

**KINETICS AND FATE OF NATURAL ORGANIC MATTER UNDER DIFFERENT
WATER MATRICES USING BASIC ION EXCHANGE RESINS**

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Chemical and Biological Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

March 2016

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Abstract

This research has investigated the factors influencing the kinetics and efficacy of natural organic matter (NOM) removal during the anionic ion exchange process (IEX). A holistic approach was undertaken to evaluate various IEX resins in terms of their NOM removal kinetics and regeneration efficiency under batch and consecutive multiple loading cycles. Initial screenings indicated the strongly basic resin as a better candidate for NOM removal, and hence it was employed for subsequent experiments.

Different treatment parameters (resin dose, contact time, NOM source) were tested and detailed kinetic evaluations were conducted to determine the affinity and removal rate of NOM as well as nitrate, and sulfate that are generally present in natural waters. Results obtained showed a substantial removal of NOM (up to 80 %) and nitrate (up to 80 %), and a superior removal for sulfate (up to 98 %). Charge density and molecular weight were found to play a major role in the removal process. Different mathematical and physical models were employed to predict the experimental data and the rate-limiting step was found to be pore diffusion which was affected by the resin dose/solute concentrations ratio. Moreover, the impact of IEX resins on NOM fractions and subsequent water quality parameters was investigated in this study. Humic (-like) substances were mainly targeted by IEX, and more hydrophilic and/or non-ionic fractions were slightly removed. Application of IEX reduced the formation potential of carbonaceous and nitrogenous disinfection by-products by 13-20 % and 3-50 %, respectively. Also, the practice of IEX treatment reduced the assimilable organic carbon levels by 30-40 %. Additionally, a positive effect of IEX, as a pretreatment to UV/H₂O₂, at reducing the •OH scavenging characteristics of the water was observed. Electrical energy per order for removing a probe compound (i.e., pCBA) showed 20-40 % reduction indicating the improvement in the efficacy of UV/H₂O₂ treatment.

Findings of this study display the robustness of IEX process for drinking water applications and lay down a quantitative approach for evaluating the kinetics of this process under various treatment conditions.

Preface

I was in charge of conducting the literature survey, identifying the research gaps and questions, developing the research proposal, design and conducting the experiments, performing the analysis (unless otherwise stated in below), and analyzing the data (unless otherwise stated in below), writing the manuscripts, and preparing the conference presentations and posters throughout the course of this research under the supervision of Professor Madjid Mohseni at the chemical and biological engineering department of the university of British Columbia, Vancouver. The followings are detailed elaboration on my role and contribution to specific chapters of this dissertation.

- A version of chapter 4 was submitted to the Journal of Environmental Engineering with the following title:

M. Bazri, B. Barbeau, and M. Mohseni, Evaluation of weak and strongly basic anion exchange resins for NOM removal, *Journal of Environmental Engineering, In Press, 2016*.

This part of the research was funded by RES'EAU-WaterNET NSERC strategic Network. I was the main researcher of this project and have designed, conducted, and analyzed the experiments and the data produced as a result. Part of the water samples used in this study was provided by Professor Benoit Barbeau from Ecole Polytechnique de Montreal and all the experiments were conducted in the advanced oxidation laboratory in the Department of Chemical and Biological Engineering, UBC. The manuscript was primarily written by myself and revised by all listed authors.

- A version of chapter 5 was submitted to the journal of Water Research with the following title:

M. Bazri and M. Mohseni, Impact of NOM properties on the kinetics of IEX process, *Water Research*, 91, 147-155, 2016.

This part of the research was funded by RES'EAU-WaterNET NSERC strategic Network. I was the main researcher of this project and have designed, conducted, and analyzed the experiments and the data produced as a result. All the experiments were conducted in the advanced oxidation laboratory in the department of chemical and biological engineering, UBC. The manuscript was primarily written by myself and revised by all listed authors.

- A version of chapter 6 has been submitted for publication with the following title:

M. Bazri, Siva Sarathy, and M. Mohseni, Impact of background water matrix on the kinetics of IEX process, *Submitted*, 2016.

This part of the research was co-funded Mitacs Canada, Trojan Technologies, and RES'EAU-WaterNET NSERC Strategic Network. I was the main researcher of this project and have designed, conducted, and analyzed the experiments and the data produced as a result. All the experiments were conducted in Research & Development department of Trojan Technologies, London, ON, under co-supervision of Dr. Siva Sarathy (Trojan Technologies) and Professor Madjid Mohseni (UBC). The manuscript was primarily written by myself and revised by all listed authors.

- A version of chapter 7 was submitted to the Chemosphere Journal with the following title:

M. Bazri, B. Martijn, J. Kroesbergen, and M. Mohseni, Impact of Anionic Ion Exchange Resins on NOM Fractions: Effect on N-DBPs and C-DBPs precursors, *Chemosphere*, 144, 1988-1995, 2016.

This part of the research was co-funded by PWN Technologies, Netherlands and RES'EAU-WaterNET NSERC Strategic Network. I was the main researcher of this project and have designed, conducted, and analyzed data produced as a result. All the experiments were conducted in Het Waterlaboratorium, Haarlem, Netherlands under co-supervision of Dr. Jan Kroesbergen (Het Water Laboratorium) and Sr. Engineer Mr. Bram Martijn (PWN-T, Netherlands). Analyses of the samples were conducted by professional staff of Het Waterlaboratorium (HWL) and final raw data was provided for further analysis. The manuscript was primarily written by myself and revised by all listed authors.

- A version of chapter 9, was submitted to the Journal American Water Works Association with the following title:

M. Bazri, S. Sarathy, and M. Mohseni, Enhancement of UV/H₂O₂ efficacy by removing DOC and NO₃⁻ using ion exchange treatment, *Journal of American Water Works Association*, In Press, 2016.

This part of the research was co-funded by Mitacs Canada, Trojan Technologies, and RES'EAU-WaterNET NSERC Strategic Network. I was the main researcher of this project and have designed, conducted, and analyzed the experiments and ~ 75% the data produced as a result. All the experiments were conducted in Research & Development department of Trojan Technologies, London, ON, under co-supervision of Dr. Siva Sarathy (Trojan Technologies) and Professor Madjid Mohseni (UBC). Analysis of the p-CBA degradation data and EEO

calculations was done by Dr. Sarathy. The manuscript was jointly written by myself and Dr. Sarathy (UV/H₂O₂ related sections) and revised by all authors listed.

The following is the list of Journal Publications as mentioned above:

- **M. Bazri, B. Martijn, J. Kroesbergen, and M. Mohseni**, Impact of Anionic Ion Exchange Resins on NOM Fractions: Effect on N-DBPs and C-DBPs precursors, *Chemosphere*, 144, 1988-1995, 2016.
- **M. Bazri, B. Barbeau, and M. Mohseni**, Evaluation of weak and strongly basic anion exchange resins for NOM removal, *Journal of Environmental Engineering*, In Press, 2016.
- **M. Bazri, S. Sarathy, and M. Mohseni**, Enhancement of UV/H₂O₂ efficacy by removing DOC and NO₃⁻ using ion exchange treatment, *Journal of American Water Works Association*, In Press, 2016.
- **M. Bazri and M. Mohseni**, Impact of NOM properties on the kinetics of IEX process, *Water Research*, 91, 147-155, 2016.
- **M. Bazri, Siva Sarathy, and M. Mohseni**, Impact of background water matrix on the kinetics of IEX process, *Submitted*, 2016.

The following is the list of the conference podium presentations:

- **M. Bazri, B. Martijn, J. Kroesbergen, and M. Mohseni**, Effect of ion exchange on different fractions of NOM and subsequent AOC, International Water Association (IWA) 6th specialty conference on NOM, 2015, Malmo, Sweden.
- **M. Bazri, B. Martijn, J. Kroesbergen, and M. Mohseni**, Control of N-DBPs and C-DBPs precursors via ion exchange process, American Water Works Association Annual Conference and Exposition (ACE), 2015, Anaheim, CA, USA.

The two above presentation are the result of the collaborative work with PWN-T and HWL as stated earlier.

- **M. Bazri, and Madjid Mohseni**, Experiences form using ion exchange process for organic removal, British Columbia Water Works Association (BCWWA) Annual conference and trade show, 2015, Kelowna, Canada.
- **M. Bazri and Madjid Mohseni**, Evaluation criteria for selection of ion exchange resins for NOM removal, AWWA Water Quality and Technology Conference 2014, New Orleans, LA.
- **I. Monosov, M. Bazri, G. Imoberdorf, G. A. Vazquez-Rodriguez, B. Barbeau, and Madjid Mohseni**, Removal of Cyanobacterial Toxins and NOM using Ion Exchange Resins, presented at the AWWA- Water Quality and Technology Conference, November 2012, Toronto, Canada.

This work was conducted under my co-supervision with Dr. Imoberdorf and Dr. Mohseni and experimental work and ~ 90 % of the data analysis was performed by an undergraduate student Ms. Monosov. I participated in the experimental design and technical lab training/coaching and ~ 50% of the materials for the presentation was provided from my own

research, and revised by Dr. Imoberdorf, Mohseni and myself. I presented the work at the conference venue.

- **M. Bazri, S. Rahmani, G. Imoberdorf and M. Mohseni**, Ion Exchange Resins for Natural Organic Matter Removal, presented at BCWWA annual conference and trade show, April 2012, Penticton, BC, Canada.

Almost 75 % of the presentation materials were provided from my research and I was responsible to write the abstract and preparing ~ 75% of the materials presented at the conference venue.

The following is the list of the conference posters:

- **M. Bazri, S. Sarathy, and M. Mohseni**, Assessing the feasibility of ion exchange as a pretreatment to UV/H₂O₂ Advanced Oxidation Applications, AWWA Water Quality and Technology Conference 2014, New Orleans, LA.

