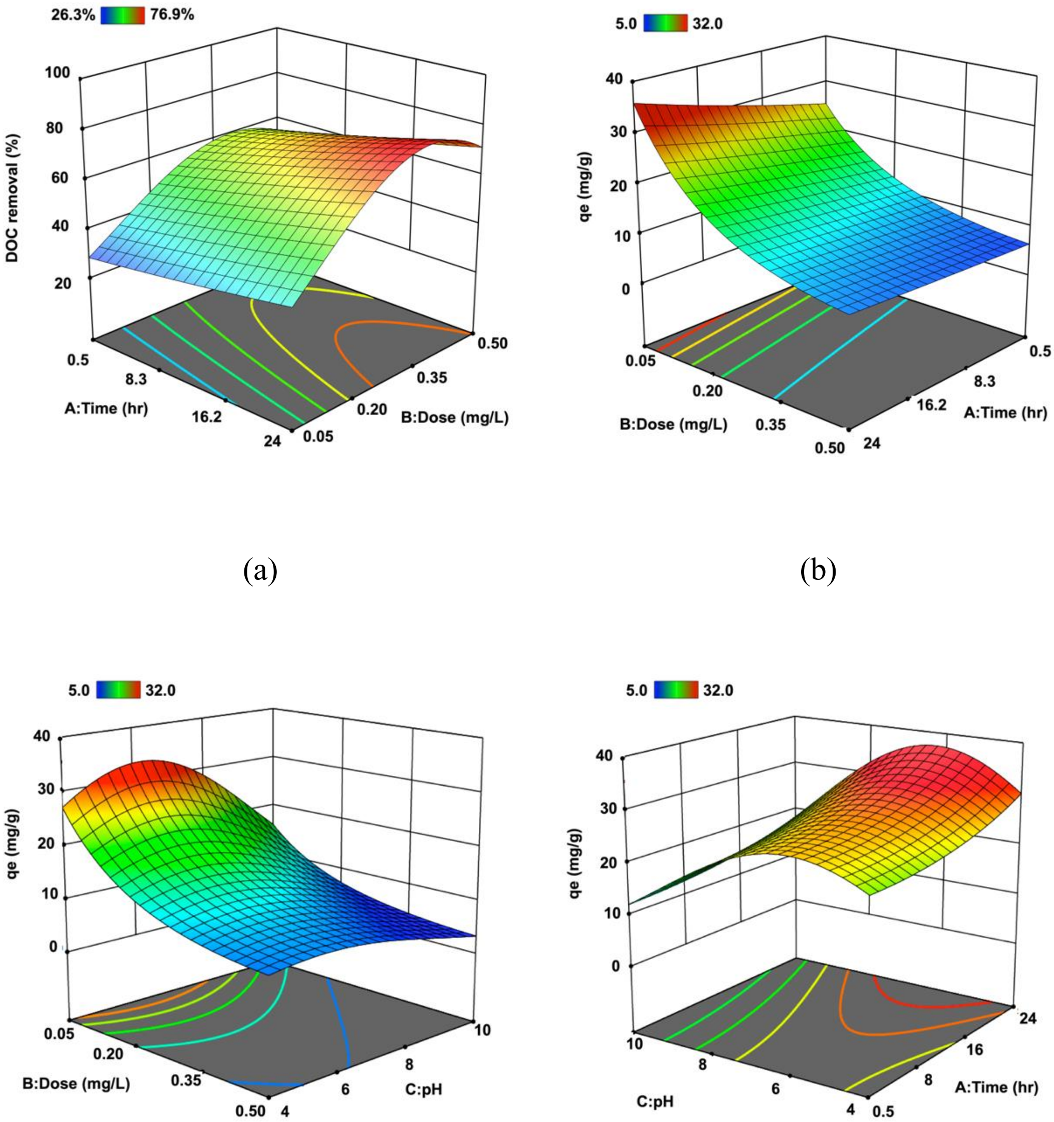
4.3.2. Optimization of Dose

Optimization was performed for finding the most efficient dosage (i.e., highest adsorption capacity and lowest dosage resulting in DOC removal > 50%) of developed ACs. The experimental design included 2^3 factorial runs, six CCD experiments, and three center points that were randomized and combined using Design Expert (version 10.0.8, 2017). Three factors of pH, dosage and contact time were investigated, where the studied ranges for variables are: pH: 4–10; time (h): 0.5–24; and dosage (g/L): 0.05–0.50. The results of the experiments on DOC removal (response 1) and adsorption capacity (response 2) are presented in Table S.4.1 in the supplementary material (SM). The maximized adsorption capacity was 18.25 mg/g that was obtained in a combination of variables (dosage: 0.14 g/L; pH: 5.26; and contact time: 19 h). The highest removal efficiency for DOC was 76.92% at pH of 7, a dosage of 0.275 g/L of AC, and a contact time of 24 h. In general, the efficiency of DOC removal increased with the increase of AC dosage (i.e., 0.25–0.50 g/L) and contact time (i.e., 24 h). A 3D plot of the responses versus time and dosage is presented in Figure 4. 7a,b. The ANOVA for q_e and DOC removal are presented in Table 4.6. The models' terms with *p*-value < 0.05 were significant and were included in the regression. However, the ANOVA table for all the main factors, two-factor interactions, and quadratic terms are presented in Tables S.4.2 and S.4.3 in SM. The $R^2_{adjusted}$, and $R^2_{predicted}$ were used to investigate the precision of the models. No substantial variation was observed between the terms, which demonstrates the precision of models in fitting data and prediction of new points using the models. The adequacy of models was investigated with the normality of residuals. The normal plots for the residuals are presented in Figure S.4.1 a,b in SM. The main significant factors in both models in the order of magnitude are concentration > pH > contact time. Moreover, the quadratic terms of Dose^2 and pH^2 had *p*-values less than 0.05 and were included in the models in Equations 4.2 and 4.3.

Table 4. 6. ANOVA results obtained for DOC removal and adsorption capacity.

Responses	R^2	$R^2_{Adjusted}$	$R^2_{Predicted}$	F-Value $_{model}$	p-Value $_{model}$
DOC removal	0.95	0.93	0.87	46.10	<0.0001
qe	0.97	0.96	0.93	92.65	<0.0001

DOC: dissolved organic carbon, qe: adsorption capacity (mg/g).



(a) (b)

(c) (d)

Figure 4. 7. 3D surface plots for (a) the effect of Dose x Time on DOC removal (%), (b) Dose and Time on adsorption capacity, qe, (mg/g), (c) Dose and pH on qe (mg/g), and (d) Time and pH on qe.

$$Ln(DOC) = 1.636 + 0.0131Time + 5.078Dose + 0.526pH - 6.756Dose^2 - 0.046pH^2, \quad (3.4)$$

$$Ln(qe) = 1.851 + 0.0131Time - 5.463Dose + 0.576pH + 4.217Dose^2 - 0.049pH^2, \quad (4.4)$$

where the actual levels of the variables are mentioned in Table 4.1. Adsorption can be an economical process if the cost efficiency of the adsorbent can be maintained. To prevent consumption of excess adsorbent, an optimization of AC was performed to minimize adsorbent dosage and maximize the efficiency of adsorption (i.e., highest adsorption capacity and lowest adsorbent dosage). A desirability function using Design-Expert software was performed to find the optimal conditions. The best result at the highest desirability value revealed that 0.141 g/L of AC and the maximum contact time of 24 h can result in a qe of 32 mg DOC/g. The results were used for the kinetic studies on AC, 0.75% Fe-AC, and 1.00% Al-AC.

4.3.3. Equilibrium adsorption isotherms

Langmuir and Freundlich are the widely used models in studies related to water treatment using AC (Menya *et al.,* 2018) and removal of HA from water using adsorption (Dehghani *et al.,* 2018). The Temkin model has also been used in previous studies (Dehghani *et al.,* 2017). In this research, Langmuir, Freundlich, and Temkin models were investigated. The models are represented as:

$$q_e = \frac{K_L q_m C_e}{1+K_L C_e}, \quad (4.6)$$

$$q_e = K_f {C_e}^{\frac{1}{n}}, \quad (4.5)$$

$$q_e = Bln(A) + Bln(C_e), \quad (4.6)$$

where, q_e (mg/g) = equilibrium adsorption capacity, q_m (mg/g) = maximum adsorption capacity, C_e (mg/L) = concentration of adsorbate (i.e., DOC) at equilibrium, K_L (L/mg) = Langmuir equilibrium constant, an indicator of affinity of the binding sites, K_f (L/g) = Freundlich constant, B = RT/b, b (J/mol) = Temkin sorption heat constant, A is isotherm constant in Temkin model (Ayawei *et al.,* 2017; Dehghani *et al.,* 2017, 2018).

The data from adsorption isotherms for 1% Al-AC, 0.75% Fe-AC, and AC-A10 were best fitted to the Langmuir model. The Langmuir isotherm is a dynamic equilibrium, which relates the adsorption to the available open sites in the surface and indicates a proportional relationship between desorption and blocked pores (Ayawei *et al.,* 2017). The adsorption isotherms for DOC removal from natural and synthetic water samples are presented in Figure 4. 8 a–f. The results indicate that the adsorption capacity of AC in natural water (i.e., the mixture of all NOM fractions (VHA, SHA, CHI, and NHI)) is higher than HA-synthesized water. Past studies showed that the adsorption of NOM to AC depended on the molecular size and NOM type (Newcombe *et al.,* 2002). NOM with low molecular weight is more prone to be removed from water by adsorption (Menya *et al.,* 2018), which is consistent with the findings in this study (Parsons *et al.,* 2014). The higher adsorption capacities of metal-modified ACs (i.e., 1% Al-AC and 0.75% Fe-AC) than non-modified AC (i.e., AC-A10) can be justified by a more positive charge on metal-coated AC. The negative surface charge of AC-A10 results in less affinity of AC to NOM. Metal ions (i.e., Al^{3+} and Fe^{3+}) on the surface of AC affect NOM adsorption positively in natural water's pH due to the negative charge of NOM molecules with carboxyl and hydroxyl groups. Thus, NOM is adsorbed to the metal-coated AC (Park *et al.,* 2015). The parameters for Freundlich and Temkin models are presented in Table S4.4 of SI.

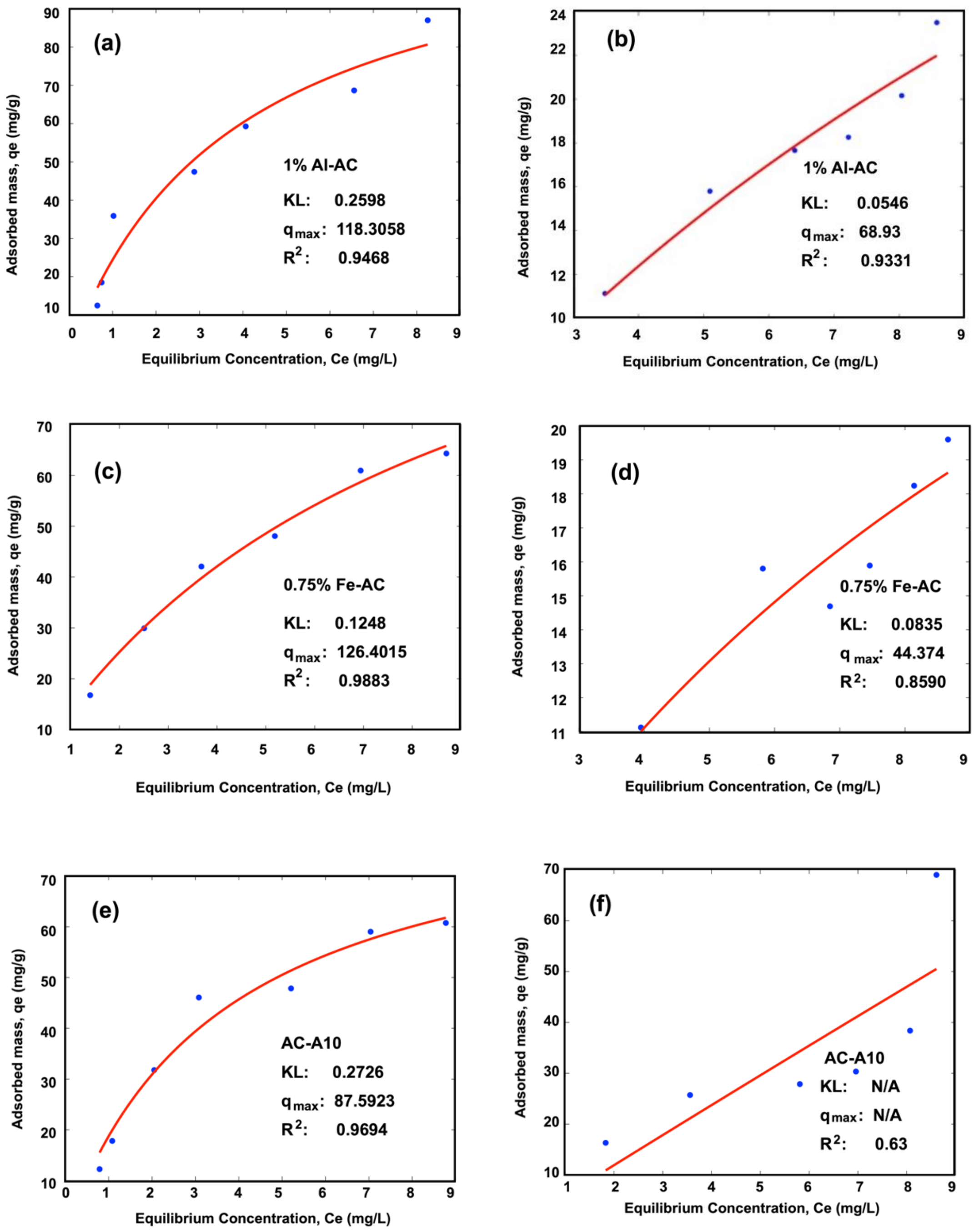


Figure 4. 8. Langmuir equilibrium isotherm models for NOM removal by (a) 1% Al-AC in natural water, (b) 1% Al-AC in synthesized water, (c) 0.75% Fe-AC in natural water, (d) 0.75% Fe-AC in synthesized water, (e) AC-A10 in natural water, (f) AC-A10 in synthesized water. AC: activated carbon, KL: Langmuir equilibrium constant (L/mg), q_{max}: maximum adsorption capacity (mg/g), R^2: coefficient of determination.

A comparison of the maximum adsorption capacity, BET, and sources of AC are presented in Table 4.7. In the past studies, q_{max} for HA and DOC adsorption was in the ranges of 18.91–76.92 and 2.21–51.81 mg/g, respectively. A comprehensive study on eight different commercial granular-activated carbons with a specific surface area of 809 to 1419 m^2/g in batch and micro column tests revealed that q_e were in a range of 1.19–27.1 mg DOC/g (Golea *et al.,* 2020). Impregnation of commercial AC with maghemite (MPAC) showed that the modified AC had a lower affinity in NOM, and the BET surface area was decreased from 769 m^2/g in non-modified AC to 575 m^2/g in MPAC (Lompe *et al.,* 2017). However, the obtained results showed that the metal impregnation on AC increased the adsorption capacity of AC by 35.06 to 44.31%.

Table 4. 7. The characteristics of AC for DOC adsorption in recent studies.

Adsorbent	Source of Adsorbent	Surface Area (BET) (m^2/g)	Water Sample	Target Adsorbate	Langmuir Constant (K_L)	qmax (mg/g)	Reference
AC-A10	Fly ash	808.29	Natural	DOC	0.2726	87.59	This study
1.00% Al-AC	Fly ash	783.29	Natural	DOC	0.2598	118.30	This study
0.75% Fe-AC	Fly ash	709.89	Natural	DOC	0.1248	126.40	This study
AC-A5	Fly ash	847.26	Natural	DOC	N/A	3.70	(Zhang, *et al.,* 2017b)
AC	Coconut palm	715.50	Synthesized	DOC	0.489	51.81	(Ribau Teixeira *et al.,* 2017)
AC	Coconut shell	808	Synthesized	DOC	1.17	2.21	(Iriarte-Velasco *et al.,* 2008)
AC	Bituminous coal	852	Synthesized	DOC	7.34	27.60	(Iriarte-Velasco *et al.,* 2008)
Non-modified GACs	8 CAC	809–1419	Synthesized	DOC	N/A	1.19 [1]– 27.1	(Golea *et al.,* 2020)
Non-modified	CAC	659	Synthesized	HA	N/A	20.39	(Eustáquio *et al.,* 2015)
H_3PO_4 AC	CAC	711	Synthesized	HA	N/A	25.64	(Eustáquio *et al.,* 2015)
H_2SO_4 AC	CAC	724	Synthesized	HA	N/A	18.91	(Eustáquio *et al.,* 2015)
$ZnCl_2$ AC	Agricultural waste	970	Synthesized	HA	0.22	76.92	(Bouras *et al.,* 2015)
GAC	CAC	1100	Synthesized	HA	0.004	16.66	(Yang and Fox, 2018)
HNO_3 PAC	CAC	N/A	Synthesized	HA	0.0086	76.92	(Yang and Fox, 2018)

AC: activated carbon, DOC: dissolved organic carbon, q_{max}: maximum adsorption capacity (mg/g), K_L: Langmuir equilibrium constant (L/mg), CAC: commercial activated carbon, GAC: granular activated carbon, MPAC: maghemite impregnated powder activated carbon, HA: humic acid [1] Equilibrium adsorption capacity is reported.

4.3.4. Kinetic studies

The performance of the developed AC (i.e., AC-A10, 0.75% Fe-AC, and 1% Al-AC) was evaluated by adding 0.15 g/L of AC (optimum dosage) to natural and synthetic water samples, and DOC was measured between 5–1440 min of dosing. The results are plotted in Figure 4.9. The widely used kinetic models, including *pseudo*-first order (PFO) (Equation 4.9) and *pseudo*-second order (PSO) (Equation 4.10), were assessed to investigate the adsorption mechanism of NOM removal (Wang and Guo, 2020).