This work is the product of collaboration with Trojan Technologies as stated earlier. I was responsible for preparing the poster and presenting it at the conference venue. The initial draft of the poster was revised by all authors.

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List of Abbreviations

AOC	Assimilable Organic Carbon
BDOC	Biodegradable Organic Carbon
Biot	Biot Number
C-DBP	Carbonous Disinfection by-Product
C_t	Concentration at t
C_0	Concentration at t=0
C_e	Concentration at equilibrium
\bar{C}	Resin Capacity
D	Diffusion Coefficient
D_a	Apparent Diffusivity
D_f	Film Diffusion Coefficient
D_p	Pore Diffusion Coefficient
$D_{p.e.}$	Effective Pore Diffusion Coefficient
D_l	Liquid Diffusivity
d	Blade Diameter
Da	Dalton (g/mol)
DBP	Disinfection by-Product
DIC	Dissolved Inorganic Carbon
DOC	Dissolved Organic Carbon
DON	Dissolved Organic Nitrogen
EEO	Electrical Energy per Order
eq	Equivalent

FA	Fulvic Acid
HA	Humic Acid
HPLC	High Performance Liquid Chromatography
HPSEC	High Performance Size Exclusion Chromatography
hr	hour
IC	Ion Chromatography
IEX	Ion Exchange
IL	Ijssel Lake
k_f	External Mass Transfer Resistance
k_1	First-Order Rate Constant
k_2	Second-Order Rate Constant
K_L	Langmuir Constant
K_F	Freundlich Constant
LC-OCD	Liquid Chromatography with Organic Carbon Detection
LP	Low Pressure
M	Resin Mass
min	minute
MIEX [®]	Magnetic Ion Exchange Process [®]
MP	Medium Pressure
MW	Molecular Weight
NSERC	Natural Sciences and Engineering Research Council of Canada
NOM	Natural Organic Matter
N-DBP	Nitrogenous Disinfection by-Product

N _{Re}	Reynolds Number
n	Freundlich Parameter
OND	Organic Nitrogen Detector
PL	Pony Lake
PLFA	Pony Lake Fulvic Acid
PSC	Scheveningen Water
q	Sorption Capacity
q _m	Maximum Sorption Capacity
q _e	Equilibrium Sorption Capacity
rps	Round per Second
R _p	Resin Radius
SBR	Strong Basic Resin
SR	Suwannee River
SRNOM	Suwannee River Natural Organic Matter
SRHA	Suwannee River Humic Acid
SRFA	Suwannee River Fulvic Acid
SMP	Soluble Microbial Product
SUVA	Specific UV Absorbance
SIX [®]	Suspended Ion Exchange Process [®]
s	Mixing Speed
TOC	Total Organic Carbon
t	Time
UV ₂₅₄	UV Absorbance at 254 nm

UVT%	UV Transmittance
U_t	Fractional Attainment (Uptake)
UV	Ultra Violet
V	Volume
\bar{V}	Resin Volume
WBR	Weak Basic Resin
X_i	Liquid Phase Concentration
Y_i	Solid Phase Concentration
α	Separation Factor
β_n	Non-zero Roots of $\tan\beta_n = \frac{3\beta_n}{3+\omega\beta_n^2}$
β	Non-removable Fraction of DOC (or TOC)
γ	Molecular weight power ($D \propto MW^\gamma$)
δ	Film Thickness
ε	Resin Porosity
μ	Dynamic Viscosity of Water
ρ	Liquid Density
ρ_a	Apparent Resin Density
ρ_s	Solid Phase Density
τ	Resin Tortuosity
ω	$\omega = \frac{VC_0}{q_e} - 1$
MGD	Mega gallon per day
ML	Mega Liter

Acknowledgements

I humbly offer my enduring gratitude to Professor Madjid Mohseni, whose expert guidance and patient mentorship is exceptional and inspiring. I cannot thank him enough for giving me the privilege to work, learn, develop, and shape my career under his supervision.

My sincerest appreciation is to Professor Benoit Barbeau and Professor Pierre Berube whose constructive comments and critical feedback shaped and tremendously enriched this work.

Also, I am extremely grateful to Dr. Bram Martijn (PWN Technologies, Netherlands) and Dr. Jan Kroesbergen (HWL) for their supervision and providing the opportunity to research in Netherlands. I am also very grateful to the staff of HWL and PWN-T for their amazing support, technical help, and their memorable hospitality.

I am sincerely thankful to my friend and supervisor Dr. Siva Sarathy (Trojan Technologies) for his kind support throughout my research at Trojan Technologies. While at Trojan Technologies, I had the opportunity to also work and benefit under supervision of Dr. Domenico Santoro whose technical and professional coaching, friendship, and critical feedback have had significant impact on my career. I also would like to thank all the experts and co-workers at Trojan Technologies in particular Dr. Ted Mao and Dr. Linda Gowman.

I also would like to offer my gratitude to Dr. Gustavo Imoberdorf for his input and immense assistance in early stages of this research.

I am truly thankful for the wonderful mentorship of Keyvan Maleki from RES'EAU WaterNET who has been a source of inspiration and unconditional help for the past seven years.

This research was privileged with superb dedication and excellent assistance of Anna Vasileva (University of Helsinki) and Melanie Radtke (University of Göttingen) who

significantly contributed to this work through experimental and analytical work as a part of their Master's internship program at UBC chemical and biological engineering department.

Dr. Nathanael Sieb and 4D LABS shared facility at Simon Fraser University are cordially thanked for the help in conducting the mercury porosimetry analysis.

Also, I would like to thank each and every member of the drinking water treatment group at CHBE as well as Timothy Ma and Joerg Winter at the environmental engineering laboratory at the civil engineering department, UBC.

During my curriculum at UBC, I had the opportunity to meet wonderful people who have become inspiring friends. In particular, I would like to thank Dr. Sona Moradi for her technical help that has enriched this work. Also, I extend my gratitude to Dr. Amir Dehkoda, Dr. Alireza Bagherzadeh, Dr. Vahid Bazargan, Dr. Mehdi Bagheri, Ramin Rezaei, Adrian Serrano Mora, Rob North, Soroush Nasser, Amin Nouri, Ata Kheirandish, Ghazal Ekram, and Reza Tafteh for all their moral support and friendship during the course of this work.

This research was funded by the premier Four-Year Fellowship from the University of British Columbia (Vancouver), and also financial support from Natural Sciences and Engineering Research Council of Canada (NSERC), RES'EAU WaterNET NSERC Strategic Network for Small Water Systems, PWN Technologies (Netherlands), Mitacs Canada, and Trojan Technologies (London, ON). Also, Purolite Canada kindly provided the ion exchange resins and supported this project. I would like to thank each and every one of these institutions for their significant contribution towards enriching this project.

My final and cordial gratitude and utmost respect is to my parents and my two wonderful sisters. They have been absolutely supporting and encouraging throughout my life and career. Words are just ineffable to express my indebtedness to them.

Dedication

To God for His enduring Grace and Bounty

To my Parents and Sisters for unconditionally believing in me

To Ali Sayad Shirazi, Mohammad Ebrahim Hemmati, and Ali Akbar Salehi

Chapter 1: Background

1.1 Natural Organic Matter (NOM)

Access to safe drinking water sources (as well as affordable water treatment technologies) is one of the major challenges for many small and remote communities across North America. In this regard, Natural Sciences and Engineering Research Council of Canada (NSERC) has financially supported RES'EAU WaterNET strategic network that has been created to understand, study, and address the challenges of small and remote communities in accessing safe and affordable drinking water. One of the challenges in treating the water sources for these communities is the presence of natural organic matter (NOM), commonly quantified as dissolved and or total organic carbon (DOC, TOC). NOM is a complex mixture of various organic substances found in surface and ground water sources and generally consists of hydrophobic, hydrophilic, and neutral fractions of varying chemical characteristics and molecular weights (Leenheer and Croué, 2003; Matilainen et al., 2002; Pelekani et al., 1999; Singer, 1999).

The presence of NOM in raw water brings about many potential issues with respect to water quality and treatment (Leenheer and Croué, 2003). High levels of NOM often lead to reduced aesthetic quality of water and taste and odour problems, as well as formation of disinfection by-products (DBPs) (Kleiser and Frimmel, 2000; Singer, 1999). It can also deteriorate biological stability and increase bacterial regrowth and biofilm formation potential within the distribution systems (Van der Kooij, 1992). Moreover, NOM is a potential cause of membrane fouling and can mitigate the efficiency of ultraviolet (UV)-based advanced oxidation

processes (AOPs), mainly used for disinfection and micropollutant removal, by screening the UV light and scavenging hydroxyl radicals (HO[•]) (Bazri et al., 2012; Sarathy et al., 2011).

1.2 Ion Exchange Process for NOM Removal

Because of its problematic presence, several chemical and physical processes have been suggested to remove NOM, thereby eliminating the associated concerns (Matilainen et al., 2002). Among those, application of anionic ion exchange (IEX) process has received considerable attention because of its effectiveness, ease of operation, scale up or down capabilities, small footprint, and relatively low cost (Bolto et al., 2002b; Chen et al., 2006; Croué et al., 1999; Drikas et al., 2002; Fu and Symons, 1990; Hongve et al., 1999). Moreover, the use of IEX technology deemed to be a promising alternative for the treatment of source waters serving small and remote communities. However, the efficacy of IEX can vary depending on resin properties (e.g., porosity, polymeric structure), process operation parameters (e.g., resin dose, contact time, regeneration ratio), and the influent water quality.