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \tag{4.7}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \tag{4.8}$$

where q_t = adsorbed amount of adsorbate at time (t); k_1 = PFO rate constant (h^{-1}); k_2 = PSO rate constant (g/mg·h); q_e = the adsorption capacity at equilibrium.

PSO describes an adsorption process corresponding to the available sites on the adsorbent. The motivating force in PSO is proportional to the non-blocked adsorbent sites. The results showed that PSO was the best fitted kinetic model for all three ACs in this study and the calculated parameters are presented in Table 4.8. The highest efficiency in DOC removal was related to 1.00% Al-AC with the lowest k_2 of 0.0011 g/mg.hr. The constant rates for 0.75% Fe-AC and AC-A10 are 0.0014 and 0.0082 g/mg.hr, respectively. The high adsorption rate of metal-coated AC is in agreement with previous studies, which showed that iron species were effective in removing NOM and HA from water through catalyzing effects on oxidation and adsorption (Kaplan Bekaroglu *et al.,* 2016). The surface chemistry of AC also influences the absorptivity of NOM. A positive charge on the surface of modified AC enhances NOM removal (Dastgheib *et al.,* 2004).

Table 4. 8. The fitted kinetic model for the adsorption.

Adsorbent	Water Sample	Model	Target Adsorbate	k_2 and k_1	R^2
0.75% Fe-AC	Natural	PSO	DOC	0.0014	0.9981
1.00% Al-AC	Natural	PSO	DOC	0.0011	0.9983
AC-A10	Natural	PSO	DOC	0.0082	0.9992
0.75% Fe-AC	Natural	30 min-PFO	DOC	0.077	0.9971
1.00% Al-AC	Natural	30 min-PFO	DOC	0.086	0.9999
AC-A10	Natural	30 min-PFO	DOC	0.048	0.9971

AC: activated carbon, PSO: *pseudo*-second order, DOC: dissolver organic carbon, k_1: PFO constant (h^{-1}), k_2: PSO constant (g/mg·h), R^2: correlation coefficient.

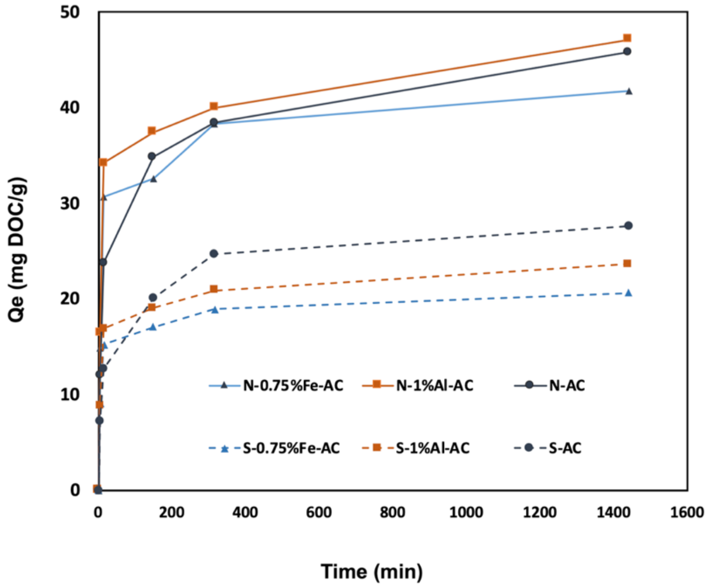


Figure 4. 9. Adsorption kinetics for 0.75% Fe-AC, 1%Al-AC, and AC-A10. N: natural water, S: synthesized water, AC: activated carbon, Qe: adsorbed mass (mg DOC/g)

Figure 4. 9 demonstrates higher adsorption rates of metal-coated AC in the first 30 min of adsorption in comparison with AC-A10. To evaluate the adsorption rates of ACs, the constant rates for the first 30 min k_1 are reported (Table 4.8) as 0.077, 0.086, and 0.048 for 0.75% Fe-AC, 1.00% Al-AC, and AC-A10, accordingly. The metal coating improved the adsorption of DOC by up to 43% in the first 30 min. Previous studies reported that iron oxide enhanced the removal of high molecular weight NOM with UV absorbance higher than 280 through adsorption. The obtained results showed a higher initial DOC uptake in iron-coated pumices (Kitis *et al.,* 2007; Swietlik *et al.,* 2015). A past study reported that 60–70% of FA were adsorbed to the magnetic oxides in the first 10–20 min, and a *pseudo*-second order kinetic model was fitted to the data showing the effect of physiochemical adsorption (Swietlik *et al.,* 2015). Their reported data showed that more than 50% of HA was adsorbed to the adsorbent in the first 10 min. This is possibly due to the break of high molecular weight because of oxidation and the ligand exchange between functional groups of NOM (i.e., carboxyl/hydroxyl) and cations (i.e., aluminum and iron oxides) (Safiur Rahman *et al.,* 2013). In addition, the break-in HMW NOM makes the hidden proper functional groups available (Swietlik *et al.,* 2015) and increases the adsorption kinetic rates. The adsorption results for DOC in natural water for all three selected ACs in the present study were higher than the synthesized water containing HA. This can be due to better adsorption of low molecular weight NOM into ACs pores comparing to HA with large molecular sizes.

To evaluate the performance of AC-A10 and metal-coated ACs on the removal of the precursors of HAA5 and THM4 from natural water samples, the formation potential of HAA5 and THM4 was measured within 72 h of chlorination. The developed AC was mixed with natural water samples at a dosage of 0.02 to 0.50 g/L for 24 h. The treated water samples were tested for HAA5 and THM4. The results showed that the maximum adsorption capacities of HAA5 precursors at equilibrium (q_e) were 39.74, 34.03, and 22.44 mg/g for 1.00% Al-AC, 0.75% Fe-AC, and AC-A10, respectively. The q_e values for THM4 were 60.20, 52.25, and 42.78 mg/g, indicating that metal-coated ACs showed enhanced removal of THM4 (22.1% and 40.7% for Fe-AC and Al-AC, respectively) and HAA5 precursors (51.6% and 77.1% for Fe-AC and Al-AC, respectively). Beyond the first 30 min, no model was found to satisfy the data (Figure 4. 9 and Table S.4.2).

4.4. Summary

Low-cost activated carbon was developed using fly ash from a local pulp and paper company for removing NOM from natural and synthetic water samples. The chemical activation using nitric acid concentration of 10% increased the surface area and improved mesoporosity of the developed AC-A10. Optimization of adsorption capacity showed that a dosage of 0.15 g/L of AC for 24 h would result in the maximized adsorption of DOC. Metal coating on AC-A10 using three valent ions of Fe and Al derived from ferric chloride and aluminum sulfate were optimized for the adsorption of DOC. The ratio of Al: AC of 1.00% and Fe: AC of 0.75% resulted in 44 and 35%, respectively, improvements in the adsorption capacities for DOC in comparison to AC-A10. However, a decrease in the surface area of the ACs was observed. The ACs were more effective in removing NOM from natural water samples than the synthetic water samples, which can be related to the better performance of AC in removing the low molecular weight NOM. The adsorption capacity of 1.00% Al-AC and 0.75% Fe-AC showed 77 and 51% improvement in HAA5 reduction, and their performances in THM4 reduction were 40.7 and 22.1%, respectively. The adsorption characteristics of 1.00% Al-AC outweigh the performance of 0.75% Fe-AC in NOM removal. The elemental analysis on the natural and treated water samples showed the ability of 1.00% Al-AC in removing Fe from water, which can be beneficial to the small water systems in NL with high levels of iron in the sources of drinking water.

4.5. References

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CHAPTER FIVE

TREATMENT OF NATURAL ORGANIC MATTER WITH ENHANCED COAGULATION AND ADSORPTION FOR CONTROLLING DBPS

This chapter has converted to a publishable paper, ready for submission. The present authos is the first and corresponding author of this manuscript. Along with the co-authors, Dr. Baiyu Zhang, Dr. Bing Chen, Dr. Shakhawat Chowdhury and Dr. Tahir Husain, the first author conceptualized, designed the experiments, performed formal analysis, investigated, visualized, and prepared the original draft, reviewed, and edited the manuscript. Tafvizi, H. collected data for studying the treatability of NOM fractions using EC and novel AC. Also, performed seasonal water sampling, collected data, and analyzed data for the effect of seasonal variation of NOM fractions on the level of DBPs. The first author prepared the original draft of the manuscript and revised it according to all the co-authors' feedback.

5.1. Introduction

The studies in North America, Europe, and North Africa illustrate the increased NOM content in freshwaters in the last two decades (Evans *et al.,* 2005; Molot and Dillon, 2008; Rodríguez-Murillo *et al.,* 2015; Worrall and Burt, 2004; Chowdhury, 2018a) due to water contamination, global warming, acute raining, soil erosion, and road salt drainage (Nkambule *et al.,* 2012; O'Driscoll *et al.,* 2018). As a result, the accumulated recalcitrant organic matter in the sources of drinking water over time not only threatened the activities of the organisms, such as heterotrophic bacteria (Imai *et al.,* 2002) but also, has caused challenges in drinking water treatment in terms of the decreased lifespan of activated carbon (Hong *et al.,* 2009), membrane fouling and reduced efficiency of coagulation (Song *et al.,* 2015). Furthermore, the worsened source water quality has led to increased toxic disinfection by-products (DBPs), many in drinking water systems, including the small ones in NL, Canada (Chowdhury, 2018b).

Many DBPs, including brominated THMs (BDCM: bromodichloromethane, DBCM: dibromochloromethane, TBM: bromoform), few HAAs (DCAA: dichloroacetic acid, TCAA: trichloroacetic acid), BrO3 (bromate), and NDMA (N-Nitrosodimethylamine), are probable human carcinogens (U.S.EPA-IRIS, 2020). Health Canada (HC) recommended the maximum acceptable concentration (MAC) (i.e., "as low as reasonably achievable" based on the locational annual rolling average) of 80 ppb for five HAAs (HAA5: monochloroacetic acids, dichloroacetic acids, trichloroacetic acids, monobromoacetic acids, and dibromoacetic acids) (HC, 2020). Also, the MAC for four regulated THMs (THM4: TCM, TBM, BDCM, DBCM) is 100 ppb (HC, 2020).

The average level of dissolved organic carbon (DOC) in some surface waters of Newfoundland (NL), Canada, is 9 mg/L with the highest reported value of 21.2 mg/L DOC in tap water in 2019–2020 (Water Resources Management Division, 2020). More than 90% of WTPs in Newfoundland use chlorination as a disinfection method in their treatment system. Seventy-nine percent of the population in Newfoundland (NL) use the public water distribution system, where 15% of the serviced population have been in contact with excessive levels of total THM4 and HAA5 in their drinking water from 2008 to 2017, a probable cause of an increasing number of cancer cases (risk ratio = 1.8) in areas with elevated levels of DBPs (Rahman *et al.,* 2020), which reveals that conventional water treatment plants in the province have been challenging with DBPs management. Variations in the characteristics of NOM (e.g., sources of water and seasonal changes) as well as methods of disinfection influence decision-making for DBPs control(Chowdhury, 2018b). Small WTPs (i.e., serving less than 3000 people) and very small WTPs (i.e., serving less than 500 capita) are more vulnerable technically and financially in terms of decision making. Small WTPs serve more than 44% of the population in Newfoundland, Canada. Previous studies revealed that Trihalomethanes (THMs) are more variable and higher in small WTPs than medium WTPs (Chowdhury, 2013, 2018b). To reduce NOM content and DBPs in supply water, some methods have shown trustable efficacy in experimental and industrial uses in the past two decades. These include enhanced coagulation (Sillanpää *et al.,* 2018a; Tafvizi and Husain, 2022); magnetic ion exchange (MIEX) resin (Levchuk *et al.,* 2018); bio-filtration (Fu *et al.,* 2017); advanced oxidation processes using ozone, hydrogen peroxide, UV, and irradiation (Sillanpää *et al.,* 2018b); membrane filtration (Lidén and Persson, 2016; Xia and Ni, 2015); and activated carbon (Jiang *et al.,* 2017; Tafvizi *et al.,* 2021).

The previous study on the optimization of EC on four surface water sources in NL showed that a reduction of 70.8% of DOC was not satisfactory for lowering DBPs to the MAC (Tafvizi and Husain, 2021) recommended by Health Canada (HC, 2020). However, the employed method resulted in 91% and 73% decrease in THM4 and HAA5, respectively. Also, through employing the tailored activated carbon (BET surface area of 808.29 m^2/g) individually, DOC removal of 76.9% was achieved. Although surface charge modification on the activated carbon improved DOC adsorption by 44%, the level of THM4 was beyond the maximum contaminant level goal required by U.S. EPA. Moreover, the developed AC showed better performance in removing NOM from natural water samples compared to synthesized water containing humic acids (Tafvizi *et al.,* 2021). Therefore, through employing a secondary treatment method (e.g., AC) in addition to EC, removal of both hydrophobic acid fractions and neutral hydrophilic NOM can be achieved, which is likely to reduce the level of DBPs. Studies to date have proved that employing adsorbents after enhanced coagulation can increase DOC removal by 2.0 - 50.2% depending on the initial DOC (i.e., 2.2-20.5 mg/L) and the characteristics of NOM. A summary of the studies on DOC removal from synthesized and natural water samples by a combination of adsorption and enhanced coagulation in recent years is presented in Table 5.1.

Table 5. 1. Recent studies on the combination of enhanced coagulation and adsorption

Type of water	Adsorbent	Initial DOC (mg/L)	Operational conditions	Removal efficiency	Reference
Synthetic	Magnetic nanoparticles (MNP)	5	750 mg/L MNP 10-70 mg/L alum	DOC =98.9% THMfp=91%	Kumari and Gupta (2020)
Natural	GAC	2.2	8mg/L Fe 3300 BV	UV254=99% DOC=24%	Sulaymon *et al.,* (2009)
Synthetic	PAC	10	60 mg/L alum 60mg/L CAC	DOC (EC)=66-83% DOC (combined)=72-89%	Watson *et al.,* (2019)
Secondary Effluent	PAC	9.3	100 mg/L CAC 1.3 mmol Fe	DOC (EC)=50-60% DOC (combined)=85%	Haberkamp *et al.,* (2007)
Natural	modified wheat straw (MWS)	2.06-2.98	0.24mmol PFC 200 mg/L MWS	DOC (EC)=20% DOC (combined)=50-55%	Zhan *et al.,* (2010)
Natural	macadamia nutshell AC (ACZ)	15	80mg/L alum 150mg/L ACZ	DOC (EC)=68% DOC (combined)=90%	Wongcharee *et al.,* (2020)
Natural	PAC	8.4	3.5 mg/L Al pre-hydrolyzed poly aluminum chloride	DOC (EC)=39.8% DOC (combined)=90%	Dabrowska, (2018)
Natural	PAC	18.8-20.5	150mg/L alum 150 mg/L PAC	DOC (EC)=73% DOC (combined)=80-95%	Kristiana *et al.,* (2011)

DOC: dissolved organic carbon, THMfp: trihalomethanes formation potential, GAC: granular activated carbon, PAC: powder activated carbon, EC: enhanced coagulation, combined: enhanced coagulation and adsorption

An investigation on the variability of NOM for learning the seasonal changes and their correlations to DBPs is necessary to address the problems in the water treatment systems (Qun shan Wei *et al.,* 2008). Moreover, aromatic compounds and polarity of organic matter in water often influence the treatability and making choices for selecting the proper method for removing NOM efficiently (Nkambule *et al.,* 2012). The chemical and physical properties of NOM depending is unique, depending on the sources of NOM, geographical location, agricultural activities, temperature, and seasonal changes (Fabris *et al.,* 2008; Liao *et al.,* 2018; Rigobello *et al.,* 2011; Sharp *et al.,* 2006a; Xia and Ni, 2015). The results of the past studies on the seasonal changes of NOM fractions based on hydrophobicity indicated an unpredictability in the seasonal changes of NOM (Table S.5.1). Recent studies on NOM variations during 9-30 months of water sampling in South Africa, the United States, and Scotland showed the highest level of DOC and very hydrophobic acids (VHA) as the dominant fraction of NOM during the summer period (i.e., July and June). In Alaskan water sources, the highest DOC and VHA were observed during winter and summer, and the lowest level of NOM was observed in spring. In two water samples in China, the highest DOC was observed in May and September. The limited data indicated that a comprehensive study is needed on the variations of NOM and its components over time for better management of the treatment processes in the conventional WTP in NL, Canada.

Studies to date have investigated the effects of adsorption after coagulation in DOC removal, but no comprehensive research has compared the capability of metal impregnated activated carbon and non-modified activated carbon on the removal of NOM fractions after coagulation. Although many studies have considered the seasonal variation of NOM over time, an investigation on the variation of NOM in NL, Canada, has not been performed by incorporating the fact that NOM characteristics vary by location and human activities. A study on NOM changes and the effects of individual NOM fractions on DBPs (i.e., THM4 and HAA5) formation is necessary to enhance conventional water treatment plants.

The objectives of this study are to investigate the seasonal variation of NOM in four different water sources in NL, Canada; identify the most effective fractions of NOM (i.e., based on hydrophobicity and charge) on the formation of THM4 and HAA5; investigate the treatability of NOM fractions using two different water treatment methods, and application of combined treatment using enhanced coagulation and activated carbon for the reduction of DBPs.

5.2. Materials and Methods

5.2.1. Water sampling and characterization

Four protected public surface water sources for drinking water supplies in Pouch Cove, Sunnyside, New-Wes-Valley, and Torbay in NL (Canada) were investigated in this study (Figure. S.5.1). These were referred to Water 1 through 4 respectively in this paper. The water sources were selected based on the higher levels of THMs in small WTPs serving less than 3000 people. Sampling was performed from May 2017 to Aug 2019 seasonally in Apr-May, Aug-Sep, Nov-Dec, and March. The water sampling date and time were selected depending on the precipitation and environmental condition (e.g., water's surface thaw). The samples were characterized by UV absorbance at the wavelengths of 254 nm and 272 nm, pH, DOC, THM4, HAA5, and NOM fractionation using resin (i.e., DAX8, XAD4, and IRA958) based on hydrophobicity. The DBPs formation potential within 72 h was measured to observe the variation of the subjected parameters. Water samples were filtered through a 0.45 μm nylon filter before analyzing by a TOC-L analyzer according to ASTM D7573 (2013).

5.2.2. Reagents, materials, and instruments

Only analytical grade chemicals were used in this study. Chemicals including hydrochloric acid 37% wt/wt and nitric acid at the concentration 10% wt/wt for oxidizing the carbon. Iodine solution (0.1 N), sodium thiosulfate (0.1 N), Methylene blue (1500 ppm) were purchased from VWR, Canada, for characterization of AC. Ferric chloride anhydrous and aluminum sulfate were used as coagulants as well as sources of metal ions for metal coating of the AC. Single point adsorption test was performed to evaluate methylene blue adsorption by AC (Raposo *et al.,* 2009). Carbon dioxide and nitrogen of 99.99% purity were purchased from Praxair Canada Inc. for AC generation. The methyl tert-butyl ether (MTBE) was purchased from J.T. Baker, U.S.A. for liquid extractions of THM4 and HAA5. NaClO at 30% wt/wt was used for chlorination. The liquid extractions of THM4 and HAA5 in MTBE were performed at North Region Persistent Organic Pollutants (NRPOP) lab following the methods: U.S. EPA 551.1 (Hautman and Munch, 1997) and U.S. EPA 552.2 (Pawlecki-Vonderheide *et al.,* 1997) respectively. An Agilent 6890 gas chromatograph equipped with ECD was used at CREAIT labs at the Memorial University of Newfoundland to analyze the samples. A Genesys 10S UV/Vis spectrophotometer (Thermo Fisher Scientific, U.S.A.) was used for the UV absorbance of water samples, while pH was measured using a benchtop FE20 pH meter (Mettler Toledo, USA).

NOM in the water samples was characterized into four fractions based on acidity and hydrophobicity. These were very hydrophobic acid (VHA), slightly hydrophobic acid (SHA), charged hydrophilic (CHI), and neutral hydrophilic (NHI), based on their adsorption to the resins (DAX 8, XAD 4, and IRA 958) according to the rapid fractionation technique (Chow *et al.,* 2004; Urbanowska and Kabsch-Korbutowicz, 2016; Vieira *et al.,* 2012). The preparation of the resins was performed as described in a previous study (Tafvizi and Husain, 2021). A schematic diagram of two stages of the experiments, including stage 1: NOM fractionation and seasonal variation, and stage 2: treatability of NOM using adsorption by AC and EC, are presented in Figure 5. 1.

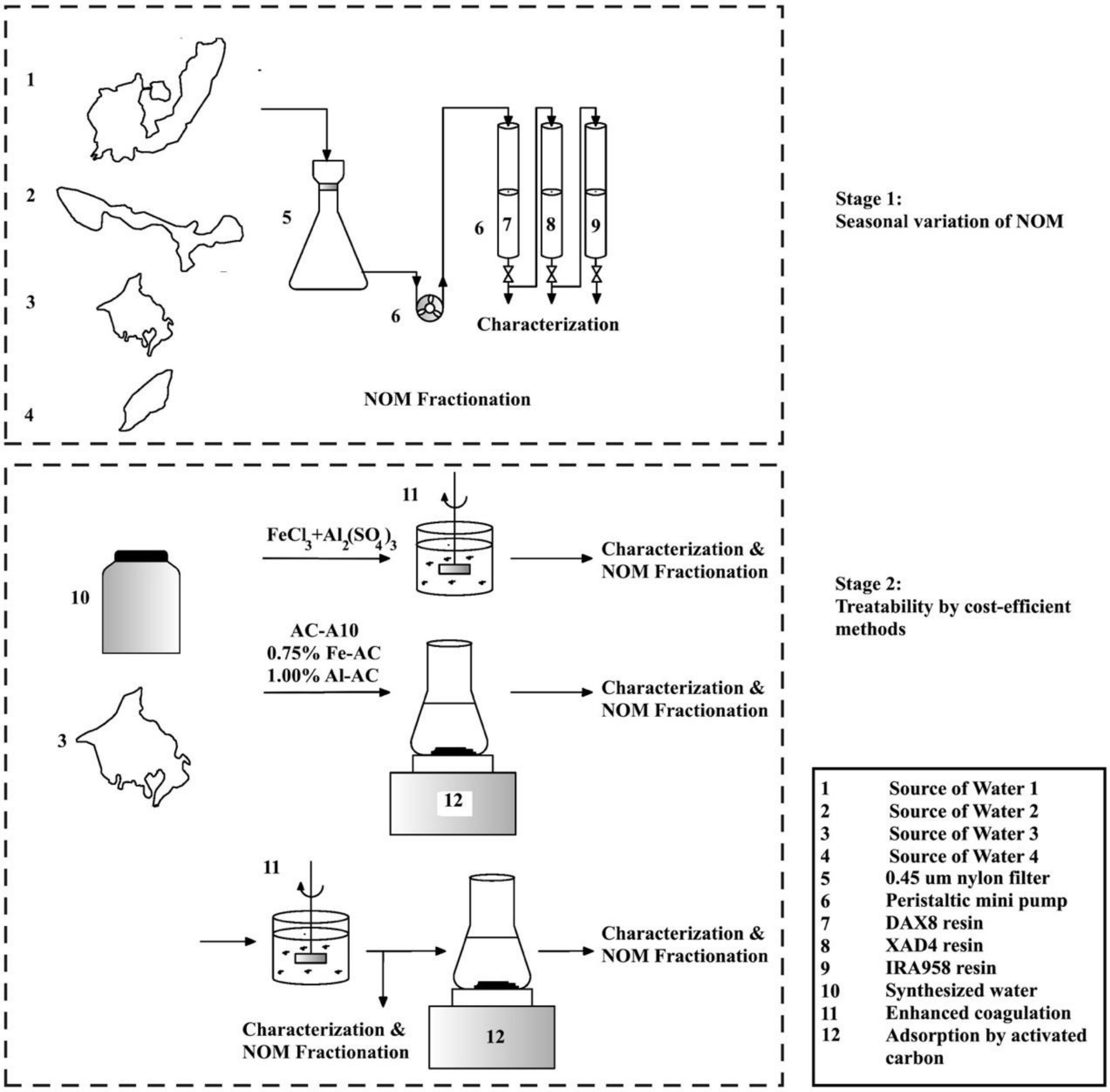


Figure 5. 1. Schematic diagram of the experimental steps (i.e., stage 1: seasonal variation of NOM within two years, Stage 2: treatability by cost-efficient methods); characterization includes measurement of UV254, UV272, DOC, THM4, and HAA5.

The removal efficiencies (E) of the parameters were calculated as follows:

$$\mathrm{E} = \frac{\mathrm{C_i} - \mathrm{C_f}}{\mathrm{C_i}} \times 100\%, \tag{5.1}$$

where $\mathrm{C_i}$ is the initial concentration (mg/L) of the studied parameter and $\mathrm{C_f}$ is the final value of this parameter after treatment (i.e., adsorption, extraction, and coagulation).

5.2.3. Activated carbon

Carbon-rich waste material (fly ash) from a local pulp and paper company was used to prepare AC. The crushed fly ash was treated for chemical activation using nitric acid at 10% wt: wt. The process was followed by physical activation using carbon dioxide and water vapor at 850 °C. Metal coating on developed AC-A10 using ferric chloride and aluminum sulfate was performed at an optimized ratio of 0.75% of Fe: AC and 1.00% Al: AC as described in detail in a previous study (Tafvizi *et al.,* 2021). The metal-coated ACs are referred to as Fe-AC and Al-AC hereafter. The characteristics of ACs are presented in Table S.5.2. Adsorption tests were performed at the dosages of 0.05 and 0.15 g/L of ACs in untreated (i.e., raw water) and treated water with EC in 250ml flasks. The mixture of activated carbon and water samples was stirred constantly using a magnetic stirrer at a speed of 200 rpm during the adsorption time (i.e., 15min and 24 hr.). The ambient temperature for all the experiments was controlled at 24 ± 2 °C.

5.2.4. Enhanced Coagulation

The method of enhanced coagulation using ferric chloride and aluminum sulfate was optimized in a previous study (Tafvizi and Husain, 2021). The desirability function in Design-Expert software (Stat-Ease, V.10.0.8.0, 2018) was used for finding the optimal conditions of the factors: pH, dosage, coagulant type, fast mixing speed, and settling time. The most cost-efficient condition was derived from the previous research

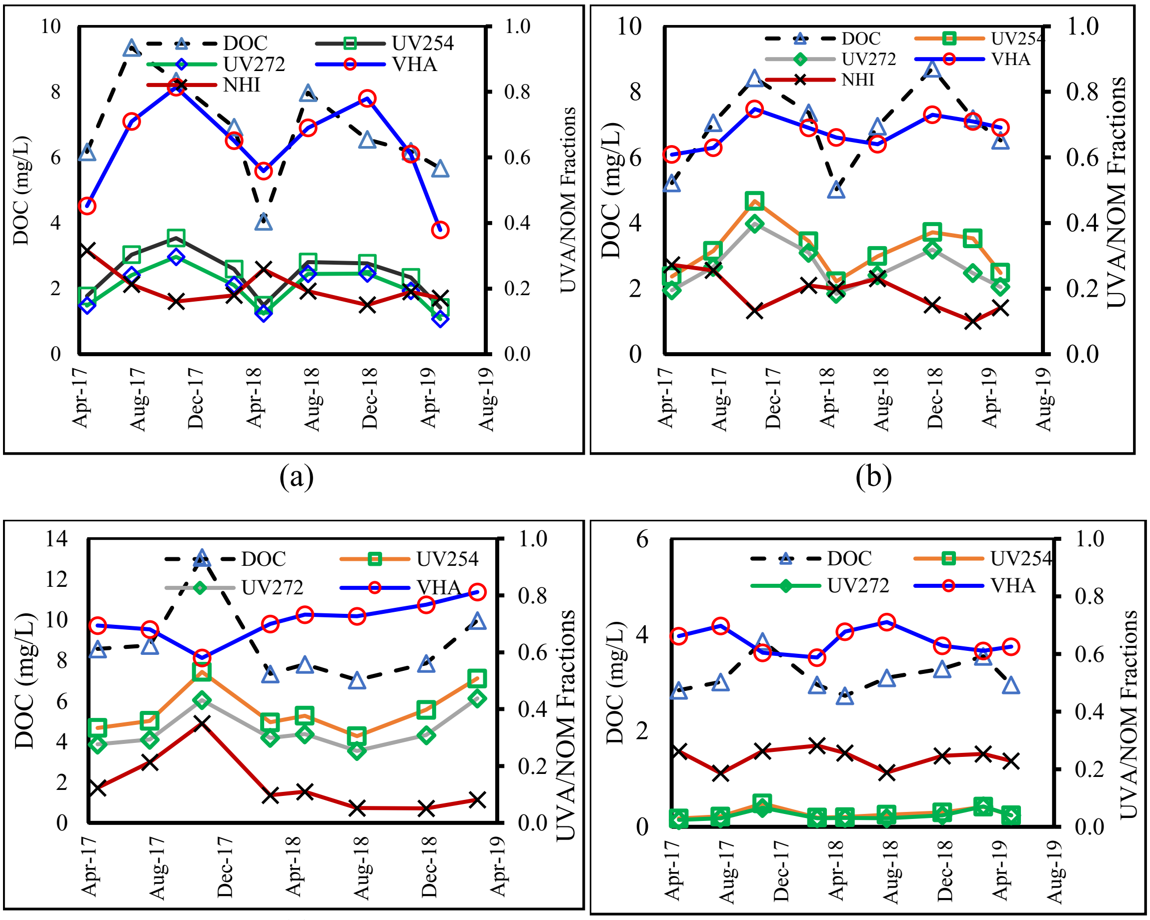
(Tafvizi and Husain, 2021). The mixing time for the rapid mixing stage was 1 min, followed by 20 min of mixing at 25 rpm for flocculation. Then the samples were rested for 20 min in the settling stage. The operational conditions of pH = 7.5, dosage = 3.83 mg/mg DOC, Fe/Fe+Al = 0.75, fast-mixing velocity gradient = 190 s^{-1}, and settling time = 20 min were used for investigating the effect of enhance coagulation in combination with adsorption. A PB-700 jar test device (Phipps and Bird, U.S.A.) was used for jar tests of the coagulation-flocculation process. The stock solutions of ferric chloride and aluminum sulfate were prepared daily and discarded after the experiments.

5.3. Results and Discussion

5.3.1. Seasonal variation of NOM

The seasonal variation of the characteristics of NOM, including DOC, UV absorbance at 254 and 272 wavelengths, and NOM fractionation based on hydrophobicity and charge, were determined for four public water supplies, and are presented in Table S.5.3 and Figures 5. 2 a–d. The sampling period for Water 1, Water 2, and Water 4 are from May 2017 to May 2019. However, sampling for the third location (Water 3) was not possible until March 2018 due to inaccessible weather conditions, and the characteristics of water were investigated from March 2018 to July 2019. The variation of DOC and NOM hydrophobicity in the water samples are presented in Figure 5. 2a–d. The highest and the lowest DOC levels for these water samples were observed as 13.08 and 2.73 for Water 3 and Water 4, respectively. The highest levels of DOC during the year (i.e., 9.35 and 7.98 mg/L) in Water 1 were observed in the third quarter, and the lowest concentrations of DOC were 6.17 and 4.05 mg/L in May (i.e., second quarter). Similar trends were observed in Water 2 and Water 4, with the lowest levels of DOC in May 2018 (i.e., 5.02 and 2.73 mg/L). The studies in England (Sharp *et al.,* 2006b), Scotland (Golea *et al.,* 2017), and Alaska (Cao *et al.,* 2016) reported similar observations of high levels of DOC in Summer. The lowest DOC concentrations were observed in April and May, which agree with the observations in Water 1 and Water 2.

Moreover, the higher levels of UV254 (i.e., 0.35 and 0.28 in 2017 and 2018) In this study were observed in the fourth quarter. The NOM fractionation in all water samples shows that VHA and NHI are the predominant fractions in all the water samples. VHA contributed more than 50% of DOC in all water samples except the samples of May 17 and May 19, with 45.2 and 37.9% of the total DOC, respectively. The NOM characterization of Water 1 and Water 2 shows that the higher percentages of VHA were observed in Nov (in the fourth quarter). The variation of NHI show lower levels of DOC during the fourth quarter and higher NHI content in the second quarter. The available climate data from four climate stations of St. John’s Airport, Arnold’s Cove, and Gander International Airport were used to analyze the precipitation and temperature changes on a quarterly basis (i.e., Jan–Mar, Apr-Jun, Jul–Sep, and Oct-Dec). The highest temperature for the selected weather stations occurred in the third quarter (i.e., Jul-Sep), and the lowest average temperature was reported in the first quarter (i.e., Jan-Mar). The highest level of precipitation was observed in the fourth quarter, and the lowest total precipitation was reported in the second quarter (Newfoundland and Labrador Statistics Agency, 2021). The higher level of VHA and UV254 in the fourth quarter may be because of the higher levels of precipitation in the third quarter of the year, as the lag period was possibly needed for the assimilation of the NOM fractions. The correlation between high contents of humic acids and higher levels of precipitation was observed in the previous research by Aschermann *et al.,* (2016).