Studies, in general, have reported that strongly basic resins (SBR) with acrylic backbone and smaller bead size perform superior at NOM removal compared to other resins (Boyer and Singer, 2008a; Fu and Symons, 1990). Resins are reused for multiple cycles and brine (NaCl ~10 % wt) is generally used to regenerate the exhausted SBRs (from NOM uptake) and restore their removal capacity. Although efficient, regeneration with brine is chemically demanding and costly, e.g., 36 kg of NaCl per 1000 m³ of treated water and or 160 kg of NaCl per 1 m³ of spent resins according to Orica Watercare[®] and Purolite[®] websites ^{*,†}. Besides, the spent regenerant (i.e., brine) is not environmentally benign for disposal (Clifford, 1999; Höll and Kiehling, 1981;

* www.miexresin.com

† www.purolite.com

Rokicki and Boyer, 2011). In this aspect, weakly basic resins (WBR) are reported to offer lower costs associated with regeneration and waste disposal, but they provide lower removal capability (Evans and Maalman, 1979; Höll and Kiehling, 1981; Höll and Kirch, 1978; Matosic et al., 2000).

Aside from resin properties, NOM properties such molecular weight (MW), polarity (i.e., hydrophobicity), and charge density could significantly influence the removal kinetics and fate of NOM removal during the IEX treatment (Bolto et al., 2002b; Boyer and Singer, 2008b; Cornelissen et al., 2008). Studies focusing on the effect of NOM properties are however inconclusive and sometimes contradictory. Moreover, inorganic anions (e.g., nitrate, sulfate) that are commonly present in natural waters could compete with NOM for adsorption/exchange on the IEX resin. This will further affect / deteriorate the overall NOM removal mechanism and efficiency under IEX resins (Hsu and Singer, 2010; Ishii and Boyer, 2011; Jelinek et al., 2004; Mergen et al., 2008; Tan and Kilduff, 2007; Walker and Boyer, 2011; Willison and Boyer, 2012).

Furthermore, despite the abundance of studies on the application of IEX treatment (in general) in batch/continuous mode at lab and pilot scales (Boyer and Singer, 2008b; Clifford, 1999; Harland, 1994; Helfferich, 1965; Höll and Sontheimer, 1977; Kukučka et al., 2011; Kunin and Myers, 1949; Nativ et al., 1975), very little attention has been given to long-term performance of IEX treatment process and/or simulating practical conditions. Moreover, recent studies focusing on commercial practice of IEX for NOM removal have suggested the use of stirred (a.k.a. suspended) mode operation as opposed to the conventional packed bed columns (Boyer and Singer, 2006; Galjaard, 2010). Packed bed resins have higher resin inventory and

also their performance is challenged under high turbidity waters (Galjaard, 2010; Slunjski et al., 2000). Moreover, they have higher pressure drop and also higher potential for biofilm formation (Flemming, 1987). Given the growing interest on the commercialization of stirred mode operation, it is necessary to understand the robustness and key factors influencing the kinetics (e.g., removal rate) and the performance of IEX process applied. In this regard, some studies have mimicked commercial applications by using consecutive loading cycles and found that the behavior/performance of IEX resins at removing NOM could change over the course of operation depending on the water source and process parameters (Drikas et al., 2011; Mergen et al., 2008; Walker and Boyer, 2011).

1.3 Kinetics of NOM Removal

Removal of NOM via anionic exchange resins may take place under two major mechanisms namely ion exchange and adsorption (Bhandari et al., 1992a; Bolto et al., 2002b; Boyer and Singer, 2008b; Heijman et al., 1999; Helfferich, 1965; Höll and Sontheimer, 1977; Kraus and Moore, 1953; Kunin and Myers, 1949; Simonnot and Ouvrard, 2005). With adsorption being one of the phenomena, size exclusion could become an important factor (depending on the resin matrix and MW distribution of NOM) influencing NOM removal thereby the treated water quality (Boyer and Singer, 2008b; Fu and Symons, 1990; Humbert et al., 2008; Tan and Kilduff, 2007).

Kinetic studies on the sorption of organic molecules have mainly concluded pore diffusion to be the rate-limiting step during the practice of IEX (Bautista et al., 2000; Boyer et al., 2008a; Chen et al., 2002; Li and SenGupta, 2000; Weaver and Carta, 1996; Wu and Gschwend, 1986). However, the effect film diffusion can become significant at low

concentrations of solute and high resin concentrations (Boyd et al., 1947; Reichenberg, 1953; Weaver and Carta, 1996; Weber Jr and DiGiano, 1996). Despite these valuable findings, detailed kinetic evaluation of IEX process for different NOM and natural water sources is rare in the literature.

1.4 Effect of IEX Treatment on Downstream Water Quality

1.4.1 Effect on disinfection by-product formation potential

Dissolved organic nitrogen (DON) comprising 0.5 – 10 % of NOM, could be a source for nitrogenous disinfection by-products (N-DBPs) formation when disinfection and/or oxidation processes are employed (Karanfil et al., 2008; W. Lee et al., 2007; Westerhoff and Mash, 2002). Recent findings indicating the higher toxicity of N-DBPs compared to carbonaceous-DBPs (C-DBPs) as well as the increased reuse of wastewater influenced water sources for drinking water production have led to more awareness and monitoring of N-DBPs in drinking water (Muellner et al., 2007; Plewa et al., 2004; Shah and Mitch, 2012).

In this respect, use of strongly basic anionic IEX resins as an effective tool for the removal of NOM, thereby reducing DBPs formation potential (FP), has received significant attention (Boyer and Singer, 2006; Fearing et al., 2004; Martijn et al., 2010; Singer et al., 2007). However, despite the advantages offered, some studies have documented nitrosamines (e.g., NDMA) and/or nitrosamines precursors (e.g., alkylamines) formation in waters treated with strongly basic anion exchange resins, with the extent of formation being dependent upon the water source (Flowers and Singer, 2013; Gan et al., 2013a; Kemper et al., 2009; Kimoto et al., 1980; Najm and Trussell, 2001). Having said that, literature showing NDMA formation as a result of IEX treatment have mainly employed packed bed columns in very extreme conditions

(e.g., very long contact time, high resin dose, use of chloramine, etc.). While these findings can be relevant to packed bed practice of IEX process, studies evaluating the suspended ion exchange process for N-DBPs (in particular Nitrosamines) formation potential are non-existent in the literature.

1.4.2 Effect on biological stability

Presence of NOM can also pose a challenge to the biological stability of water within the distribution system, a parameter that is mainly monitored by measuring the Assimilable Organic Carbon (AOC) fraction of NOM (Bazri et al., 2012; Smeets et al., 2009; van der Kooij et al., 1999). IEX resins are reported to preferentially remove hydrophobic-transphilic NOM with low-medium molecular weights (Boyer et al., 2008b; Drikas et al., 2003) and therefore, one can expect to see a reduction in AOC after IEX treatment (Bazri et al., 2012). Historical data and other observations available to PWN Technologies, Netherlands, suggested that IEX removes larger portion of non-biodegradable NOM fractions (e.g., humic substances) compared to the biodegradable ones (e.g., biopolymers), hence posing a challenge to the AOC of IEX treated water. Nonetheless, the extent of reduction and contribution of various NOM fractions to AOC is not well documented and also very limited data is available in the literature concerning the effect of IEX treatment on AOC of waters.

1.4.3 Effect on UV and hydroxyl radical scavenging properties

Under the application of UV/H₂O₂ for micropollutant removal, the presence of NOM and nitrate can be problematic. Both NOM (measured as DOC) and nitrate absorb UV irradiation from 200-300 nm, thereby reducing the photons available for hydroxyl radical production resulting in higher operating cost. Moreover, DOC is a major scavenger of hydroxyl radicals,

thereby reducing the oxidant available for target contaminant destruction. Meanwhile, the photolysis of nitrate (under the application of medium pressure UV) leads to the formation of nitrite, another strong scavenger of hydroxyl radical, posing further and more serious health concerns. In this regard, IEX treatment process could be utilized as pre-treatment to UV/H₂O₂ in order to remove DOC and nitrate simultaneously. This could lead to potential cost savings by improving the water scavenging properties. For instance, Martijn et al., (2010) investigated applying ion exchange followed by ultrafiltration upstream of UV/H₂O₂ and reported a 50% improvement in the electrical energy per order (EEO).

1.5 Statement of Research Rational

Despite the presence of studies evaluating IEX resins for NOM removal, a holistic approach for selecting and comparison of strongly and weakly basic anionic resins in terms of NOM removal capability, kinetics, and regeneration efficiency is missing in the literature. Moreover, the source of NOM (e.g., hydrophobic, hydrophilic) and the background water matrix (e.g., presence of NO₃⁻, SO₄²⁻) can influence the finished water quality and also the long-term performance of the treatment process. Therefore, it is of paramount importance to understand the governing kinetics of IEX process (and its limitations) and scrutinize its effect on various NOM fractions (as well as other water constituents) and its subsequent impact on key water qualities such as DBPs FP and biological stability. Moreover, given the promise of IEX as an efficient pre-treatment for AOPs (e.g., UV/H₂O₂), it is of great interest to study how the use of IEX can increase the performance of such oxidation processes thereby contributing to potential energy savings.

1.6 Thesis Layout

The objectives of this study were achieved through a series of well controlled experimental work carried out at UBC, PWN Technologies (Netherlands), and Trojan Technologies (London, ON). The results of all these studies along with the pertinent information gathered from the literature are presented in this dissertation which is structured as follows:

Chapter 1: Presents a general background on research topic and concerning issues.

Chapter 2: Provides a comprehensive literature review around the application of IEX for NOM removal and its challenges. Research objectives and rationale are spelled out and significance of the research is articulated.

Chapter 3: Provides detailed description of the experimental plan and research methodology as well as all the assays and analytical techniques employed in this study.

Chapter 4: Discusses the findings related to the selection of the best performing resin for NOM removal in terms of kinetics, regeneration efficiency, and simulated long-term performance.

Chapter 5: Studies the key NOM characteristics that influence the IEX process performance and scrutinizes the governing removal mechanism and rate-limiting steps during IEX process by evaluating various mathematical and physical models for predicting the results obtained.