(a)

(b)

(c)

(d)

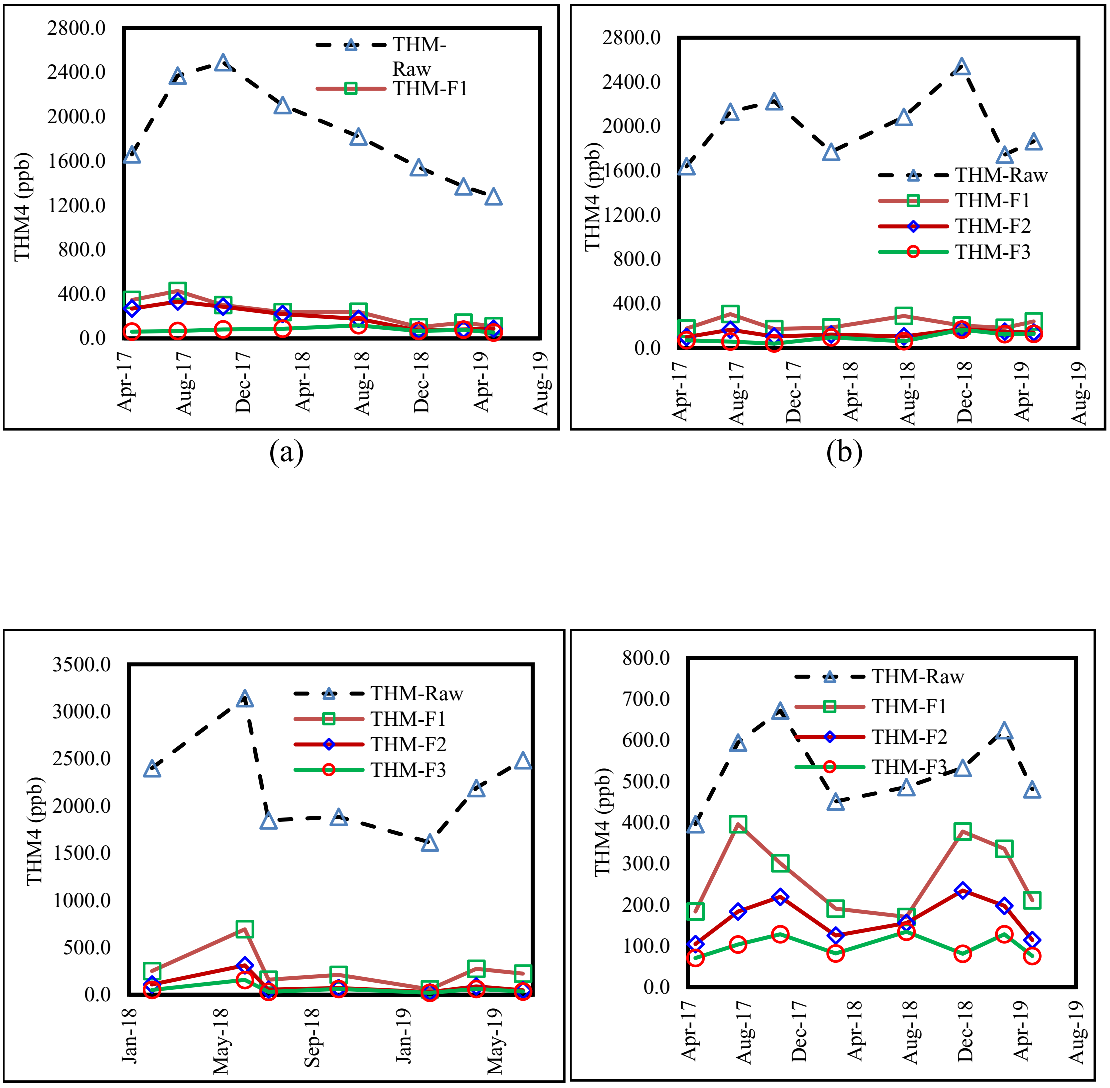
Figure 5. 2. Seasonal variation of NOM fractions, UV absorbances, and DOC over sampling duration for (a) Water 1, (b) Water 2, (c) Water 3, and (d) Water 4.

DOC: dissolved organic carbon, UV254: UV absorbance at the wavelength 254nm, UV272: UV absorbance at the wavelength of 272 nm, VHA: very hydrophobic acids, SHA: slightly hydrophobic acid, CHI: charged hydrophilic, NHI: neutral hydrophilic.

5.3.2. DBPs formation and NOM fractionation

The effects of NOM hydrophobicity on the formation of THM4 and HAA5 were investigated through chlorination of the filtrates of each column of resins (i.e., DAX8, XAD4, and IRA958). THM4 and HAA5 were extracted after 72 hours, and the results are illustrated in Figure 5.3a–d and Figure 5.4a–d, respectively, for Water 1–4. The concentrations of THM4 for Water 1–4 showed the minimum of 396 ppb and the maximum of 3144 ppb in Water 4 and Water 3, respectively (in unfiltered sample). The level of THM4 formation potential (FP) for Water 1 in the filtrate of DAX8 and after the removal of VHA was in the range of 102 – 428 ppb. The obtained results indicate a decrease of 87.33 ± 4.7% in the THM4-FP comparing the THM4 level of 1281-2491 ppb in unfiltered Water1, as presented in Figure 5.3a. The results for the filtrates of XAD4 and IRA958 showed 2.76 ± 1.6% and 5.58 ± 4.7% removal of the precursors of THM4-FP during the NOM fractionation due to the removal of SHA and CHI accordingly. The average of THM4-FP for the filtrate of IRA958, which contained NHI fraction of NOM, was 4.32 ± 1.22%.

The effects of the removal of NOM fractions in Water 2–4 showed an average decrease of 88.93 ± 2.49, 88.98 ± 32.99, and 49.49 ± 12.4 with the elimination of VHAs, as illustrated in Figures 5.3b–d. The reductions for SHA and CHI were less than 10% for all water samples with an average of 8.38 ± 8.4 for SHA removal (i.e., filtration with XAD4 resin) and 5.46 ± 6.1 for NOM fraction containing CHI. NHI contributed an average of 4.34, 4.71, and 2.46% in Water 1–3 while it contained an average of 19.02 ± 3.9% of THM precursors in Water 4. Among the investigated water samples in this research, removal of the VHA fraction of NOM resulted in an average decrease of 78.25 ± 18.6% of the precursors of THM4. Previous studies on untreated and treated water samples in 30 water treatment works in Scotland revealed that the most reactive fraction of NOM in the formation of THMs are hydrophobic acids (Golea *et al.,* 2017). The observation by Chen et al., (2008) on the influence of algal bloom in the levels of DBPs in North China showed that humic acids and fulvic acids had a 66.6 ug/mg C yield in THM-FP and contained 60% of DBPs precursors. However, various sources of water showed different potentials of NOM reactivity for the formation of DBPs (Chen *et al.,* 2008). The results of the present study are consistent with the findings of previous research. The findings show that the removal of the VHA fraction of NOM is likely to significantly reduce the THM4-FP.



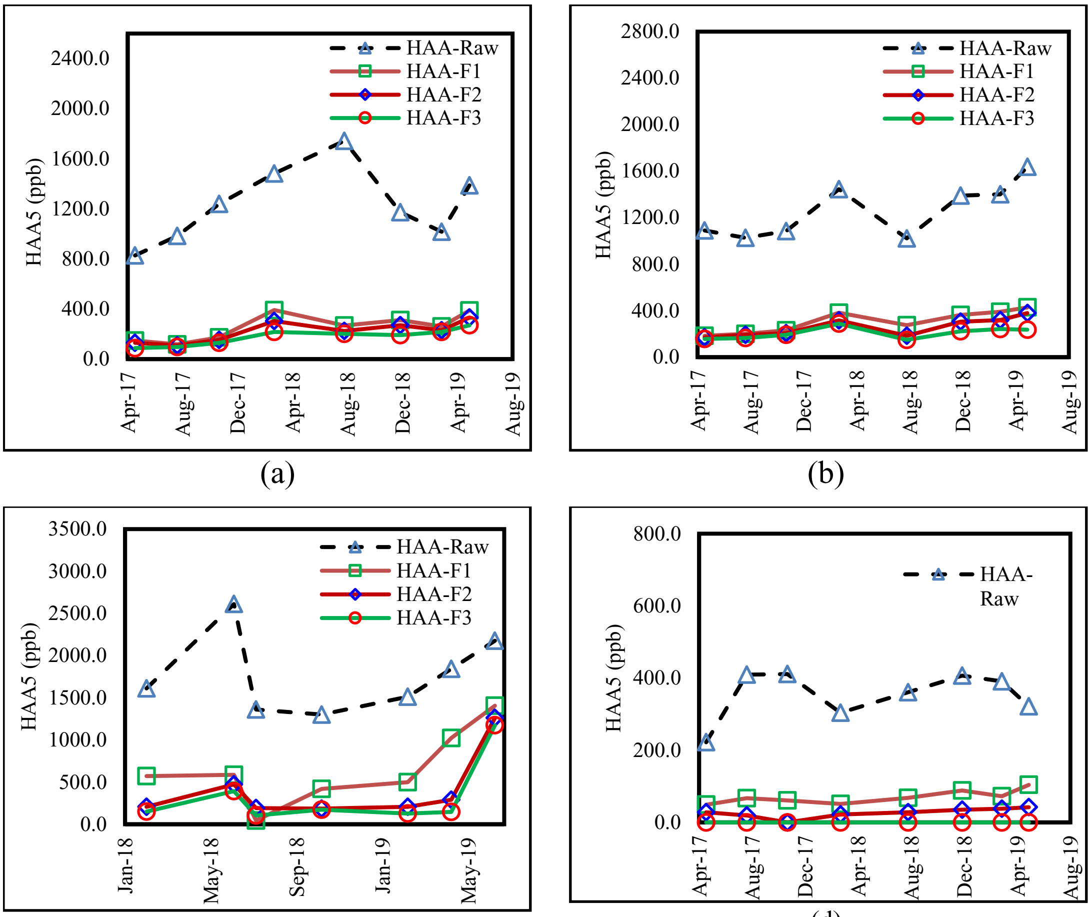
(a) (b)

(c) (d)

Figure 5. 3. Alterations of THM4 formation potential by NOM fractionation within the sampling period (a) Water 1, (b) Water 2, (c) Water 3, and (d) Water 4.

THM4: four regulated Trihalomethanes by U.S. EPA, Raw: untreated water, F1: DAX8 filtrate, F2: XAD4 filtrate, F3:IRA958 filtrate.

The variation of HAA5 with the removal of NOM fractions of VHA, SHA, CHI, and NHI are depicted in Figure 5.4 a–d. The levels of HAA5 in unfiltered samples of Water 1–4 were within 222.0 to 2611.0 ppb. The obtained results for the HAA5 of filtrates of the first column of NOM fractionation showed an average of 79.2 ± 6.57, 76.1 ± 4.0, 64.7 ± 25.5, and 79.8 ± 5.5% decrease in the levels of HAA5 in Water 1 – 4 respectively. The results indicate the high capability of VHA fraction in the formation of HAAs, which agrees with the results by Chen et al., (2008). The results of HAA5 formation on the filtrates of XAD4 showed that SHA (i.e., transphilics) contained 2.97 ± 1.5, 3.3 ± 2.6, 14.3 ± 13.1, and 12.2 ± 3.5% of HAA5 in Water 1 – 4, respectively. The results by Karapinar *et al.,* (2014) showed that transphilics possessed high reactivity properties in the formation of HAAs. The NOM fraction of CHI contained an average of 4.94 ± 3.38 in all water samples. The filtrates of IRA958 contained 14.3 ± 4.4, 16.3 ± 1.9, and 16.5 ± 17.35% of HAA5 in Water 1–3, which showed the high reactivity of NHI in the formation of HAA5. The results indicate that the significant removal of NHI is likely to reduce the HAAs-FP.



(a) (b)

(c) (d)

Figure 5. 4. Alterations of HAA5 formation potential by NOM fractionation within the sampling period (a) Water 1, (b) Water 2, (c) Water 3, and (d) Water 4. HAA5: five regulated Trihalomethanes by U.S. EPA, Raw: untreated water, F1: DAX8 filtrate, F2: XAD4 filtrate, F3:IRA958 filtrate.

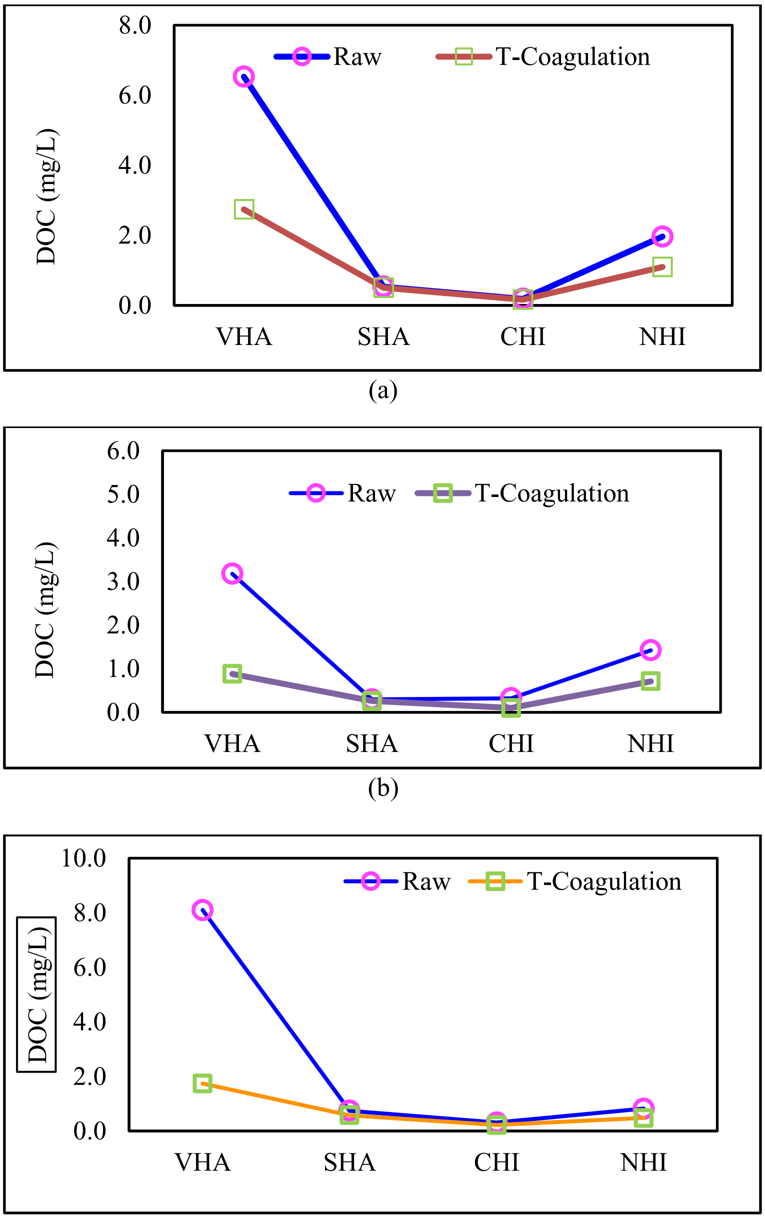
5.3.3. NOM fractionation of EC

Enhance coagulation is a cost-efficient water treatment process for the removal of DOC and DBPs. However, to minimize the consumption of coagulants and the cost of the treatment process and for lowering the amount of sludge, optimization was investigated by modeling the results of two sets of jar test data shown in the previous research by Tafvizi and Husain (2021). The efficiencies of coagulation processes for the removal of NOM fractions were investigated using the resin fractionation technique on natural and synthetic water samples with various ratios of VHA and NHI fractions. Synthetic water samples containing humic acids and polysaccharose were treated at the optimized combination of variables (i.e., pH = 7.5, dosage = 3.83mg/mg DOC, Fe/Fe+Al = 0.75, fast-mixing velocity gradient = 190 s^{-1}, and settling time = 20 min). Also, selected treated water samples with the highest DBPs removal and minimum coagulant dosage from Tafvizi and Husain (2021) were examined. The obtained results for NOM fractionation in terms of DOC contents in VHA, SHA, CHI, and NHI fractions are presented in Figure 5a–c. The resin fractionation of Water 1 exhibited the following results: VHA = 6.53 mg/L, SHA = 0.53 mg/L, CHI = 0.18 mg/L, and NHI = 1.96 mg/L, whereas for Water 2 the fractions of NOM were VHA = 3.18 mg/L, SHA = 0.29 mg/L, CHI = 0.32 mg/L, and NHI = 1.42. The NOM profile for Water 3 were: VHA = 8.10 mg/L, SHA = 0.74 mg/L, CHI = 0.31mg/L, and NHI = 0.82 mg/L. VHA and NHI are the predominant fractions in all water samples, with 70.92 and 21.30 % in Water 1, 60.86 and 27.2 % in Water 2, and 81.19 and 8.21% in Water 3, respectively. These water samples were used for the investigation of the performance of EC on the removal of NOM fractions.

The EC results for Water 1 indicate that the level of VHA decreased from 6.53

mg/L in raw water to 2.74 mg/L in an optimized treated water sample. These results represent the removal of 58.03 % of the VHA from water by optimized coagulation. In addition, 5.96, 11.65, and 43.91 % of the SHA, CHI, and NHI fractions were removed during EC, respectively. Figure 5a-c shows that most of the DOC reduction was achieved via VHA removal. The NOM fractions of SHA and CHI were not significantly reduced by EC, as the maximum removal of SHA and CHI in Water 1, 2, and 3 were less than 0.2 mg/L. EC removed 72.30 and 50.06% of VHA and NHI in Water 2, and the removal efficiencies were 78.53% and 41.46%, respectively, in Water 3.

The NOM profiling results for the treated samples of Water 1, Water 2, and Water 3 in Fig. 5 a-c show that VHA and NHI have the highest and second-highest removal efficiencies in all samples. The DOC removal of NHI is, however, significantly lower than that of VHA. Ghernaout et al., (2009) reported that the coagulation process was more efficient in removing hydrophobic and aromatic compounds. Hussain *et al.,* (2013) and Archer and Singer (2006) showed that enhanced coagulation could remove up to 80 % of the hydrophobic matter. In contrast, the removal efficiencies for the hydrophilic and lower molecular weight compounds were not satisfactory. However, the concentration of VHA's fraction was considerably higher than NHI in all water samples in this research (i.e., VHA = 6.64 mg/L and NHI = 1.99 mg/L in Water 1, VHA = 3.18 mg/L and NHI = 1.42 mg/L in Water 2, and the VHA and NHI contents in Water 3 were 8.10 and 0.82 mg/L). The results of the EC on the samples containing VHA and NHI representatives (i.e., humic acids and polysaccharose) revealed an 89.48% decrease in the VHA content of humic acids and a 40.98% decrease of polysaccharose (i.e., NHI). The results are consistent with the reduction of VHA contents in Water 1 and Water 3 and the previous studies (Hussain *et al.,* 2013; Archer and Singer, 2006).