Chapter 6: Demonstrates the impact of background water matrix on IEX performance by evaluating four natural water sources under various IEX treatment conditions. Similar to chapter 5, removal mechanism of NOM, NO_3^- , and SO_4^{2-} are investigated and empirical and mathematical models are used to predict the data obtained.

Chapter 7: Shows the impact of IEX treatment on NOM fractions of various standard organic isolates and determines the subsequent effect on disinfection by-product formation potential of the IEX-treated water.

Chapter 8: Shows the impact of IEX treatment on NOM fractions of various standard organic isolates and determines the subsequent effect on biological stability (i.e., AOC) of the IEX-treated water.

Chapter 9: Evaluates the feasibility of using IEX as a pre-treatment for UV/H₂O₂ process and gauges its subsequent impacts on key water quality parameters in particular OH radical scavenging.

Chapter 10: Presents overall conclusions, summarizes the key findings of the work, and provides recommendations for future research.

Chapter 2: Literature Review

2.1 Natural Organic Matter (NOM)

Natural Organic Matter (NOM) is a complex mixture of various organic substances found in surface and ground water sources, adversely affecting aesthetic quality of water and the performance of water treatment processes. Originating from the breakdown of plants, dead animal bodies and other natural species within the environment (Leenheer and Croué, 2003), NOM consists generally of hydrophobic, hydrophilic, and neutral fractions with varying chemical characteristics and a wide range of molecular weights (Leenheer and Croué, 2003; Matilainen et al., 2002; Pelekani et al., 1999; Singer, 1999). In fact, NOM is not a well-defined chemical entity and as a result of its complexity several characterization methods have been developed to study NOM each focusing on a specific attribute. Of those, one can refer to UV spectroscopy, chemical fractionation, molecular weight distribution analysis (size exclusion chromatography), and excitation-emission matrix (EEM) fluorescence spectroscopy. Each of these methods is used to study/monitor a particular property of NOM and therefore, is not solely comprehensive to characterize its structure (Frimmel, 1998; Leenheer and Croué, 2003). Total and dissolved organic carbon (TOC, and DOC) are major parameters that are used to quantify the amount of organic carbon (in water) associated with NOM. Also, UV absorbance at 254 nm (UV_{254}) is another surrogate parameter to measure the amount of conjugated double (carbon-carbon) bonds within the NOM structure.

NOM is recognized as a precursor of disinfection by-products and its presence in water can reduce the aesthetic quality of water, and sometimes causing taste and odour problem (Kleiser and Frimmel, 2000; Singer, 1999). It can also deteriorate biological stability and

increase bacterial regrowth and biofilm formation potential within the distribution systems (Van der Kooij, 1992). Moreover, NOM can lead to some problems during the treatment of water. It leads to membrane fouling and can mitigate the efficiency of ultraviolet (UV)-based advanced oxidation processes (AOPs), mainly used for disinfection and micropollutant removal, by screening the UV light and scavenging hydroxyl radicals (HO^\bullet) (Bazri et al., 2012; Sarathy et al., 2011).

Given the challenges posed by NOM to treatment processes and subsequent water quality, various chemical and physical processes have been proposed to address the issue of NOM, thereby eliminating its associated concerns (Matilainen et al., 2002). Chemical processes such as Ozonation and UV-based advanced oxidation are often costly and would lead to partial removal of NOM and could result in the generation of by-products (Graham, 1999; Sarathy and Mohseni, 2009; Thomson et al., 2004; Toor and Mohseni, 2007; von Gunten, 2003). In this regard, physical processes such as coagulation/flocculation and filtration have gained attention and among those, application of anionic ion exchange (IEX) process for the removal of NOM has been shown to be effective due to its excellent performance and simplicity of operation (Bolto et al., 2002b; Chen et al., 2006; Croué et al., 1999; Drikas et al., 2002; Fu and Symons, 1990). IEX has been demonstrated as an effective pretreatment process for high DOC waters prior to the application of other treatment processes such as coagulation, activated carbon, advanced oxidation or membrane reducing the coagulant dose, disinfection by-products formation potential, or fouling rate, respectively (Bond et al., 2011a; Cornelissen et al., 2009; Huang et al., 2009; Humbert et al., 2008, 2005; Singer and Bilyk, 2002).

2.2 Ion Exchange Process for NOM Removal

The reversible exchange of negatively charged anions (e.g., Cl^- , OH^- , HCO_3^-) a.k.a. counter ion, from the surface of a polymeric resin to a surrounding liquid (e.g., water) in return for the uptake of (an)other anionic specie(s) (e.g., DOC, SO_4^{2-}) is called anion exchange process (Figure 2.1) (Cornelissen et al., 2008; Harland, 1994). NOM consists largely of negatively charged poly-electrolytes; therefore, it could be removed effectively using IEX, depending on the characteristics of NOM and the background water matrix undergoing the IEX treatment (Bolto et al., 2004, 2002b). Effectiveness, ease of operation, scale up or down capabilities, small footprint, relatively low cost, and being a by-product free treatment are among the factors attracting considerable attention towards IEX for NOM removal (Chen et al., 2006; Clifford, 1999; Hongve et al., 1999). As a result, several types of resins have been manufactured specifically to remove organic matter. However, the efficacy of IEX can vary depending on resin properties, process operation parameters, and the influent water quality as discussed in the following sections.

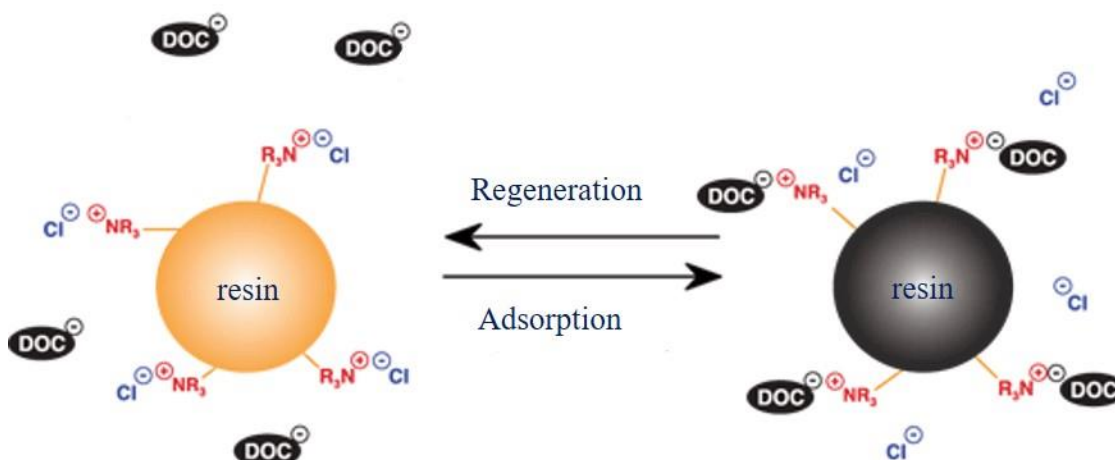


Figure 2.1, Schematic of reversible anionic ion exchange process for NOM removal (modified from Orica)

2.2.1 Effect of ion exchange resin

Ion exchange resins manufactured for NOM removal generally differ in terms of various properties including (Chen et al., 2006; Harland, 1994); Polymeric matrix and degree of cross-linking (Acrylic or styrene), functional group (Quaternary ammonium Type I or II (i.e., strongly basic) or tertiary ammonium (i.e., weakly basic), ionic form and/or counter-ion (Cl^- , OH^-), ion exchange capacity, water content, and particle size. Studies in general, have reported that quaternary ammonium strongly basic resins (SBR) with acrylic backbone and smaller bead size (i.e., higher surface area) to show superior performance at NOM removal compared to other resins (Boyer and Singer, 2008a; Fu and Symons, 1990). The presence of a hydroxyl group close to the quaternary nitrogen, or a low ratio of carbon to quaternary nitrogen would further improve the IEX process efficacy at NOM removal (Bolto et al., 2002b; Chen et al., 2006). Weakly basic resins (WBR) with tertiary ammonium functional groups may have a greater affinity for hydrophilic organic molecules than SBRs, but generally there are fewer charged sites in the resin at neutral pH providing lower removal capability (Evans and Maalman, 1979; Höll and Kiehling, 1981; Höll and Kirch, 1978; Matosic et al., 2000).

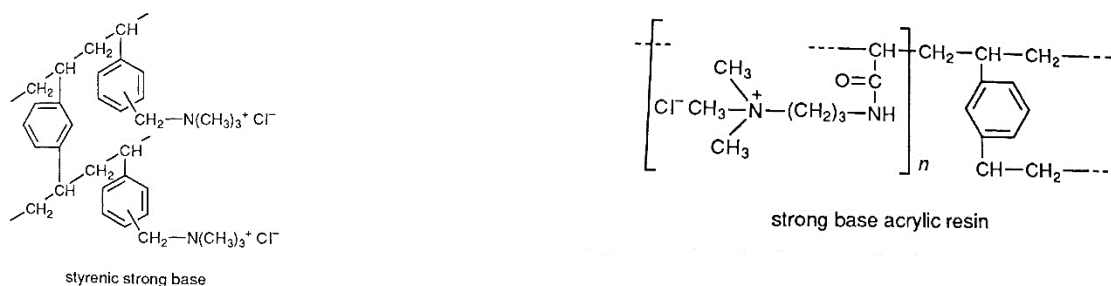


Figure 2.2, Schematic for styrenic and acrylic quaternary ammonium strongly basic anion exchange resins (Harland, 1994)

In terms of polymeric backbone, polystyrene resins (Figure 2.2) are more selective towards smaller size organics (i.e., <1 kilo Dalton, kDa) and aromatic moieties than acrylic species, which is attributed to a combination of electrostatic interactions and hydrophobic bonding (Bolto et al., 2002b; Fu and Symons, 1990; Humbert et al., 2008). Generally, for DOC with MW >1 kDa, hydrophilic acrylic resins are preferred for DOC removal compared with the relatively hydrophobic polystyrene resins (Fu and Symons, 1990). Also, higher water content and more open structure (i.e., macroporous) have been found to increase the resin performance at NOM removal, especially those of smaller molecular size (Bolto et al., 2002b; Cornelissen et al., 2008; Fu and Symons, 1990).