(a)

(b)

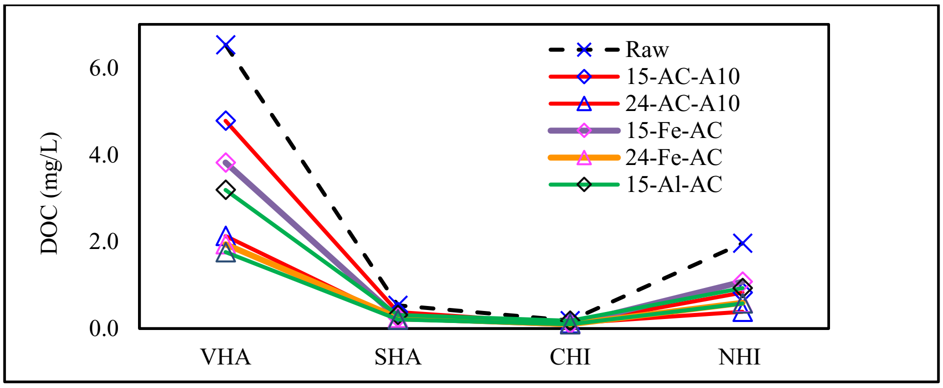
(c)

Figure 5. 5. The removal of NOM fractions by optimized enhanced coagulation in (a) Water 1, (b) Water 2, (c) Water 3. VHA: very hydrophobic acids, SHA: slightly hydrophobic acid, CHI: charged hydrophilic, NHI: neutral hydrophilic, Raw: untreated water, T-Coagulation: treated water by enhanced coagulation.

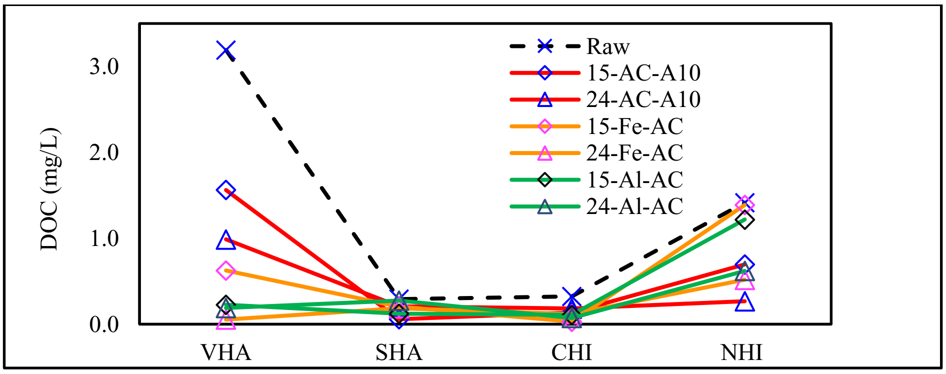
5.3.4. NOM fractionation by activated carbon

The efficiency of AC in the removal of water pollutants depends on the surface charge and available surface functional groups (Tanthapanichakoon *et al.,* 2005). The NOM removal relies on the surface charge of AC as investigated in the previous research (Tafvizi *et al.,* 2021). The metal coating using aluminum sulfate and ferric chloride on the AC showed improvements in the affinity of NOM molecules to the AC. The optimized metal-coated AC of 0.75% Fe-AC, 1.00% Al-AC and non-modified AC were used for the investigation of the performance of AC in the removal of NOM fractions. The ACs were mixed with natural and synthetic water at 0.15 mg/L. The combined solution was mixed for 15 minutes and 24 hours; then, rapid NOM fractionation was performed on filtered water to recognize the performance of ACs on the removal of NOM fractions. The results of NOM fractionation on untreated and treated water samples using three types of ACs are presented in Fig 6 a-c. Within the 1st 15 minutes, VHA content in Water 1 reduced from 6.53 mg/L to 4.78, 3.82, and 3.19 mg/L by AC-A10, 0.75%Fe-AC, and 1.00%Al-AC, respectively. The VHA contents in Water 2 and treated water samples were obtained as 3.191, 1.562, 0.626, and 0.226 mg/L, respectively. The VHA content in Water 3 was 8.103 mg/L (Raw water), while in treated water samples, VHA was 5.77, 4.13, and 3.89 mg/L for AC-A10, 0.75%Fe-AC and 1.00%Al-AC treatment, respectively, after 15 minutes. In all the water samples, metal-coated activated carbons showed better performance in the removal of VHAs. However, non-modified AC (i.e., AC-A10) led to a better performance in the removal of NHI in comparison with metal-coated ACs. The removal of SHA and CHI fractions was in the range of 0.07 to 0.50 mg/L.

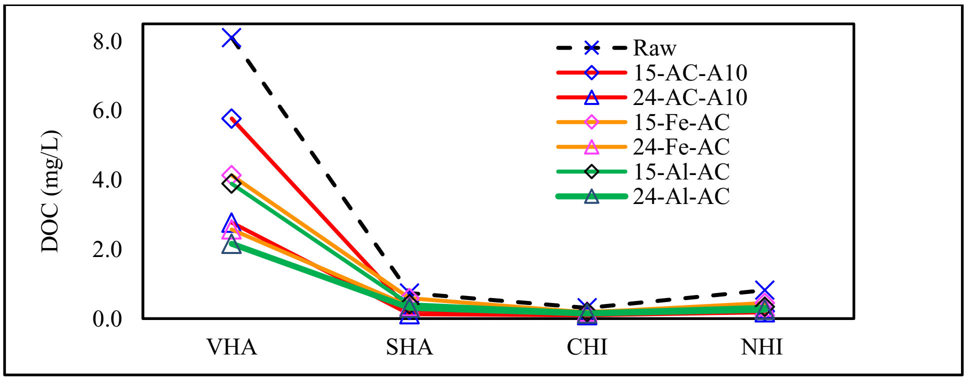
The higher removal of NOM compounds with high molecular weight to iron oxide in the first 30 minutes of adsorption (Kitis *et al.,* 2007) as well as up to 70% uptake of fulvic acids to magnetic oxides through physiochemical adsorption in research by Swietlik *et al.,* (2015) are consistent to the results in the present study. Rahman *et al.,* (2013) reported that more than half of the humic acid contents were adsorbed in the first 10 minutes of adsorption as a result of oxidation of NOM and ligand exchange between the carboxyl and hydroxyl functional groups of NOM and the metal cations in the surface of the adsorbent. Moreover, oxidation of NOM with high molecular weight (i.e., VHA fraction) increases the adsorption due to an increase of the proper functional groups. However, the results for the removal of this by three different ACs show that non-modified AC removed higher fractions of NHIs in comparison to metal-coated ACs, which can be due to the decrease in the micropore surface area because of blockage by metal impregnation in 0.75% Fe-AC and 1.00% Al-AC. The removal efficiency for both fractions of NHI and VHA after 24 hours of contact time shows slight variations between the three types of ACs. However, still 1.00% Al-AC shows higher VHA removal in Water 1 and Water 3 in comparison with two other ACs. The concentrations of VHA in Water 1 after 24 hours of treatment by AC-A10, 0.75%Fe-AC, and 1.00%Al-AC were 2.13, 1.94, and 1.76 mg/L, respectively. In Water 2, the concentrations were 0.98, 0.06, and 0.19 mg/L, respectively, while in Water 3, these were 2.77, 2.57, and 2.16 mg/L, respectively.



(a)



(b)



(c)

Figure 5. 6. The removal of NOM fractions by AC-A10, 1.00% Al-AC, and 0.75%Fe-AC in (a) Water 1, (b) Water 2, (c) Water 3 after 15 minutes and 24 hours of contact time. DOC: dissolved organic carbon, 15: 15 min, 24: 24 min, AC: activated carbon, VHA: very hydrophobic acids, SHA: slightly hydrophobic acid, CHI: charged hydrophilic, NHI: neutral hydrophilic

5.3.5. Combined treatment

To evaluate the performance of the combination of EC and AC on NOM removal, Water 3, treated by coagulation, was used for the next stage of the investigation. The AC-A10 and metal-coated ACs at the dosages of 0.05 and 0.15 g/L, respectively, were mixed with treated Water 3 for 24 hours to reach the adsorption equilibrium. The DOC of the treated water (by coagulation) was 3.095 ± 0.10 mg/L at the optimized combination of the coagulation factors. The results of UV254, UV272, DOC, THM4, and HAA5 removal for six different treatment conditions are presented in Table 5.2. The lowest observed DOC by secondary treatment was obtained by applying AC-A10 at dose = 0.15 g/L. However, applying ACs as low as 0.05 g/L resulted in a satisfactory removal of DOC (i.e., DOC < 1.0 mg/L). The higher performance of AC-A10 in the removal of DOC (following coagulation) can be due to the higher removal of high molecular weight NOM and VHAs during coagulation (Hussain *et al.,* 2013) and high content of NHI in the treated water. The results of combined treatment agree with the findings in NOM fractionation in this study.

Table 5. 2. Performance of combination of coagulation and adsorption in DOC removal

Sample	AC Type	AC Dose (gL^{-1})	UV254 (cm^{-1})	UV272 (cm^{-1})	DOC (mgL^{-1})	THM4	HAA5
Untreated Water 3	N/A	N/A	0.508±0.05	0.438±0.05	9.97	2485	2187.1
Coagulated	N/A	N/A	0.105±0.02	0.096±0.01	3.091	618	626.4
EC and AC	AC-A10	0.05	<0.01	<0.01	0.878	<10	107.7
EC and AC	1.00% Al-AC	0.05	<0.01	<0.01	1.298	28	187.1
EC and AC	0.75% Fe-AC	0.05	<0.01	<0.01	1.325	51	196.7
EC and AC	AC-A10	0.15	<0.01	<0.01	0.769	<10	59.7
EC and AC	1.00% Al-AC	0.15	<0.01	<0.01	0.807	<10	62.3
EC and AC	0.75% Fe-AC	0.15	<0.01	<0.01	1.129	<10	105.3

DOC: dissolved organic carbon, UV254: UV absorbance at the wavelength 254nm, UV272: UV absorbance at the wavelength of 272 nm, VHA: very hydrophobic acids, SHA: slightly hydrophobic acid, CHI: charged hydrophilic, NHI: neutral hydrophilic, EC: enhanced coagulation, AC: activated carbon

Moreover, the DBPs formation potential was measured in the untreated, single treatment, and combined treated water samples. The results showed that the enhanced coagulation with optimized dosages of alum and ferric chloride resulted in 68.9, 75.1, and 71.35% removal of DOC, THM4, and HAA5, respectively, while the levels of THM4 and HAA5 were much higher than the recommended values for drinking water (HC, 2020). However, the combination of coagulation and adsorption using three different types of ACs resulted in the reduction of THM4 by 98.4, 95.46, and 91.74% using AC-A10, 1.00%Al-AC, and 0.75% Fe-AC respectively, at a dosage of 50 mg/L. The final concentrations of THM4 and HAA5 were lower than the recommended values by U.S. EPA and Health Canada (U.S.EPA, 2020; HC, 2020).

The AC-A10 increased THM4 removal by 23.2%; however, HAA5 levels of treated samples (by adsorption) were still unsatisfactory. An increase of the dose to 0.15 g/L for AC-A10 and 1.00% Al-AC showed satisfactory results for both THM4 and HAA5 (i.e., THM4 <100 ppb and HAA5 <80 ppb). The obtained results in the current study showed that the EC is effective in the removal of VHA but does not remove NHI efficiently. Moreover, the addition of ACs to the treated water samples with EC resulted in the removal of THMs as high as 98.38% by AC-A10. The total DOC removal in the combined treatment was as high as 91.2%. The previous studies reached the THM4 removal of 91% and DOC removal of 98% by adding a dosage of 60-750 mg/L of adsorbents (Dabrowska, 2018; Kristiana *et al.,* 2011b; Kumari and Gupta, 2020; K. Watson *et al.,* 2019). Considering the competitive method of enhanced coagulation with 3.83 mg coagulant/mg DOC (Tafvizi and Husain, 2021) in this study, a dosage of 50 mg/L of AC-A10 shows a 91.2% removal of DOC, 98.5% reduction in THM4, and 82.8% reduction of HAA5, which appears to be the more efficient treatment of water with high levels of NOM which will result in more cost-efficiency in terms of coagulant and activated carbon consumption.

5.4. Summary

Seasonal variation of the fractions of NOM was studied in four surface waters located in Newfoundland, Canada, through two years of sampling following the rapid resin fractionation technique. The results showed that the highest levels of DOC and VHA fraction varied tempo-spatially at different locations of sampling while the highest values of VHA were obtained in Nov and Dec. The reactivity of NOM fractions in the formation of THM4 and HAA5 was examined by investigating the levels of DBPs formation potential within 72 hours of chlorination. The most reactive components of NOM in all water samples were VHAs forming 78.35% of THM4, and a combination of VHAs and NHIs were reported as the influencing compounds on the formation of HAAs with 75.32% and 15.67% shares, respectively. The NOM fractions of SHA and CHI were not as effective as VHAs and NHIs in DBPs formation. The treatability of NOM was investigated by performing NOM fractionation on untreated and treated water samples with adsorption and enhanced coagulation. The results showed that the addition of AC-A10 at a dosage of 50 mg/L to the coagulation improved the removal of precursors of THM4 and HAA5 by 23%. Adsorption with ACs was more efficient for the removal of the precursors of THM4 rather than HAA5. AC-A10 showed better performance in the reduction of DOC and DBPs than the metal-coated ACs. The present study showed better performance through combined treatment by applying lower dosages of coagulants and adsorbents, which is likely to reduce the cost of water treatment processes.

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CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

To better explain and to improve the removal of NOM from drinking water sources with cost-efficient methods, the study performed an in-depth investigation on seasonal variation of NOM in several water sources in NL, developed activated carbon from industrial waste, optimized enhanced coagulation to improve the performance in NOM removal and decrease the power consumption, and applied the combined techniques in water treatment.

The technological achievements to date were reviewed and the scopes of research were identified. During this study, the following research activities were performed.

- **Enahncing the optimization conditions of the enhanced coagulation by decreasing chemical and power consumption based on DBPs removal.**

The simultaneous effects of operational factors including pH, coagulant type ($Fe^{3+}/Fe^{3+} + Al^{3+}$ ratio), coagulant dosage, fast-mixing rate, and settling time were investigated using a response surface methodology design in two sets of experiments (i.e., 50 runs in triplicate and two blocks) were investigated. Statistical models were developed using experiments on two natural water samples of NL, which were validated by four natural and two synthetic water samples. The multivariate optimization on THM4 and HAA5 resulted in a significant reduction in the fast-mixing energy consumption by 59.9%, and a reduction of 23.4–41.1% in coagulant dosage in comparison with DOC removal. The optimized coagulant dosage of 3.83–5.95 mg/mg DOC could remove up to 91.0, 72.6, and 70.8% of THM4, HAA5, and DOC, respectively, in natural water samples with a very hydrophobic acid fraction (VHA) of 0.67–0.81 VHA/DOC. The results of this study were used for further investigation on the treatability of NOM using combined methods later.

- **Improving the removal of NOM by developing low-cost activated carbon with enhanced adsorption capacity and modified surface charge by the metal coat of Al and Fe**

Activated carbon was developed from waste materials of a pulp and paper company in NL using optimization of chemical activation by nitric acid (at concentrations of 0%, 5%, and 10% (wt: wt%) followed by physical activation (i.e., steam and carbon dioxide) and metal coating (i.e., Al and Fe) in a ratio of 0.25% to 10.0% (wt: wt%). The factors of dosage, pH, and time were optimized to achieve the highest adsorption capacity. The results of the study showed 35-44%improvement in DOC removal using AC containing 0.75% Fe coating and 1.0% Al. Moreover, THM4 and HAA5 removals were improved by 40.7% and 77.1% in HAAs compared to non-modified AC. The kinetic studies on the AC in this study showed a physiochemical mechanism of adsorption.

- **Investigating the seasonal variation of NOM in water sources of drinking water in NL**

Seasonal changes of NOM, including polarity and hydrophobicity was studied in four locations in NL for two years by applying the resin fractionation technique. NOM fractionation revealed that very hydrophobic acids are the main contributors to the formation of THM4 while the neutral hydrophilic played a crucial role in forming haloacetic acids. The highest levels of DOC were observed in summer in three out of four sampling locations.

- **Improving the performance of enhanced coagulation and adsorption (i.e., solely and in combination) on the removal of NOM**

The performance of EC and AC derived from the waste material of pulp and paper company with/without metal coatings were investigated on the removal of NOM fractions and DBPs reduction on three natural water samples individually and in a series combination. The combined method using non-metal AC and EC improved THM4 reduction by 23.3% and reduced THMs up to 98.4% in comparison to EC alone. Also, the combined treatment technique removed up to 91.2% and 82.8% of DOC and HAA5, respectively. The NOM fractionation on raw and treated water samples showed the effectiveness of EC and metal-coated AC on the removal of very hydrophobic acids, while the non-modified AC removed higher concentrations of neutral hydrophilic NOM. The study assisted in a better understanding of the performance of EC and AC on the removal of NOM fractions in water samples with high levels of DOC.

6.2. Recommendations

The current research improved the removal of THM4 and HAA5 precursors using two methods of EC and AC by applying batch tests in laboratory conditions. Also, the effects of five factors on EC and three factors on adsorption have been studied. This study can be extended to the following research areas to overcome the challenges in water treatment facilities.

- Pilot-Scale study on the application of EC and AC in series combination: This study showed an enhancement in the removal of DBPs precursors and significantly improved the reduction of THM4 in the lab environment. However, the performance of the proposed water treatment technique needs to be applied in the real water system through a pilot-scale plant for further development.

- The effects of temperature variation on the removal of DBPs in EC and AC: The temperature in the current study was in the ambient range of the laboratory while lower temperatures during the winter season can be challenging for the water treatment facilities. Batch and pilot-scale studies in the lab and field environment can help to improve the models developed for EC in this study.

- Extended water sampling from drinking water resources with higher levels of bromide: Studies to date have shown the importance of Br^- in the formation of more hazardous DBPs in water. The four sources of drinking water in this study contained lower concentrations of Br. Therefore, an investigation on the seasonal variation of Br in drinking water sources with higher levels of Br can fill the scientific gap in the formation of DBPs. Moreover, the interaction effects of DOC and Br on NOM removal by EC and AC can be studied to improve the performance of the models and in more efficiently removing DBPs.

APPENDIX 1

SUPPLEMENTARY INFORMATION FOR CHAPTER THREE: ENHANCED COAGULATION FOR REMOVAL OF NATURAL ORGANIC MATTER AND DISINFECTION BYPRODUCTS: MULTIVARIATE OPTIMIZATION

S.3.1. U.S. EPA suggestions for TOC removal in EC

Table S.3. 1. Required TOC removal in EC as requested by U.S. EPA

Raw water TOC (mg/L)	Alkalinity (mg/L as $CaCO_3$)		
	0-60	>60-120	>120
>2.0-4.0	35%	25%	15%
>4.0-8.0	45%	35%	25%
>8.0	50%	40%	30%

(EPA, 1999)

The analysis of water samples, Water 1 and Water 2, in Newfoundland's water portal indicate that the levels of alkalinity are 0–60 mgL^{-1} as $CaCO_3$ (Water Resources Management Division, 2020). The levels of DOC in Water 1 and Water 2 are 9.35 mgL^{-1} and 5.22 mgL^{-1}, respectively. Accordingly, a TOC removal of 45%–50% is suggested by the U.S. EPA.

S.3.2. Materials and methods

S.3.2.1. Preparation and analysis of NOM Fractions

The virgin resins of DAX-8 and XAD-4 were conditioned for the experiment by immersing them in HPLC-grade methanol for a minute of mixing using a magnetic stirrer and an hour of settling. The process was followed by immersion in pure water following the same procedures of stirring and rest for three successive washes and careful decantation. Resins were left in pure water to rest overnight and then were given three successive washes with pure water the next day. Resin IRA-958 was washed by subsequent acetonitrile after methanol conditioning, and the preparation was followed by pure water washes.

Three borosilicate columns with length x ID dimensions of 200 mm x 25 mm (Kimble, US) equipped with flex-columns economy flow adaptors (Kimble, US), stopcock valves, and PTFE tubing were used for the fractionation. Water samples with a volume of 500 ml were first filtered through a 0.45-µm nylon membrane (Millipore, Ireland). The water sample was acidified to pH=2 and passed through columns containing DAX-8 and XAD-4 at 5 ml/min and 0.2-bed volume per minute, respectively. The first 50 ml, the two-bed volume of resin, of the sample was disposed of from each column. The pH of the outflow of XAD-4 was adjusted to 8, and was passed through the IRA958 column. The water samples were taken for DOC, HAA5, THM4, and UV measurements from the inlet and outflow of each column. Each column containing resin was rinsed with 100 mL of pure water at 5 ml/min before the fractionation to decrease the errors in the results of DOC.

S.3.3. Experimental design and results of tests

In this study, the type of coagulant, a qualitative parameter, was defined as a numerical variable to reduce the number of runs, which decreased the number of tests from 38 runs, $(2^4 + 3) \times 2$, to 19. As a result, the interaction effect of ferric chloride and aluminum was investigated.

The number of extended tests for the CCD method is calculated in Equation S.3.1. The number of runs for a BBD, as presented in Equation S.3.2, with more than five factors, is higher than that by a CCD combined with fractional factorial design (Ferreira et al., 2007).

$$\text{Total number of runs for CCD } = \left(2^{k-1} + \text{center points}\right) + 2k + \text{center points} + \text{replications} = 19 + 2 \times 5 + 1 + 1 = 31 \qquad \text{(S.3.1)}$$

$$\text{Total number of runs for BBD } = 2k(k-1) + \text{center points} = 2 \times 5 \times 4 + 3 = 43 \qquad \text{(S.3.2)}$$

A CCD design provides an orthogonal, rotatable, and sequential design, which is crucial for the prediction ability of the developed models and the reduction of variables; however, a D-optimal design does not possess these crucial features (Montgomery, 2013).

Table S.3. 2. Fractional factorial design (2^{5-1}) showing the coded levels of five independent variables and the experimental results.

						Responses (Removal Efficiency ± 5%)							
						Water 1				Water 2			
Std	X_1:pH	X_2:Dose	X_3:Fe: (Fe + Al)	X_4:Fast Mixing	X_5:Settling Time	DOC	UV254	HAA5	THM4	DOC	UV254	HAA5	THM4
1	–1	–1	–1	–1	–1	38.05	54.70	63.80	72.30	23.7	33.20	34.591	37.68
2	+1	–1	+1	–1	–1	58.10	6.06	64.10	78.74	50.8	64.80	68.1387	62.20
3	–1	+1	+1	–1	–1	22.90	–300.00	49.30	51.00	52.6	60.00	60.3537	58.18
4	+1	+1	–1	–1	–1	54.60	68.50	67.12	76.47	60.2	66.00	75.6706	83.89
5	–1	–1	+1	–1	+1	46.98	20.30	45.10	55.76	43.5	47.30	67.6379	55.28
6	+1	–1	–1	–1	+1	61.90	68.80	60.30	76.25	38.9	53.60	37.7868	52.23
7	–1	+1	–1	–1	+1	48.64	61.49	51.00	71.30	57.4	54.00	29.1304	78.79
8	+1	+1	+1	–1	+1	41.48	–359.00	68.60	78.80	61.9	58.00	77.505	86.37
9	–1	–1	+1	+1	–1	40.39	61.47	38.90	50.47	46.8	58.40	71.3869	61.37
10	+1	–1	–1	+1	–1	51.85	60.40	67.00	73.98	38.5	40.40	31.8573	58.50
11	–1	+1	–1	+1	–1	46.50	68.50	46.14	63.25	52.7	44.40	29.0054	71.15
12	+1	+1	+1	+1	–1	35.77	–303.40	66.80	73.10	69.7	76.00	80.2575	69.33
13	–1	–1	–1	+1	+1	46.9	67.50	65.10	70.80	33.1	37.60	31.0701	34.97
14	+1	–1	+1	+1	+1	51.55	12.50	67.92	82.05	58.6	65.20	33.1537	86.8
15	–1	+1	+1	+1	+1	26.30	–329.00	40.30	52.44	51.3	53.20	39.3014	59.10
16	+1	+1	–1	+1	+1	52.60	30.74	59.10	73.20	56.9	63.60	43.7784	67.29
17	0	0	0	0	0	53.26	12.50	64.05	76.60	62.0	66.00	75.8549	88.04
18	0	0	0	0	0	48.90	–25.00	55.20	69.33	64.2	70.4	60.3584	86.05
19	0	0	0	0	0	43.27	–81.00	58.88	71.66	58.1	68.8	74.5254	75.80

All samples were triplicate tested for DOC, HAA5, THM4 and UV measurements.

Table S.3. 3. Central composite design (CCD-RSM) with coded levels for the independent factors for Water 2 and the results for four responses.

Std	X_1:pH	X_2:Dose	X_3:Fe: (Fe + Al)	X_4:Fast Mixing Speed	X_5:Settling Time	Responses (Removal Efficiency ± 5%)			
						DOC	UV254	HAA5	THM4
1	$-\alpha^1$	0	0	0	0	57.27	55.67	58.25	68.06
2	$+\alpha$	0	0	0	0	68.35	69.15	73.00	82.43
3	0	$-\alpha$	0	0	0	30.90	17.38	22.93	5.76
4	0	$+\alpha$	0	0	0	54.38	32.62	49.98	57.50
5	0	0	0	0	$-\alpha$	72.66	54.61	75.30	79.72
6	0	0	0	0	$+\alpha$	72.22	53.55	78.80	77.57
7	0	0	0	$-\alpha$	0	69.85	51.48	71.56	81.33
8	0	0	0	$+\alpha$	0	71.65	50.71	70.05	77.14
9	0	0	$+\alpha$	0	0	70.67	34.75	59.50	88.17
10	0	0	$-\alpha$	0	0	35.90	23.05	31.56	88.01
11	0	0	0	0	0	55.91	57.80	67.74	87.27
12	0	0	0	0	0	56.96	69.15	61.55	85.38

$\alpha^1 =$ 1.3

The obtained results from RSM and fractional factorial stages show that the maximum removal efficiency for DOC was 72.66 ± 4.97 % for Water 2 in run 5 of the RSM block, with a pH of 6.5, coagulant dose of 7.18 mg /mg DOC, Fe/(Fe + Al) of 0.5, fast mixing speed of 165 rpm, and settling time of 0 min. The highest UV254 reduction and HAA5 removal were obtained in run 12 of the first stage of the experiments for Water 2 (R = 76.00 ± 5.42 % for UV254 and R = 80.25 ± 3.90 % for HAA5), with a pH of 7.5, coagulant dose of 10.53 mg /mg DOC, Fe/(Fe + Al) of 0.75, fast mixing speed of 210 rpm, and settling time of 20 min. The maximum reduction in the level of THM4 (R = 88.17 ± 4.60 %) was obtained at a pH of 6.5, a coagulant dose of 7.18 mg /mg DOC, an identical dosage of $FeCl_3$ and $Al_2(SO_4)_3$, Fe/(Fe + Al) of 1.00, fast mixing speed of 165 rpm, and settling time of 40 min. The maximum DOC removal, as well as the HAA5 and THM4 reductions, for Water 1 were 61.90, 68.60, and 82.05 %, respectively. In general, the efficiency of the coagulation process at the reduction of DOC and DBPs was higher in the experimental combinations with a basic pH in Water 2 than Water 1. However, the CFS in both water samples, with different SUVA and NOM characteristics, resulted in an ~70 % reduction in both the THM4 and HAA5. SUVA in water samples range from 3.15 to 4.54 (L mg^{-1} cm^{-1}) and according to Matilainen *et al.,* (2011), the moderate level of SUVA (2<SUVA<4) in Water 1 show that EC can remove 25 to 50 % of DOC, while SUVA level more than 4 in Water 2 indicate the water samples is very hydrophobic and EC is probably an effective method for removing NOM (efficiency>50%).

Table S.3. 4. ANOVA Results.

	Water 1				Water 2			
Variable	DOC(%)	$HAA5$(%)	$THM4$ (%)	$UV254$(%)	DOC (%)	$HAA5$(%)	$THM4$ (%)	$UV254$(%)
R^2	0.85	0.954	0.97	0.97	0.85	0.84	0.89	0.86
$R^2_{Adjusted}$	0.81	0.88	0.95	0.97	0.81	0.79	0.85	0.82
$R^2_{Predicted}$	0.641	0.61	0.90	0.94	0.68	0.64	0.71	0.74
Sum of Squares	1,519.94	1,626.8	1,664.9	4,177	4,047.35	8,809.63	9,369.84	6,290.76
P-Value Model	0.0001	0.0009	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
P-Value Lack of Fit	0.87	0.69	0.90	0.99	0.0957	0.4382	0.3363	0.433
Curvature	Not Significant	Not Significant	Not Significant	Not Significant	Significant	Significant	Significant	Significant

The assessment of the existence of a linear relationship between the responses and a combination of variables in the regression models was performed via a null hypothesis test. A rejection of the null hypothesis implied that at least one regression coefficient for the parameters was not zero, and, consequently, the model could be deemed significant (Montgomery, 2013).

$R^2_{adjusted}$ is the sum of variances in the model adjusted with the non-significant terms in the model, and $R^2_{predicted}$ represents the regression model's ability to define the points not included in the model. The values of $R^2_{adjusted}$, according to the ANOVA results for all of the produced models for the two tested waters, differ from each other by less than 20 % for all of the developed equations (Equations 3.4 to 3.11). Based on the p-value of the lack of fit, the best regression model was that of the UV254 removal (%), with a calculated $R^2_{adjusted}$ of 0.97, and $R^2_{predicted}$ of 0.94.

S.3.4. Adequacy of the produced models for Water 1

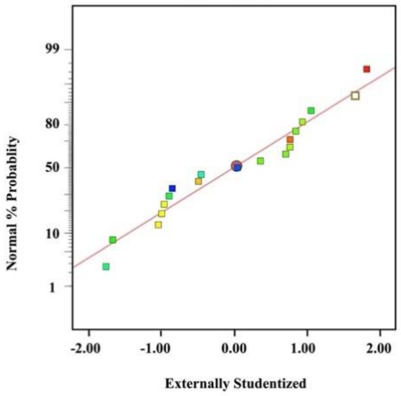


Figure S.3. 1. Normal plot of residuals for DOC removal in Water 1

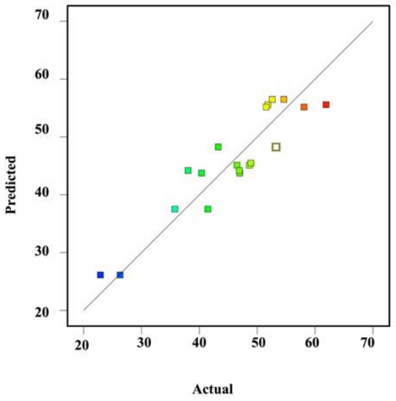


Figure S.3. 2. Predicted values vs. actual data for DOC removal in Water 1

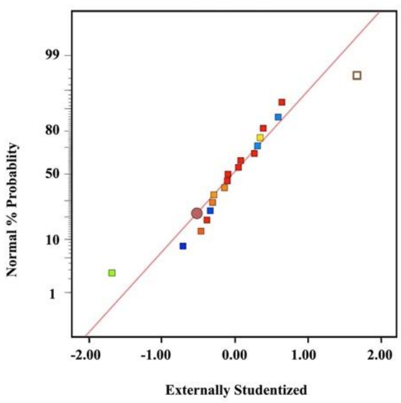


Figure S.3. 3. Normal plot of residuals for UV254 reduction in Water 1

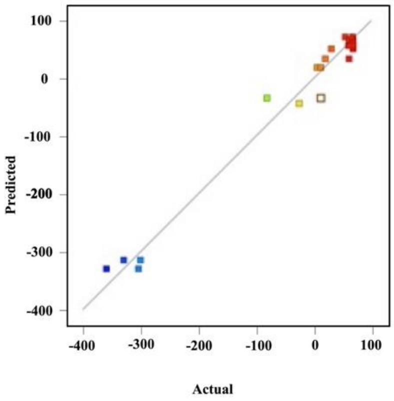


Figure S.3. 4. Predicted values vs. actual data for UV254 removal in Water 1

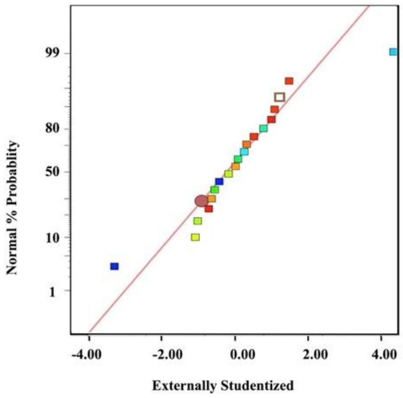


Figure S.3. 5. Normal plot of residuals for HAA5 removal in Water 1

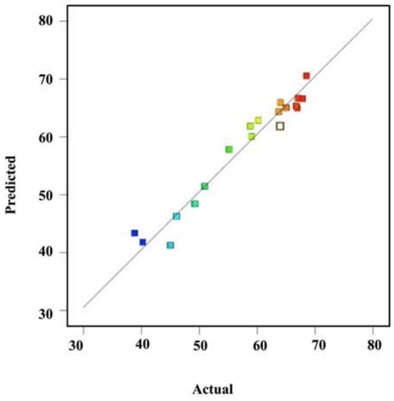


Figure S.3. 6. Predicted values vs. actual data for HAA5 removal in Water 1

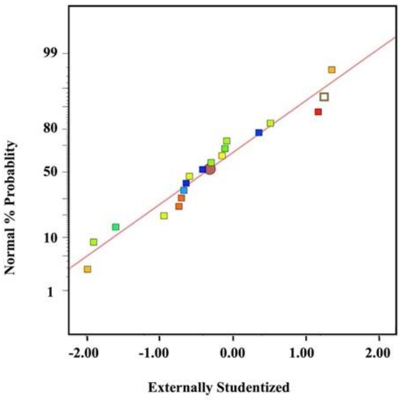


Figure S.3. 7. Normal plot of residuals for THM4 removal in Water 1

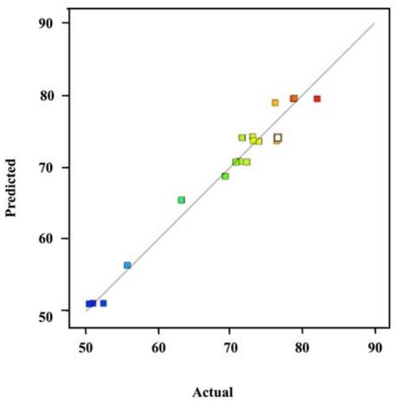


Figure S.3. 8. Predicted values vs. actual data for THM4 removal in Water 1

S.3.5. Adequacy of the produced models for Water 2

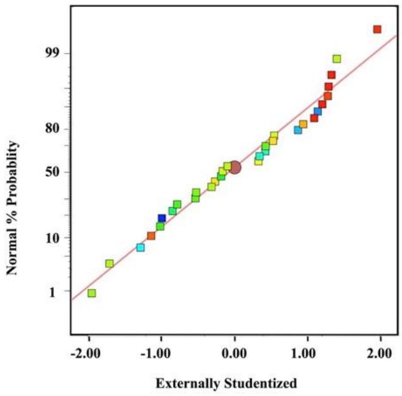


Figure S.3. 9. Normal plot of residuals for DOC removal in Water 2

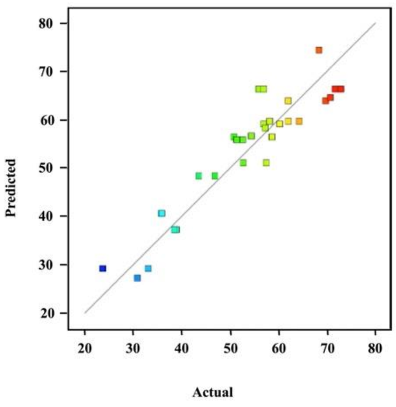


Figure S.3. 10. The plot of predicted values vs. actual data for DOC removal in Water 2