2.2.2 Effect of NOM source and background water matrix

Aside from resin properties (Bolto et al., 2002b; Boyer and Singer, 2008b; Cornelissen et al., 2008), NOM properties such as molecular weight (MW), polarity (i.e., hydrophobicity), and charge density could significantly influence the kinetics and fate of NOM removal (i.e., treatment efficacy) during the IEX treatment. For instance, IEX process is reported to be more effective towards removing low to medium molecular weight organics and a cheaper alternative to granular activated carbon (GAC) (Drikas et al., 2003; Heijman et al., 1999; Mergen et al., 2009). Studies focusing on the effect of NOM properties are however inconclusive and sometimes contradictory. Croué et al., (1999) observed an inverse correlation between hydrophobicity of NOM and its removal performance while Mergen et al., (2008) and Boyer and Singer, (2008a) reported the hydrophobic-transphilic fractions of NOM as the main targets of IEX resins. The effect of molecular weight of NOM was investigated by Fu and Symons, (1990) for various resins where results observed showed that organic fraction with MW of larger than

10 k dalton (Da) were not removed due to size exclusion by the resins. Similar observations have been reported by Mergen et al., (2008), and Tan and Kilduff, (2007) where higher molecular hydrophobic fractions are not removed by ion exchange resins. Charge density of organic molecules, basically representing combined effects of MW and polarity (i.e., hydrophobicity), has been suggested as a more comprehensive parameter to predict the behavior of organic matter and a key factor in determining the removal efficiency (Boyer et al., 2008b; Boyer and Singer, 2008a, 2008b).

During the application of IEX, anions are adsorbed on exchange sites with different affinities (i.e., preferences). The charge, the size of hydrated ion, acidity, and the chemistry of the target ions are among the factors affecting the uptake of anions by anionic exchangers (Boari et al., 1974). Inorganic anions such as nitrate and sulfate that are commonly present in natural waters can also compete with NOM for adsorption/exchange on IEX resins. Anion exchange resins are reported to have a higher affinity toward sulfate compared to NOM components and hence the presence of SO_4^{2-} ions (at high concentrations) could adversely the removal of NOM by IEX resins (Hsu and Singer, 2010; Ishii and Boyer, 2011; Jelinek et al., 2004; Mergen et al., 2008; Tan and Kilduff, 2007; Walker and Boyer, 2011; Willison and Boyer, 2012). For instance a typical value reported for the relative affinity of strong basic IEX resin for SO_4^{2-} compared to CH_3COO^- and OH^- is 9.2 : 0.14 : 0.65, respectively (Chen et al., 2006; Clifford, 1999). Nitrate is not a strong competitor for NOM under IEX resin application; however, at high concentrations its presence might influence the removal of organic matter (Boyer and Singer, 2008a; Clifford, 1999). Bicarbonate and chloride are shown to have equal affinity for anion exchangers and lower preference compared to organic molecules (Boyer and Singer, 2008a; Walker and Boyer, 2011; Willison and Boyer, 2012). Having said that, presence of bicarbonate and chloride can result in

dehydration of organic molecules (salting out effect) thereby reducing their size and consequently improving their removal efficiency (Cornelissen et al., 2008; Croué et al., 1999; Tan and Kilduff, 2007).

2.3 Regeneration of IEX Resins

The resins exchange sites (pores) become depleted (occupied) as a result of NOM uptake over the course treatment. Therefore, resin regeneration is frequently required to restore the performance of the process and maintain the treated water quality. That said, regeneration of resins has always been a challenge for the application of IEX process (Bae et al., 2002; Clifford, 1999; Greenleaf et al., 2009; McAdam and Judd, 2008).

For anionic exchanges, brine (NaCl ~10 % wt) is generally used to elute the ions adsorbed from the resins and restore their capacity for further cycles. Although efficient, regeneration with brine is a chemically demanding process e.g., 20 - 36 kg of NaCl per 1000 m³ of treated water[‡] (Grefte et al., 2013) that also requires subsequent handling and disposal (Clifford, 1999; Höll and Kiehling, 1981; Rokicki and Boyer, 2011). In this aspect, WBRs are reported to offer lower costs associated with regeneration and waste disposal, but they provide lower removal capability (Evans and Maalman, 1979; Höll and Kiehling, 1981; Höll and Kirch, 1978; Matosic et al., 2000). Because of economic considerations, strategies have been taken to reuse/treat the spent brine and utilize it for further regeneration cycles. For instance, membrane biofilm reactors (McAdam et al., 2010; Van Ginkel et al., 2011), biological reduction processes alone (McAdam and Judd, 2008) or in combination with activated carbon (Bae et al., 2002), biological activated carbon combined with capacitive deionization (Ng et al., 2008), and

[‡] www.miexresin.com

nanofiltration (Schippers et al., 2004; Vaudevire et al., 2013) are among the alternatives proposed for brine treatment and recycling. It is also important to note that implementation of these brine treatment modules requires further capital investments and operating costs (McAdam and Judd, 2008; Ng et al., 2008; Schippers et al., 2004).

Bicarbonate salt is another alternative to regenerate IEX resins. In fact, chloride-form IEX resin can be converted to bicarbonate-form resin using bicarbonate salt. In comparison to brine, bicarbonate is more expensive (200-250 \$/tonne vs. 50-75 \$/tonne, respectively[§]), but it is environmentally benign and also eliminates the concern of excess chloride in the treated water that in turn affects downstream biological processes as well as pipelines (Höll and Kiehling, 1981; Ishii and Boyer, 2011; Jelinek et al., 2004; Matosic et al., 2000; Rokicki and Boyer, 2011; Walker and Boyer, 2011). Despite its promise, bicarbonate-form IEX resins have not attracted enough attention in the literature for NOM removal likely because of its higher price (4-5 times) in the global market (Rokicki and Boyer, 2011; Walker and Boyer, 2011).

2.4 Simulating Practical Operation of Ion Exchange Process

Despite the higher water quality produced by conventionally used packed bed columns, recent studies focusing on commercial practice of IEX for NOM removal have suggested the use of stirred (a.k.a. suspended) mode operation (Figure 2.3) as opposed to the conventional packed bed columns (Boyer and Singer, 2006; Galjaard, 2010). This is because stirred mode has a lower resin and salt usage and also their performance is not challenged under high turbidity waters i.e., no clogging (Galjaard, 2010; Slunjski et al., 2000). More importantly, suspended IEX has a significantly lower pressure drop and biofilm formation potential inside the mixing reactor

[§] Source: www.alibaba.com

(Flemming, 1987). Despite the increasing studies on the use of IEX resins in the stirred mode at lab and pilot scales (Bolto et al., 2004; Boyer and Singer, 2006, 2005; Drikas et al., 2002; Johnson and Singer, 2004; Mergen et al., 2009), only a few studies have mimicked commercial IEX applications by using consecutive loading cycles and found that the behavior/performance of IEX resins at removing NOM could change over the course of operation depending on the water source and process parameters (Drikas et al., 2011; Mergen et al., 2008; Walker and Boyer, 2011).

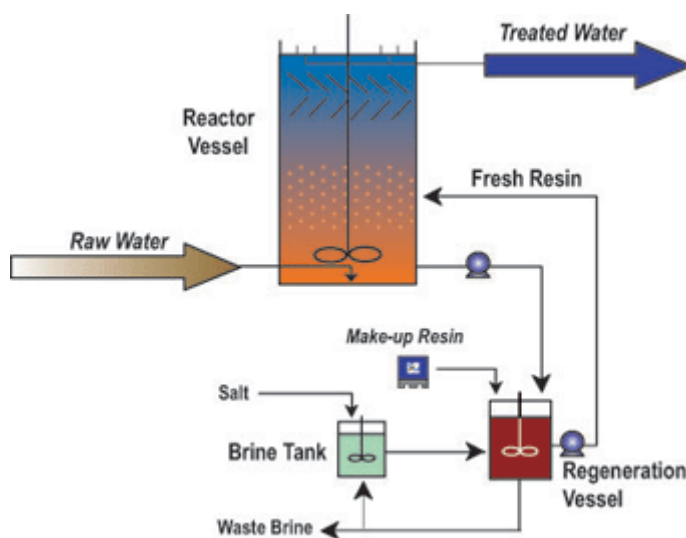


Figure 2.3, Schematic of Orca's proprietary MIEX® process (Courtesy of Orca Watercare)

2.5 Kinetics of NOM Removal

Removal of NOM via anionic exchange resins takes place via two major mechanisms. The reversible electrostatic exchange of resins' counter-ions (e.g., Cl^- , OH^- , HCO_3^-) with anions in the surrounding solution (Boyer and Singer, 2008b; Helfferich, 1965; Höll and Sontheimer, 1977; Kunin and Myers, 1949; Simonnot and Ouvrard, 2005) and or adsorption of ions on the resins' surface (Bhandari et al., 1992b; Bolto et al., 2002b; Clifford, 1999; Heijman et al., 1999;

Kraus and Moore, 1953). Good removal (40-70 %) was observed for intermediate molecular weights organics (500 - 1500 Da) under the application of IEX (Humbert et al., 2005; Mergen et al., 2008). Also, for the molecular weight range of 1 to 5 kDa, Fu and Symons (1990) found balanced equivalent exchange of chloride for the NOM captured from the solution. Overall, their results showed that the sorption mechanism for DOC removal was ion exchange with only a small percentage of the DOC in the <1 kDa and >10 kDa fractions being removed by adsorption. Similar conclusion was made by Bolto et al., (2002b) where hydrophobic interactions appeared to be responsible for only a small proportion of NOM adsorption (Bolto et al., 2002b). Furthermore, it has been shown that anionic exchangers poorly remove very large organic molecules composed of hydrophobic humic compounds due to size exclusion (Allpike et al., 2005; Fearing et al., 2004; Fu and Symons, 1990) or small neutral organics (Humbert et al., 2005; Mergen et al., 2008). Therefore, the molecular size of the organic matter can play a significant role resulting in size exclusion that could impede adsorption (depending on the resin matrix and MW distribution of NOM) and influence NOM removal and the treated water quality (Boyer and Singer, 2008b; Fu and Symons, 1990; Humbert et al., 2008; Tan and Kilduff, 2007).