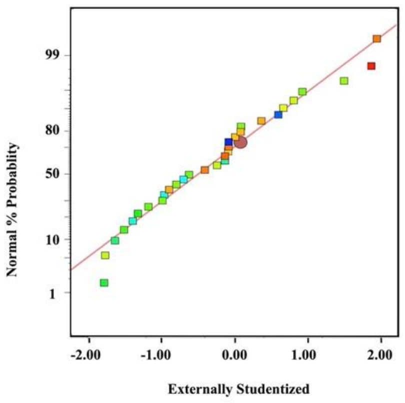


Figure S.3. 11. Normal plot of residuals for UV254 in Water 2

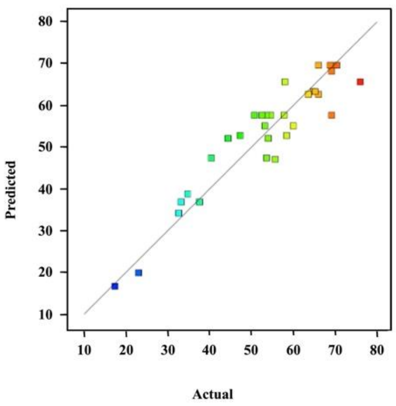


Figure S.3. 12. Predicted values vs. actual data for UV254 in Water 2

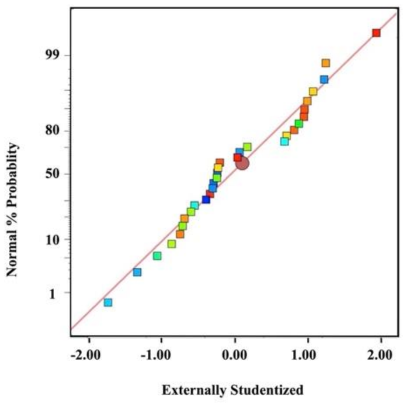


Figure S.3. 13. Normal plot of residuals for HAA5 reduction in Water 2

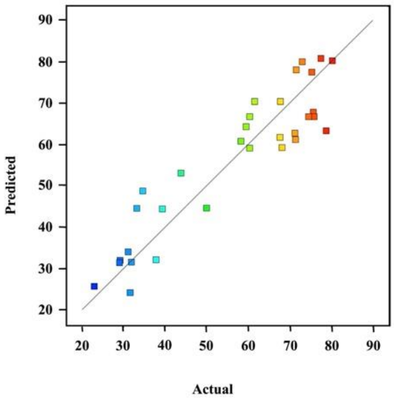


Figure S.3. 14. Predicted values vs. actual data for HAA5 reduction in Water 2

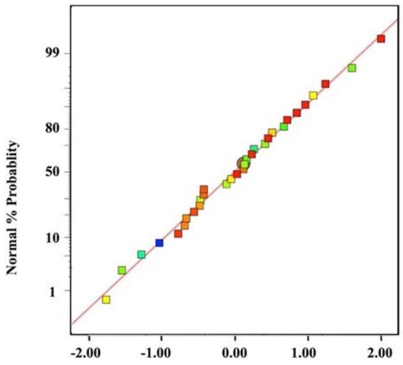


Figure S.3. 15. Normal plot of residuals for THM4 reduction in Water 2

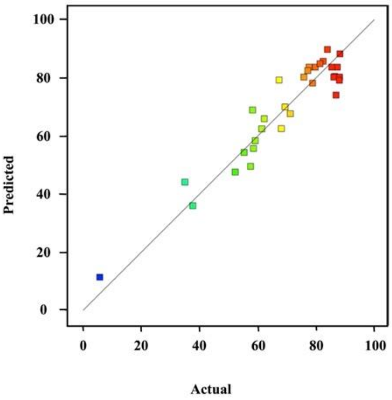


Figure S.3. 16. Predicted values vs. actual data for THM4 reduction in Water 2

S.3.6. The effect of factors on the DOC removal

The contour plots (Figures S.3.17a,b) illustrate that the quadratic terms of the variables, i.e., pH and dose, as well as the interaction effect between the coagulant type and dose, are significant at DOC removal in the contour plots. Racar *et al.,* (2017) found that the quadratic terms of the concentration of Fe^{3+} and pH are significant in DOC removal. Their analysis resulted in a mathematical model with quadratic and cubic terms of iron concentration, pH, and their interaction effect. Li *et al.,* (2016) developed a regression model for TOC concentration based on dosage, pH, basicity, and all of the variables' quadratic terms. In another study, Alfaro *et al.,* (2016) found the term pH × coagulant dosage of high importance in eliminating DOC via charge neutralization and sweeping processes.

The results of this study are in agreement with the previous studies so far in terms of DOC removal. The positive contribution of pH to DOC removal in the obtained models for both water samples (Equations 3.4 and 3.5) in this study is related to an increasing dissociation of humic materials in water with an increasing pH (from 5.5 to 7.5). With higher dissociation levels of humic substances, higher adsorption to positively charged coagulant hydroxide compounds occurs (Alfaro *et al.,* 2016) that enhances DOC removal.

Contour plot for Water 1 (Figure S.3.17a) and Equation 3.4 illustrate that increase in the coagulant dosage and pH as well as a decrease in the ratio of Fe/(Fe + Al) (i.e., using alum as a coagulant), contributes positively to DOC removal which illustrate the dominance of sweeping mode for DOC removal. Increasing the dosage of alum and the pH results in the polymerization of aqueous hydroxyl Al^{3+} in water. Consequently, DOC is adsorbed on the polymerized hydroxide Al^{3+} (Tang *et al.,* 2015). The type of coagulant is the most significant factor in the produced model of DOC removal in both sweeping and charge neutralization processes in this study. Dose^2 and Dose in charge neutralization mode is more significant than pH as an increase in the optimal concentration of ferric chloride increases the charge neutralization for the deprotonated carboxylic functional groups of the humic substances and increases the level of aggregation of the particles (Siéliéchi *et al.,* 2008). In contrast the effect of dose-coagulant interaction is of higher significance in sweeping mode of Water 1 because the hydroxide species of alum in the solution are affected by the pH and dosage, defining the sweeping or charge neutralization domination in the coagulation mechanism. Amorphous monomeric Al hydroxide, $\mathrm{Al(OH)_{3(amp)}}$, contributes to the adsorption of the precipitated particles and floc growth in the sweeping mechanism at high pH and dosage.

The contour plot of the dose and coagulant type for DOC removal in Water 2 (Figure S.3.17b) represents the optimal conditions with increasing dosage of ferric chloride, i.e., 7.85 < Dose (mg/mg DOC) < 9.19, and a low dosage of alum under 5.5 < pH < 7.5. Increasing the amount of coagulant dosage in this case will increase the level of destabilization of the DOC fraction with a negative charge (Alfaro *et al.,* 2016). This holds true for both of water samples in this study.

S.3.7. Effect of factors on UV254 removal

The fitted models for the removal of UV254 are presented in Equations 3.6 and 3.7 for Water 1 and Water 2, respectively. The most significant model terms in order of importance are $\frac{\mathrm{Fe}}{\mathrm{Fe+Al}} > \mathrm{Dose} \times \frac{\mathrm{Fe}}{\mathrm{Fe+Al}} > \mathrm{Dose} > \mathrm{pH}$ for both produced models. The contour plot of UV254 removal (Figure S.3.17c) represents the optimal condition for decreasing the UV254 of Water 1 based on dose and Fe/(Fe + Al). The maximum removal efficiency of UV254 was obtained at high levels of alum (increasing the dose to 10.53). The optimal conditions for UV254 removal in Water 2 occurred with $7.85 < \text{dosage} < 10.53$ and $0.5 < Fe/(Fe + Al) < 0.75$, suggesting that ferric chloride removes UV254 more effectively than alum.

Similarities were observed between the fitted models of UV245 and DOC removal in terms of the effective coded factors and optimal conditions. Previous studies have shown that UV254 is an indicator of humic substances in water (Leenheer and Croue, 2003), such that differential UV254 ($\Delta UV254$) absorbance is a rapid and precise measurement of the removal of hydrophobic NOM, e.g., humic acids, in an enhanced coagulation process (Ghernaout *et al.,* 2009). Dlamini et al., (2013) suggested $\Delta UV254$ as a surrogate parameter for the efficiency of water treatment methods for the removal of NOM, finding that the factors that influence DOC removal are effective at UV254 removal. The significant factors (i.e., pH, dose, and Fe/Fe + Al) in removing humic substances via charge neutralization and sweeping in Water 1 and Water 2 (discussed in section 3.3) were also found effective at decreasing the level of UV absorbance at 254 nm.

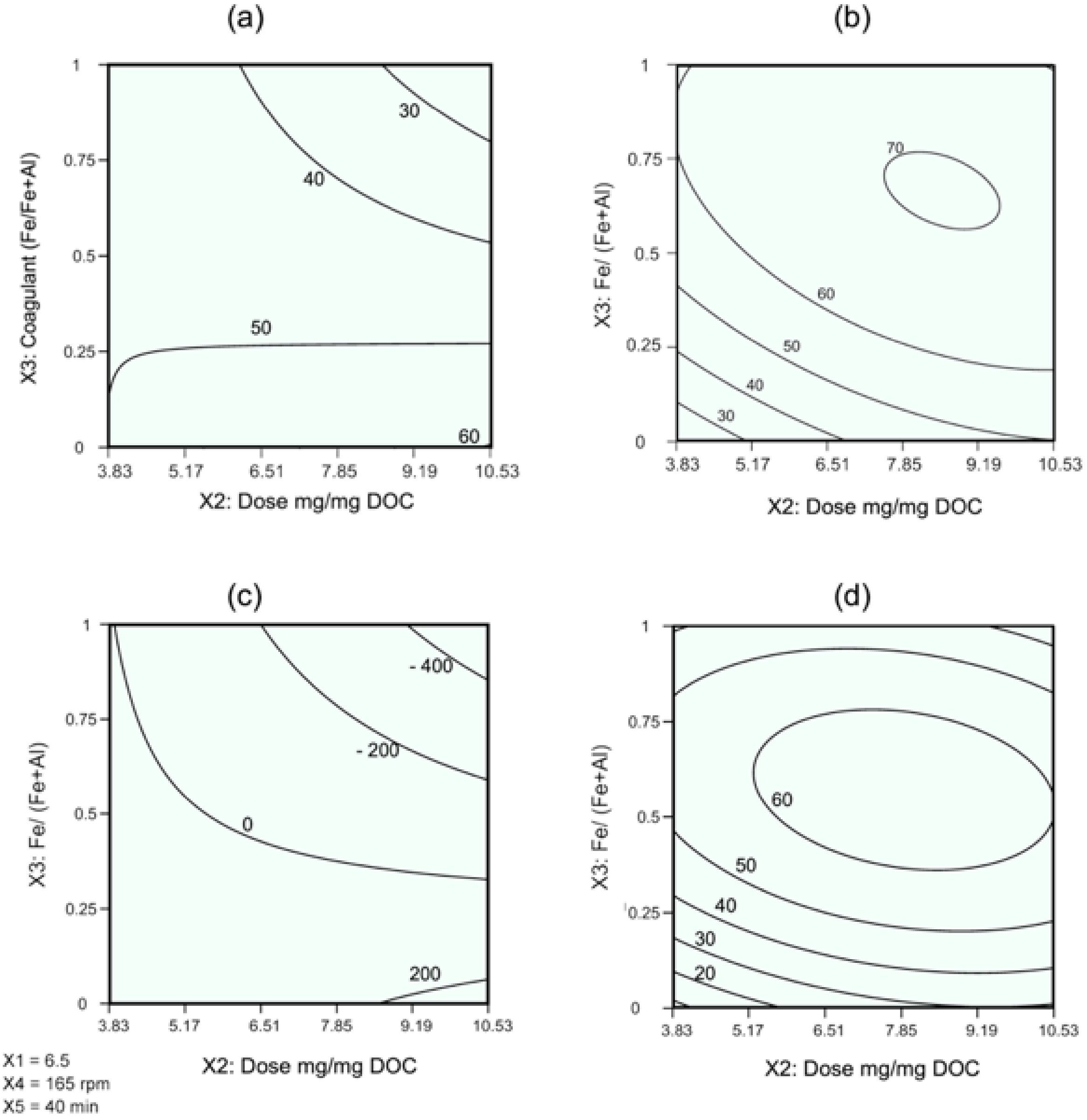


Figure S.3.1 Contour plot (a) DOC removal in Water 1 (b) DOC removal in Water 2 (c) UV254 reduction in Water 1 (d) UV254 in Water 2.

S.3.8. Optimization and Validation

Humic acids and polysuccharose were used for the preparation of two water samples containing 100% of VHA and NHI fractions respectively as decribed in previous studies (Alfaro *et al.,* 2016). The water samples characteristics are presented in Table S.3.4. The validation results for optimal conditions are presented in Table S.3.5.

Table S.3. 5. Raw water characterization.

Source	Origin	DOC (mg L^{-1})	HAA5 (ppb)	THM4 (ppb)	UV254 (cm^{-1})	VHA (ppm)	SHA (ppm)	CHI (ppm)	NHI (ppm)	VHA (%)
Water	Natural	9.35	327.69	2317.1	0.297	6.64	0.54	0.18	1.99	71.02
Water	Natural	5.22	545.76	1639.35	0.237	3.50	0.29	0.12	1.31	67.05
Water	Natural	9.98	2175.42	2485.12	0.518	8.10	0.74	0.31	0.82	81.16
Water	Natural	7.38	1359.73	1849.47	0.305	5.06	0.96	0.59	1.26	68.56
Water	Synthetic	9.05	2213.49	1088.38	1.03	8.90	0.32	<0.10	<0.10	98.34
Water	Synthetic	9.22	1495.8	345.08	0.018	0.00	0.00	0.00	9.7	0.00

VHA: Very hydrophobic acid; SHA: slightly hydrophobic acid; CHI: charged hydrophilic; NHI: neutral hydrophilic. HAA5 and THM4 are measured based on a formation potential within 72 H; ppb: part per billion; ppm: part per million; VHA%: VHA (mg L^{-1})/ DOC (mg L^{-1}).

Table S.3. 6. Validation results for the optimization conditions.

Source	DOC (%)	HAA5 (%)	THM4 (%)	error (%)		
				DOC	HAA5	THM4
Water 1	51.87	62.10	80.55	-5.61	-3.94	-1.08
Water 2	64.36	70.30	91.00	-4.38	-10.03	8.33
Water 3	70.79	72.64	82.73	5.17	-7.04	-1.51
Water 4	68.14	70.95	78.57	1.24	-9.21	-6.46
Water 5	89.48	88.79	94.42	32.94	13.63	12.41
Water 6	44.98	45.51	68.38	-33.18	-41.75	-18.59

S.3.9. Mixing Energy and Cost Estimation

The jar tests were performed using a flat paddle phipps and bird jar testing device. The velocity gradient (G) curves of the device are presented in Figure S.3.18. The optimum fast mixing rotary speed of 120 rpm in this study equals a velocity gradient of 95 s^{-1} shown in the curves. Equation S.3.3 correlates the velocity gradient with the power consumption in the jar testing.

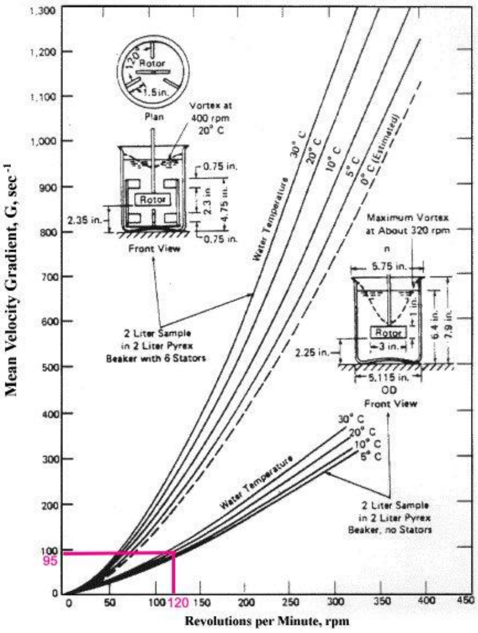
$$G = \sqrt{\frac{P}{V.\mu}} \qquad (S.3.3)$$

where, G is the velocity gradient (s^{-1}); P is the input power (W); μ represents the dynamic viscosity ($N\ s\ m^{-2}$), and V is the volume (m^3) (Cornwell and Bishop, 1983). The velocity gradient for proper mixing in a full-scale water treatment facility is suggested to be 300–1000 s^{-1} (EPA, 1999). Then, referring to Equation S.3.4, an increase in velocity gradient from 95 to 300 for a WTP will increase the power as follows:.

$$\frac{G_1^2 V_2}{G_2^2 V_1} = \frac{P_1}{P_2} \qquad (S.3.4)$$

where, G_1 equals 95 s^{-1}; G_2 equals 300 s^{-1}; V1 = 500 mL in this study ; V2 = 2000 mL in the graph. P1 is the input power in the jar test and P2 is the input power for the velocity gradient of 300 s^{-1} in the WTP. Under these conditions, $P_2 = 2.49 \times P_1$. Thus, the power consumption in a fast mixing unit of the WTP can be reduced up to 59.88%. A study by Vadasarukkai and Gagnon, (2017) showed that DOC removal is achievable with velocity gradients less than 200 s^{-1} because ligand complexation of iron and DOM are not depdependent on the rotation speed in fast mixing. AWWA recommends a G value of 600–1000 s^{-1} (Randtke and Horsley, 2012) that results in 90% more power consumption comapred to the results obtained by Vadasarukkai and

Gagnon (2017).



Velocity gradient calibration curves for water.