Weakly basic resins in the free-base form remove organic acids from solution following a sorption process rather than a true ion exchange (Helfferich, 1965; Nativ et al., 1975). Weakly basic amino groups may have a greater affinity for hydrophilic counter ions (fractions) than quaternary ammonium groups, but generally there are fewer charged sites on the resin at neutral pH. Some studies have reported high NOM uptake for WBRs (as high as SBRs) with the same water content, even though the choice of the NOM source can potentially affect this conclusion (Bolto et al., 2002b; Chen et al., 2006).

Regardless of the removal mechanism being ion exchange and or adsorption, some kinetic studies on the sorption of organic molecules have identified pore diffusion to be the rate-limiting step during the practice of IEX (Bautista et al., 2000; Boyer et al., 2008a; Chen et al., 2002; Li and SenGupta, 2000; Weaver and Carta, 1996; Wu and Gschwend, 1986); however, film diffusion can also become significant at low concentrations of solute and or high resin concentrations (Boyd et al., 1947; Reichenberg, 1953; Weaver and Carta, 1996; Weber Jr and DiGiano, 1996).

2.6 Effect of IEX Treatment on the Downstream Water Quality

2.6.1 Effect on disinfection by-product formation potential

NOM is a known precursor for disinfection by-products (DBPs) formation in drinking water sources (Singer, 1994). Studies have reported 0.5 – 10 % of NOM to be dissolved organic nitrogen (DON) which could be a source of nitrogenous DBPs (N-DBPs) formation when disinfection and or oxidation processes are employed (Karanfil et al., 2008; W. Lee et al., 2007; Westerhoff and Mash, 2002). High DON content during chlorination/chloramination could lead to higher disinfectant demand, production of haloacetic acids (HAAs) and trihalomethanes (THMs), and more importantly formation of halogenated (i.e., halonitromethanes (HNMs), haloacetonitriles (HANs, cyanogen halides)) and non-halogenated (i.e., nitrosamines) N-DBPs (Bond et al., 2012, 2011b; Dotson and Westerhoff, 2009; Krasner et al., 2012; W. Lee et al., 2007). Recent findings indicating the higher toxicity of N-DBPs compared to carbonaceous-DBPs (C-DBPs) and also the increased reuse of wastewater influenced water sources for drinking water production have led to more awareness and monitoring of N-DBPs in drinking water (Muellner et al., 2007; Plewa et al., 2004; Shah and Mitch, 2012).

In this respect, use of strongly basic anionic IEX resins as an effective tool for the removal of NOM, thereby reducing DBPs formation potential (FP) has received significant attention (Boyer and Singer, 2006; Fearing et al., 2004; Martijn et al., 2010; Singer et al., 2007). Despite the advantages offered, some studies have documented nitrosamines (e.g., NDMA) and/or nitrosamines precursors (e.g., alkylamines) formation in waters treated with strongly basic anion exchange resins, with the extent of formation being dependent upon the water source (Flowers and Singer, 2013; Gan et al., 2013a; Kemper et al., 2009; Kimoto et al., 1980; Najm and Trussell, 2001). The formation of nitrosamines (especially NDMA) in IEX treated waters is generally attributed to the presence and thereby reaction of reactive disinfectants (i.e., Chlorine, Chloramine, ClO_2) with the amine-containing functional groups of polymeric resins (Flowers and Singer, 2013; Gan et al., 2013b; Kemper et al., 2009; Najm and Trussell, 2001). However, significant NDMA release from resins was also reported as a result of soaking (4 hr) in distilled water (Najm and Trussell, 2001). Flowers and Singer (2013) also evaluated a large pool of anionic resins and found that most of the nitrosamines were released during the first 50-100 bed volumes (BV) of operation. Flow interruption (i.e., soaking resins) and regeneration were found to increase nitrosamines precursors release mainly due to resins swelling (i.e., more open structure).

Even though the potentially formed N-DBPs could be removed via downstream UV/ H_2O_2 and granular activated carbon (GAC) installations, the risk associated with their formation due to final disinfection (i.e., disinfectant reaction with DON) could remain in place (Karanfil et al., 2008; Kristiana et al., 2013). Furthermore, literature showing NDMA formation as a result of IEX treatment have mainly employed packed bed columns in very extreme conditions (e.g., very long contact time, high resin dose, use of chloramine, etc.) which in turn influences the

conclusion. Hence, additional research is needed to determine the relative importance and fate of various NOM fractions (DON as well) and subsequent implications on C-DBPs FP and N-DBPs FP during the practice of IEX process.

2.6.2 Effect on biological stability

Presence of NOM can also pose a challenge to the biological stability of water within the distribution system. Biological stability is mainly monitored by measuring the Assimilable Organic Carbon (AOC) fraction of NOM (Bazri et al., 2012; Smeets et al., 2009; van der Kooij et al., 1999). AOC levels higher than 10 µg/L acetate-C (measured by conventional AOC bioassay) could deteriorate biological stability of water leading to bacterial regrowth and biofilm formation within the distribution system (Van der Kooij, 2002, 1992, 1987). IEX resins are reported to preferentially remove hydrophobic-transphilic NOM with low-medium molecular weights (Boyer et al., 2008b; Drikas et al., 2003) and therefore, one can expect to see a reduction in AOC after IEX treatment (Bazri et al., 2012). Having said that, the extent of reduction and contribution of various NOM fractions to AOC is not well documented and also very limited data is available in the literature concerning the effect of IEX treatment on AOC of waters. Historical data and other observations available to PWN Technologies, Netherlands, suggested that IEX removes larger portion of non-biodegradable NOM fractions (e.g., humic substances) compared to the biodegradable ones (e.g., biopolymers), hence posing a challenge to the AOC of IEX treated water. Hence, to ensure producing superior water quality for utilities that employ IEX, it is important to investigate the impact of ion exchange resins on AOC of several waters.

2.6.3 Effect on hydroxyl radical properties

The combination of ultraviolet (UV) irradiation and hydrogen peroxide (UV/H₂O₂) is increasingly being applied to the removal of trace contaminants from drinking water supplies. When UV/H₂O₂ is applied for drinking water treatment of surface water, DOC and nitrate play a very important role. Both DOC and nitrate absorb UV irradiation from 200-300 nm; thereby reduce the photons available for hydroxyl radical production which in turn result in higher operation cost. Moreover, DOC is a major scavenger of hydroxyl radicals, reducing the oxidant available for target contaminant destruction (Rosenfeldt and Linden, 2007; Sarathy et al., 2011). Meanwhile, the UV photolysis of nitrate (under the application of medium pressure UV and high UV dosages) leads to the formation of nitrite, another strong scavenger of hydroxyl radical, posing further and more serious health concerns (Hofman-Caris et al., 2015; Lu et al., 2009; Martijn and Kruithof, 2012; Peldszus et al., 2004; Sharpless and Linden, 2001). For instance, presence of nitrate in blood can result in failure of the oxygen transport process in body causing blue-baby syndrome (Lu et al., 2009). United States Environmental Protection Agency (US EPA) has reported the maximum contaminant levels (MCLs) for nitrate^{**} and nitrite^{††} to be 10 and 1 mg/L, respectively. In addition, there have been reports of increases in AMES II mutagenicity for surface waters containing DOC and nitrate when subjected to polychromatic UV/H₂O₂ treatment (Heringa et al., 2011; Kolkman et al., 2015; Martijn and Kruithof, 2012; Martijn et al., 2015). Nonetheless, this issue can be addressed by reducing nitrate prior to UV/H₂O₂ (Martijn et al., 2015) and or via downstream treatment with granular activated carbon (Heringa et al., 2011; Martijn and Kruithof, 2012).

^{**} <http://water.epa.gov/drink/contaminants/basicinformation/nitrate.cfm>

^{††} <http://water.epa.gov/drink/contaminants/basicinformation/nitrite.cfm>

While downstream treatment can be effective to ameliorate potential health concerns, it does not have any potential to improve UV/H₂O₂ performance. In this regard, IEX treatment process could be utilized as pre-treatment to UV/H₂O₂ in order to remove DOC and nitrate simultaneously. For instance, Martijn et al., (2010) investigated applying ion exchange followed by ultrafiltration upstream of UV/H₂O₂ (medium pressure UV) and reported a 50% improvement in the electrical energy per order (EEO).

2.7 Knowledge Gaps and Research Questions

Despite the studies evaluating IEX resins for NOM removal, a holistic approach for selecting and comparing strongly and weakly basic anionic resins in terms of NOM removal capability, kinetics, long-term performance, and regeneration efficiency is missing the literature. In fact, it is not clear whether the potentially lower regeneration demand of WBRs can compensate for their lower efficiency and place them as competitors to SBRs for NOM removal. Therefore, the following first research question was formulated to answer this knowledge gap:

Question 1: How are SBRs and WBRs compared in terms of NOM removal capacity, kinetics (i.e., rate), long-term performance, and regeneration efficiency?

The primary hypothesis for this question is that the use of various kinetic and adsorption experiments along with different regeneration scenarios can enable us to compare and select the best performing IEX resin for a given application.

Moreover, process parameters (e.g., resins dose, contact time) and characteristics of the influent water (e.g., NOM source, background anions) can influence the resins performance and consequently finished water quality, especially over long-term application of IEX process. Therefore, it is of great interest to gauge the robustness of this process and also understand the

effect of IEX on different NOM fractions and its subsequent implications of key water quality parameters such as DBPs FP and biostability. Moreover, it is equally significant to investigate parameters that affect kinetics (and efficacy) of the removal process and use that understanding toward efficient design of IEX contactors. It is important to note that very few studies have tried to tackle these objectives and a holistic research looking at these key factors is missing in the literature. Hence, the second and third research questions were formulated upon this knowledge gap:

Question 2: How would the performance and robustness of IEX process change under different water sources and process parameters (e.g., resin dose, contact time, long-term operation)?

It is hypothesized that there is an optimum range for the process parameters such as treatment time and resin dose when applying IEX process in the stirred mode. Also, there are certain limitations (e.g., lack of removal for non-ionic species) that are intrinsic to the nature of the removal process and may not be addressed. Therefore, different waters from various sources will be tested under different kinetic experiments with varying process parameters such as treatment time, resin dose, as well as resin reuse to answer this question.

Question 3: What are the governing factors on the kinetics of NOM removal under IEX application?

It is postulated that the properties of NOM play a significant role in the efficacy of the IEX process for DOC removal. These properties are mainly charge density, molecular weight, and hydrophobicity. Having said that, it is further hypothesized that depending on the intensity of each of this parameter one may dominate and determine the fate of organic matter removal

during the treatment. Also, given the stirred mode application of the ion exchange resins, it is hypothesized that the mass transfer resistance is minimal and hence the removal rate is highly dependent on the properties of the resins used (e.g., macroporous vs. gel) as well as NOM (e.g., molecular weight). The use of mathematical and physical model could validate this hypothesis.

Given the increasing interest to utilize IEX as a tool to reduce DBP precursors, the growing concern over N-DBPs formation in drinking water sources, and (ironically) some concerns over the formation of N-DBPs under application of IEX, it is of paramount importance to examine thoroughly the effect of IEX on various fractions of NOM and its subsequent impacts on key water qualities such as DBPs FP. Biological stability (i.e., AOC) is another key water quality parameter that is a function of organic matter type and level in drinking water sources. AOC is receiving considerable attention and is routinely monitored by many water utilities in Europe. With the growing attention toward using IEX for organic matter removal, there is a need to understand the effect of IEX on various NOM fractions and a resulting AOC.

Moreover, because of the promise of IEX as an efficient pre-treatment for advanced oxidation process (e.g., UV/H₂O₂), studies are needed to understand how the use of IEX can increase the performance of the oxidation process as well as energy savings. To the best of our knowledge at the time of this research, studies looking into the impact of IEX on various fractions of NOM and correlation between the changes in NOM molecular distribution and subsequent water qualities such as DBPs, AOC, and OH scavenging are rare/non-existent in the open literature. Hence, the fourth research question is intended to address the above mentioned knowledge gap:

Question 4: How does the effect of IEX on various fractions of NOM influence DBPs FP (in particular N-DBPs), AOC, and •OH scavenging properties of the treated water.

It is expected that IEX process reduces DBP precursors (also N-DBPs) and the preparation and operation conditions of the treatment process can influence the finished water quality. Similarly, AOC is expected to decrease via ion exchange, even though the extent of that may depend on inlet water quality and NOM source. Lastly, the overall scavenging properties of IEX-treated water will improve; however, the extent of that improvement depends on the operating conditions and the influent water quality.

2.8 Scope and Objectives

Given the concern over the presence of NOM in surface waters and the need for its removal, the overall objective of this work is to study the removal kinetics and fate of NOM under different water matrices using anionic ion exchange resin. This research intends to carry out holistic sets of experiments and analyses to address the questions (unknowns) that are deemed to be both fundamental and practical in nature; hence, are of great importance for efficient design and utilization of the IEX process. This will be achieved through a holistic and detailed experimental work focusing on the following sub-objectives:

1. Study, compare and select the best performing anionic basic resin (i.e., strongly or weakly basic) in terms of:
 - i. NOM removal kinetics and long-term efficacy
 - ii. Regeneration efficiency
2. Study and predict the effect of NOM source and background water matrix on the kinetics and efficacy of IEX process using the resin selected from sub-objective 1, under:

- i. Different operating conditions (i.e., resin dose and contact time)
 - ii. Different NOM sources and water matrices
 - iii. Batch and consecutive loadings (simulating practical long-term operation)
3. Investigate the correlation between changes in MW distribution of NOM during IEX and its effects on important water quality parameters namely:
 - i. Disinfection by-products formation potential
 - ii. Biological stability i.e., AOC
 - iii. OH radical scavenging and UV transmittance (when IEX is used as a pretreatment for AOPs)

2.9 Significance of This Work

The first stage of this study will take a holistic approach to compare and select SBR and WBR resins for NOM removal based on NOM removal, simulated long-term performance, and regeneration efficacy. In the next steps, understanding the behaviour of IEX process under different treatment conditions (e.g., resin dose and contact time) and water matrices will help to gauge the robustness of the process applied for various water sources and also to efficiently combine IEX with other processes (e.g., filtration, oxidation processes) within a treatment train. Kinetic data obtained could be used to understand the kinetics (as well as limitations) of the removal process and use that to simulate, design, and fabricate efficient reactor set-up configuration in order to maximize NOM removal as well as regeneration efficiency. Information obtained from this study will enhance the existing knowledge on IEX application and potentially open new opportunities towards efficient utilization of IEX process for treating natural waters.

Chapter 3: Experimental Methodology

This chapter describes the common experimental methodology and procedures followed to fulfill the stated objectives of this research. Methodologies and experimental work specific to certain tasks will be presented as part of the respective chapter (chapters 4 to 9).

3.1 Preparation of Glassware, and Tools

All glassware and tools (i.e., Buchner funnels, glass filters) were thoroughly washed, triple rinsed with Milli-Q water, and baked at 550°C for 5 hrs. Pipette tips were autoclaved and kept away from potential contamination. All tools (glassware, flasks, funnels, glass filters 1.6 μm) were heated at 550°C for 5 hrs according to the method described elsewhere (Mitch et al., 2003; Mitch and Sedlak, 2002). Filter papers used for water filtration and or separation of resins from water samples were tripled rinsed with Milli-Q water prior to use.

3.2 Preparation of Water Samples

Synthetic test water samples made from standard natural organic matter isolates (i.e., Suwannee River NOM, Suwannee River Fulvic Acid, Suwannee River Humic Acid, and Pony Lake Fulvic Acid) were prepared on the day of experiments and filtered through 0.45 μm pre-rinsed membrane filters. For experiments longer than two days requiring larger water volumes (e.g., more than 20 L) a stock solution of 700 mg/L was prepared, filtered (0.45 μm), and stored in dark at 4°C for up to two weeks. The pH of raw synthetic water samples was adjusted to neutral range (~ 7.5) by buffering with NaHCO_3 (40 mg/L), and adding NaOH (0.1 N) and NaCl (1 mg/L) prior to the experiments. Only synthetic waters in chapters 7 and 8 were made using phosphate buffer (10 mM, pH ~ 7.5).

Natural water samples (chapters 6, and 9) were filtered (0.45 μm) within 24 hrs of collection and stored at dark at 4°C for up to a month. Dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), NO_3^- , and SO_4^{2-} levels of the raw samples were monitored throughout the experiments to ensure minimal impact from organics degradation on the experimental results.

3.3 Resins Preparation

To eliminate any potential for cross contamination from manufacturing process, virgin resins received from the manufacturer (in the chloride form) were initially regenerated using brine (NaCl, 10 % wt.) for 1hr with a resin to regenerant ratio of 1 mL/10 mL. Thereafter, the regenerant was decanted and resins were triple rinsed with Milli-Q water (resin to Milli-Q water ratio of 1 mL/10 mL) and mixed with Milli-Q water at least three times for 30 minutes. This was continued until the amount of Cl^- (mg/L) released from resins (200 mL) was below the detection limit (~ 0.2 mg/L).

To gauge the effect of counter ion, resins were evaluated in both chloride and hydroxyl (OH^-) forms. For this reason, $-\text{Cl}^-$ and $-\text{HO}^-$ forms of both SBR and WBR resins were initially prepared by regenerating the virgin resins with NaCl (10 % wt.) or NaOH (4% wt.), ratio of 1 mL/10 mL, followed by triple rinsing with Milli-Q water. Resins intended to use for isotherm experiments were air dried overnight and stored in desiccator for at least 24 hrs prior to use.

3.4 Mercury Porosimetry

Porosity of the Purolite A860 resin was measured using the mercury porosimetry technique (AutoPore IV 9500 V1.09) at 4D LABS shared facilities at the Simon Fraser University.

3.5 Jar Test Procedure

To standardize the Jar test procedure across all experiments the following conditions were maintained throughout all stages. A standard Phipps and Bird standard jar test equipped with flat blades (blade diameter 7.6 cm) was employed. Round glass 2L glass beaker were filled with 1L of water sample and mixed at 150 rpm with desired resin dose. The mixing speed of 150 rpm was selected through a preliminary test where the impact of mixing speed between 100 rpm and 150 rpm was determined to be insignificant. This is consistent with the report of Lai et al., (1975) where they reported 100 rpm as the minimum speed to achieve turbulent mixing. Reynolds number for the selected condition was calculated to be 14400 using the following equation:

$$N_{Re} = \frac{D^2 \times s \times \rho}{\mu}$$

Where N_{Re} is the Reynolds number, D is the blade diameter (7.6×10^{-2} m), s is the mixing speed (round per second, rps), ρ is the liquid density ($\sim 1 \text{ kg/m}^3$) and μ is the dynamic liquid viscosity ($\sim 10^{-3} \text{ kg/m.s}$). The mean velocity gradient (G value) at 150 ppm for the configuration used in this study was estimated by Lai et al., (1975) to be $\sim 90 \text{ s}^{-1}$.