Figure S.3. 17. Velocity gradient calibration curve for Jar-testing device by Phipps and Bird, USA

An estimation of the consumed energy and corresponding costs at two velocity gradients of 190 s^{-1}, 300 s^{-1}, and 600 s^{-1} are presented in Table S.3.7. The calculations are based on a hypothetical WTP with an average flow of 1 m^3s^{-1} using Equation S.3.5. An average water temperature of $15℃$, an efficiency of 85% for motor (Vadasarukkai and Gagnon, 2017), and a 60 s mixing time were used for the average power utilization in kWh/year. The average cost of 0.13 CAD/ kWh^{-1} is used for costs estimations.

$$\text{Power (kWh/year)} = G^2 \times \mu \times Q \times t \times 8760\, {}^{h}/_{year} \times 0.001\, {}^{W}/_{kW} \div EF$$

(S.3.5)

Where power is the consumed power in the fast-mixing stage ($kWh.year^{-1}$), G is the velocity gradient (s^{-1}), μ is dynamic viscosity of water (Nsm^{-2}), Q is the average flow rate (m^3s^{-1}), t is the mixing time (i.e., 60 s), EF is the motor efficiency.

Table S.3. 7. Energy reduction and power cost by fast mixing speed optimization

G values (s^{-1})	190	300
energy (kWh/year)	21,579	53,798
Power Cost (CAD)	2,805	6,993

An estimation of the cost efficiency for the reduction of coagulant dosage for two optimization condition: DOC removal, and DBPs reduction are presented in Table S.3.8. The consumed coagulants and related costs at two dosages of 5.95 and 7.81 mg /mg DOC at a ratio of Fe/Fe+Al=0.76 mol/mol were considered for the calculations of an imaginary WTP with an average capacity of 1 m3s-1. The DOC level of 10 mgL^{-1} , and an average price of 300, and 425 CAD per ton of ferric chloride and aluminum sulfate respectively, are assumed for costs estimations:

Table S.3. 8. Coagulant consumption and corresponding costs by coagulant optimization for DBPs reduction

Coagulant dosage (mg/mg DOC)	5.95	7.81
Ferric chloride (ton/year)	1407.6	1847.6
Aluminum Sulfate (ton/year)	468.8	615.4
Total Cost (CAD)	621,519.9	815,810.1

The optimization of coagulant dosage for DBPs reduction resulted in a cost reduction of 194,920.25 CAD per year. The obtained results for a total cost reduction from power consumption in the fast-mixing stage and the coagulant dosage contribute to a 198,478.25 financial saving in a typical WTP.

S.3.10. References

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APPENDIX 2

SUPPLEMENTARY INFORMATION FOR CHAPTER 4

LOW COST ACTIVATED CARBON FOR REMOVAL OF NOM AND DBPS: OPTIMIZATION AND COMPARISON

Table S.4. 1. Experimental results for the optimization of adsorption capacity considering time, dose, and pH in terms of actual levels.

Std	Time A	Dose B	pH C	R1: DOC removal	R2: qe (mg/g)
1	5.26	0.14	5.20	46.76	17.25
2	19.23	0.14	5.20	49.48	18.26
3	5.26	0.40	5.20	61.86	7.88
4	19.23	0.40	5.20	76.87	9.80
5	5.26	0.14	8.80	29.42	10.86
6	19.23	0.14	8.80	39.87	14.59
7	5.26	0.40	8.80	42.11	5.37
8	19.23	0.40	8.80	45.37	5.78
9	0.50	0.27	7.00	53.78	10.19
10	24.00	0.27	7.00	76.93	14.55
11	12.25	0.05	7.00	28.69	32.05
12	12.25	0.50	7.00	61.42	6.40
13	12.25	0.27	4.00	57.89	10.97
14	12.25	0.27	10.00	26.30	4.98
15	12.25	0.27	7.00	58.93	11.16
16	12.25	0.27	7.00	57.58	10.91
17	12.25	0.27	7.00	55.99	10.61

[1] Std: standard run number, R: response, a:1.68, qe: adsorption capacity (mg/g).

Table S.4. 2. ANOVA for quadratic model of DOC removal.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1.59	9	0.1763	27.00	0.0001	significant
A-Time	0.1147	1	0.1147	17.57	0.0041	significant
B-Dose	0.4537	1	0.4537	69.48	< 0.0001	significant
C-pH	0.6238	1	0.6238	95.53	< 0.0001	significant
AB	0.0006	1	0.0006	0.0882	0.7751	
AC	0.0013	1	0.0013	0.2064	0.6634	
BC	0.0068	1	0.0068	1.04	0.3411	
A^2	0.0199	1	0.0199	3.05	0.1243	
B^2	0.1327	1	0.1327	20.33	0.0028	significant
C^2	0.2036	1	0.2036	31.18	0.0008	significant
Residual	0.0457	7	0.0065			

df: degree of freedom

Table S.4. 3. ANOVA for quadratic model of qe.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3.64	9	0.4048	40.00	< 0.0001	significant
A-Time	0.1132	1	0.1132	11.18	0.0123	significant
B-Dose	2.42	1	2.42	238.66	< 0.0001	significant
C-pH	0.6274	1	0.6274	61.98	0.0001	significant
AB	0.0004	1	0.0004	0.0438	0.8403	
AC	0.0011	1	0.0011	0.1126	0.7471	
BC	0.0063	1	0.0063	0.6257	0.4549	
A^2	0.0074	1	0.0074	0.7294	0.4213	
B^2	0.0777	1	0.0777	7.68	0.0276	significant
C^2	0.2564	1	0.2564	25.33	0.0015	significant
Residual	0.0709	7	0.0101			

df: degree of freedom

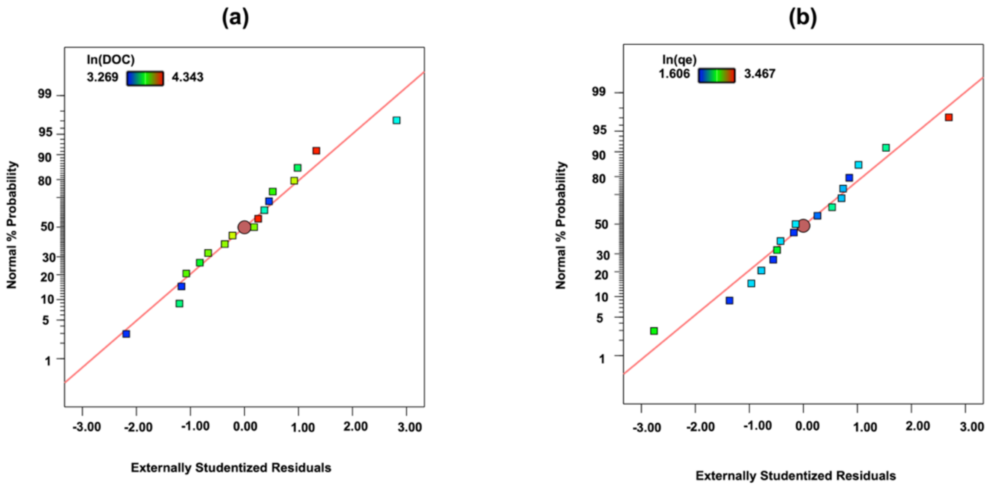

Figure S.4. 1. Plots of normal probability of residuals (a) DOC removal, (b) adsorption capacity (qe)

Table S.4. 4. Modeling results for equilibrium isotherms of natural and synthesized water sample

Model	Adsorbent	Water sample	Parameters		R^2
Freundlich	1.00% Al-AC	Natural	K_f=25.75,	n=1.78	0.95
	1.00% Al-AC	Synthesized	K_f=4.39,	n=1.33	0.94
	0.75% Fe-AC	Natural	K_f=16.56,	n=1.54	0.97
	0.75% Fe-AC	Synthesized	K_f=4.51,	n=1.51	0.87
	AC-A10	Natural	K_f=20.54,	n=1.90	0.93
	AC-A10	Synthesized	K_f=N/A,	n=N/A	0.63
Temkin	1.00% Al-AC	Natural	B=25.01		0.95
	1.00% Al-AC	Synthesized	B=11.95		0.93
	0.75% Fe-AC	Natural	B=26.71		0.99
	0.75% Fe-AC	Synthesized	B=9.47		0.85
	AC-A10	Natural	B=20.54		0.98
	AC-A10	Synthesized	B=N/A		0.52

APPENDIX 3

SUPPLEMENTARY INFORMATION FOR CHAPTER 5:

TREATMENT OF NATURAL ORGANIC MATTER WITH ENHANCED COAGULATION AND ADSORPTION FOR CONTROLLING DBPS

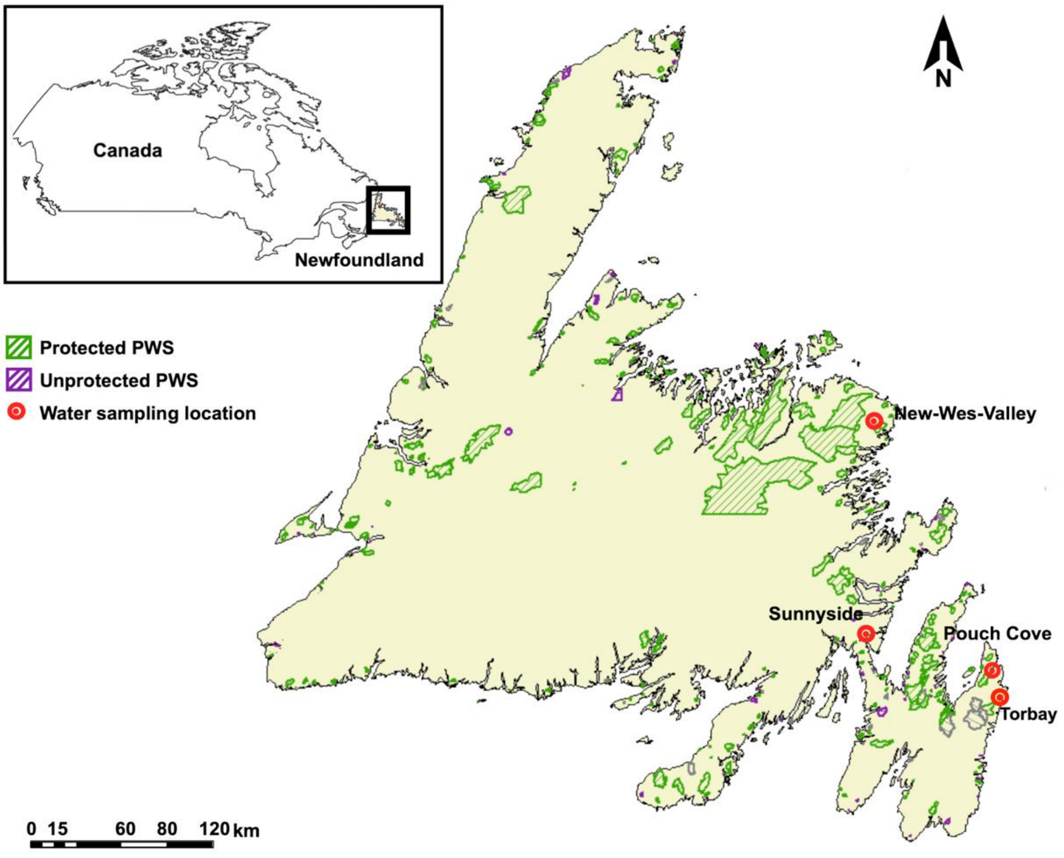

Figure S.5. 1. Public water supplies (PWS) in Newfoundland and locations of water sampling adapted from (Water resources portal 2021)

Table S.5.1. A review of the recent studies on the seasonal changes of NOM

Location	Sampling Duration	Fractionation Method	DOC Trend and Fractions	Reference
South Africa and Belgium	9 months	N/A	summer DOC>winter DOC	Ndiweni et al., (2019)
Scotland	18-30 months	XAD	highest TOC, UV, and THMfp in July HPO was the main fraction of TOC and most reactive part for THMfp	Golea et al., (2017)
Alaska	11 months	XAD	high DOC in summer and winter, lower DOC in spring	Cao et al., (2016)
Alaskan Beaufort Sea	30 months	N/A	lowest DOC in April, high DOC in June	Connelly et al., (2015)
Turkey	9 months	XAD	TPI the precursor of HAAs, TPI and HPI the dominant part of DOC	Karapinar et al., (2014)
Finland	11months	XAD	highest DOC in May most of DOC related to HOA	Mikola et al., (2013)
United States	11 months	N/A	DOC was high in summer and low in winter	Brinkman and Hozalski (2011)
China	9 months	XAD	highest TOC in May most of TOC related to HOA and HIM	Wei et al., (2008)
China	12 months	XAD	highest DOC in Sep most of THMs and HAAs were formed from HOA	Chen et al., (2008)
England	11 months	XAD	highest DOC in Dec, highest HOA in winter	Sharp et al., (2006a)
England/Albert WTP	20 months	XAD	highest DOC in Aug, highest HOA in Jan the most variable part is fulvic acids	Sharp et al., (2006b)
Japan	22 months	XAD	HOA and HIA were the dominant part of DOC	Imai et al., (2001)

DOC: dissolved organic carbon, TOC: Total organic carbon, UV: Ultraviolet absorbance at wavelength 254 nm, THMfp: formation potential for trihalomethanes, HAAs: five regulated haloacetic acids, HOA: hydrophobic acids, HIA: hydrophilic acids, HIM: hydrophilic matter, TPI: transphilics, WTP: water treatment plant, XAD: XAD resins for fractionation

Table S.5.2. Characteristics of activated carbons

Sample	Surface Area (BET) (m^2/g)	Micropore Volume (cm^3/g)	Methylene blue value (mg/g)	Iodine Number (mg/g)	qmax (mgDOC/g)
AC-A10	808.29	0.21	265	1212	87.59
1.00% Al-AC	783.29	0.18	234	925	118.30
0.75% Fe-AC	709.89	0.19	226	931	126.40

AC: activated carbon, DOC: dissolved organic carbon, q_{max}: maximum adsorption capacity (mg/g); Adapted from (Tafvizi et al., 2021a)

Table S.5.3. Characteristics of raw water during the sampling period

Source	Date month-YY	DOC (mgL^{-1})	UV254 (cm^{-1})	UV272 (cm^{-1})	VHA (%)	SHA (%)	CHI (%)	NHI (%)
Water 1	May-17	6.17	0.18	0.15	45.2%	4.4%	18.9%	31.6%
	Aug-17	9.35	0.30	0.24	71.0%	5.8%	2.0%	21.2%
	Nov-17	8.32	0.35	0.30	81.4%	1.6%	0.9%	16.1%
	Mar-18	6.92	0.26	0.21	65.0%	14.0%	3.0%	18.0%
	May-18	4.05	0.15	0.12	55.8%	17.0%	1.2%	25.8%
	Aug-18	7.98	0.28	0.25	69.0%	10.7%	1.1%	19.2%
	Dec-18	6.55	0.28	0.25	78.0%	6.0%	1.0%	15.0%
	Mar-19	6.19	0.23	0.19	61.0%	18.0%	2.0%	19.0%
	May-19	5.67	0.14	0.11	37.9%	1.0%	19.8%	17.1%
Water 2	May-17	5.22	0.24	0.20	60.9%	5.7%	6.2%	27.2%
	Aug-17	7.06	0.32	0.27	63.0%	8.6%	2.9%	25.6%
	Nov-17	8.43	0.47	0.40	74.8%	8.8%	3.2%	13.3%
	Mar-18	7.36	0.34	0.31	69.0%	7.0%	3.0%	21.0%
	May-18	5.02	0.22	0.18	66.0%	12.4%	1.7%	19.9%
	Aug-18	6.95	0.30	--	64.0%	10.0%	3.0%	23.0%
	Dec-18	8.72	0.37	0.32	73.0%	9.0%	3.0%	15.0%
	Mar-19	7.18	0.35	0.25	71.0%	14.1%	4.9%	10.0%
	May-19	6.52	0.25	0.21	72.1%	13.1%	5.8%	9.0%
Water 3	Mar-18	8.56	0.33	0.28	69.4%	10.7%	7.4%	12.3%
	May-18	8.74	0.36	0.29	68.1%	1.5%	9.0%	21.3%
	Jul-18	13.08	0.53	0.43	58.0%	1.9%	4.3%	35.0%
	Aug-18	7.34	0.35	0.30	70.0%	18.1%	10.9%	9.8%
	Nov-18	7.81	0.38	0.31	73.2%	7.9%	7.9%	11.0%
	Mar-19	7.04	0.31	0.25	72.6%	17.1%	16.3%	5.2%
	May-19	7.86	0.40	0.31	76.8%	9.4%	8.7%	5.1%
	Jul-19	9.97	0.51	0.44	81.2%	8.6%	3.6%	6.3%
Water 4	May-17	2.85	0.03	0.02	66.2%	5.5%	2.1%	26.2%
	Aug-17	3.02	0.04	0.03	69.8%	10.6%	0.8%	18.6%
	Nov-17	3.87	0.08	0.07	60.5%	10.4%	2.7%	26.3%
	Mar-18	2.96	0.03	0.03	58.8%	8.1%	4.9%	28.2%
	May-18	2.73	0.03	0.03	67.8%	6.6%	0.0%	25.6%
	Aug-18	3.11	0.04	0.03	71.1%	8.8%	1.2%	18.9%
	Dec-18	3.29	0.05	0.04	62.9%	10.4%	2.1%	24.6%
	Mar-19	3.56	0.07	0.07	61.1%	10.1%	3.5%	25.3%
	May-19	2.96	0.04	0.04	62.6%	8.7%	5.8%	22.9%

DOC: dissolved organic carbon, UV254: UV absorbance at the wavelength 254nm, UV272: UV absorbance at the wavelength of 272 nm, VHA: very hydrophobic acids, SHA: slightly hydrophobic acid, CHI: charged hydrophilic, NHI: neutral hydrophilic.

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