3.5.1 Kinetic and isotherm experiments

For the initial screening, resins amounts of 200 – 1000 mg/L (dry) were mixed with SRNOM (using a Phipps & Bird 9900 Jar tester) for up to 8 hrs and their TOC removal performance was compared to select the best two performing resins. For other experiments a practical resin dose of 2.5-15 mL (Boyer and Singer, 2006; Galjaard, 2010; Mergen et al., 2008) was mixed with 1 L of water for various contact times from 5 minutes (min) to 24 hrs using a Jar tester.

For adsorption isotherms, 10 to 1000 mg of dried resins were carefully weighed and mixed with 1L of water to equilibrium (i.e., 24 hrs). Resins were filtered from the treated water using a pre-rinsed fast coarse filter (Whatman 113- 30 μm) and samples underwent subsequent water quality analyses.

All experiments were repeated for three times with coefficient of variation (CV) < 5 % and water samples were duplicated (CV < 2 %) to improve the statistical power and significance of the results.

3.5.2 Simulating practical conditions: consecutive multiple loadings test (MLT)

To understand and simulate the effect of NOM properties on IEX performance under realistic operating conditions, consecutive batch loadings were carried out using 10 mL/L (for organic matter isolates) and 7.5 mL/L (for RW water, chapter 4) of resins and 30 minute contact time. This condition was selected based on previous evaluations presented elsewhere (Boyer and Singer, 2006; Galjaard et al., 2011; Slunjski et al., 2000). At the end of each batch, resins were removed by a 30 μm pre-rinsed filter and then reloaded to another liter of raw water. The number of bed volumes (BV) of water treated in each cycle was calculated as $L_{\text{water}}/\text{mL}_{\text{resin}}$ equal to 100 BV and 130 BV for SRNOM and RW, respectively. Multiple loadings were continued for 6 to 10 cycles corresponding to treating ~ 700 to 1400 BV of raw water.

3.5.3 General analytical techniques

Total and dissolved organic carbon (i.e., TOC and DOC), and dissolved inorganic carbon (DIC) measurements were performed in all stages using a TOC analyzer (Shimadzu VCPH). TOC and DOC are measured as surrogate parameters to quantify the amount of NOM. All spectrophotometric measurements (e.g., UV_{254}) were carried out using a UV-Vis spectrophotometer (Shimadzu UV mini 1240) with a cell path length of 1 cm. Specific UV

absorbance (SUVA:UV₂₅₄/DOC) was also monitored in all the experiments. pH was routinely monitored using a pH-mV meter (Denver Instruments UB-10). Chloride (Cl⁻) was measured using Dionex 1100 ion chromatography unit equipped with electrical suppressor and Dionex AS22 Fast column, according to the methods of Environmental Protection Agency (EPA) 300.0 and Standard Method (SM) 4110B (Pfaff, 1993; Rice et al., 2012).

For the natural waters sources (FPW, MAN, RLW, and WEW) in chapters 6 and 9, DOC and dissolved inorganic carbon (DIC) of waters were measured (GE Sievers 5310C TOC analyzer) and monitored during the storage and experimentation period. All spectrophotometric measurements (e.g., UVT %, UV₂₅₄) were carried out using a UV-Vis spectrophotometer (Agilent Varian Cary 50 UV-Vis spectrophotometer) with cell path lengths of 1 and 5 cm. Specific UV absorbance (SUVA) defined as the ratio of UV₂₅₄ to DOC was also monitored in all the experiments. Anions (Cl⁻, NO₃⁻, and SO₄²⁻) were measured using ion chromatography (Cecil Instruments IonQuest ion chromatography equipped with Dionex AS22 column and Chemical suppressor) according to the EPA 300.0 and Standard Method (SM) 4110B methods⁶ (Pfaff, 1993; Rice et al., 2012).

Apparent Molecular Weight (AMW) distribution analysis was performed using high performance size exclusion chromatography (HPSEC) technique (WATERS 2695 HPLC system equipped with a 2998 photodiode array detector set to detection at 260 nm) as described by Sarathy and Mohseni, (2007). Further to AMW distribution assessment, a Waters 600E Multisolvant Delivery System (TSK HW-50S column, 35 cm X 2 cm, Tosoh, Japan), equipped with a Waters 486 Tunable Absorbance Detector followed by a GE Sievers 900 Portable TOC Analyzer Turbo was utilized to perform the Liquid Chromatography coupled with Organic Carbon Detector (LC-OCD) analysis.

Molecular weight distribution of SRNOM, SRHA, SRFA, and PLFA presented in chapters 7 and 8 was assessed through liquid chromatography equipped with size exclusion and organic carbon and nitrogen detectors using a DOC-LABOR system at Het Waterlaboratorium, Netherlands according to the method of Huber et al., (2011). The classification of NOM into various fractions was performed using the embedded software in the system and the basis for that has been previously discussed by others (Amy and Her, 2004; Cornelissen et al., 2008; Grünheid et al., 2005; Huber et al., 2011).

Specific water quality analyses such as disinfection byproducts formation potential (DBPs FP) test, nitrosamines quantification and measurement, assimilable organic carbon bioassay (AOC), and UV/H₂O₂ related measurements (e.g., UV fluence, H₂O₂, pCBA measurement) are elaborated in their relevant chapters.

Chapter 4: Evaluation of Weak and Strongly Basic Anion Exchange Resins for NOM Removal

This chapter presents the results of the experiments conducted to assess the feasibility of using either a strongly or weakly basic ion exchange resin for the removal of natural organic matter (NOM) from surface water. Resins were compared in terms of their removal kinetics and regeneration efficiency under batch and simulated commercial conditions. The dominant mechanism for NOM removal with the strongly basic A860 resin was ion exchange whereas a combination of ion exchange and surface adsorption governed the removal with the weakly basic A847. Adsorption isotherms obtained were thoroughly analyzed and the estimated limiting capacity (q_m) and the equilibrium constant (α) for A860 were higher than the ones for A847, showing greater affinity of A860 for organic matters. Also, under the consecutive batch loadings (i.e., simulated commercial condition) the strongly basic resin showed greater removal (by about 10%) compared to A847. Different regeneration scenarios were also examined and A860 resins showed a superior regeneration efficiency (by about 20%) compared to A847. Overall, findings indicated the strongly basic resin (Purolite A860) as a better candidate for the removal of NOM from surface water. As a result, this resin was used for subsequent experiments throughout the rest of this research.

4.1 Introduction

Taste and color, reduction of treatment efficacy, formation of disinfection by-products, and potential regrowth of biofilm within the distribution system are among the problems resulting from the presence of natural organic matter (NOM) in surface waters serving as drinking water sources (Bazri et al., 2012; Kleiser and Frimmel, 2000; Singer, 1999; Van der

Kooij, 1992). One feasible solution to address this challenge is the use of anionic ion exchange (IEX) process that has been shown to be simple in operation and effective at removing NOM and other inorganics such as nitrate and arsenate (Chen et al., 2006; Clifford, 1999; Harland, 1994). The performance of IEX process is, however, affected by resin characteristics such as functional group (strongly basic, weakly basic), backbone structure (acrylic or styrenic), and porosity (gel or macroporous) as well as the influent water quality (Bolto et al., 2004, 2002b; Harland, 1994). For instance, strongly basic resins (SBR) are very effective at removing a wide range of anionic species (e.g., NOM, NO_3^-) and are commonly regenerated using brine (NaCl ~10 % wt.); a chemically demanding and costly process with environmental concerns over the disposal of the spent regenerant (Clifford, 1999; Greenleaf et al., 2009; Harland, 1994; Höll and Kiehling, 1981; Rokicki and Boyer, 2011). On the other hand, weakly basic resins (WBR) offer lower costs associated with regeneration and waste disposal by using caustic solution (e.g., Ca(OH)_2 , NaOH ~4% wt.), but exhibit lower NOM removal capability compared to SBRs (Bolto et al., 2002b; Cornelissen et al., 2008; Evans and Maalman, 1979; Rook and Evans, 1979). That said, the use of caustic solution is not favorable due to its handling risks and disposal issues (Höll and Kiehling, 1981; Evans and Maalman, 1979; Höll and Kirch, 1978; Matosic et al., 2000).

Resins are generally reused (a few times) within an operational cycle prior to their regeneration and therefore some variations may be observed in their removal efficacy (Drikas et al., 2011; Mergen et al., 2008; Walker and Boyer, 2011). Additionally, the use of stirred (a.k.a. suspended) mode operation as opposed to the conventional packed bed columns has gained considerable attention in recent studies on the removal of NOM via IEX resins (Boyer and Singer, 2006; Cornelissen et al., 2009; Drikas et al., 2002; Galjaard, 2010; Gan et al., 2013a; Grefte et al., 2013; Martijn et al., 2010; Slunjski et al., 2000). However, the variability in the

performance of IEX resins under consecutive batch loading conditions and different water sources have seldom been investigated (Mergen et al., 2008; Walker and Boyer, 2011). Given the growing interest on commercialization of the stirred mode operation (e.g., recent opening of Andijk III plant, Netherlands treating 120000 m³/day using suspended ion exchange SIX[®] technology), it was motivating for the authors to evaluate and compare the resins under stirred mode batch and consecutive batch loading conditions (simulating commercial applications).

Given the lack of a holistic scheme to assess IEX resins for NOM removal in the literature, this research intended to look at key important criteria such as NOM removal performance, kinetics, and regeneration efficiency under anionic IEX resins during batch and consecutive multiple cycles for different water qualities. The purpose of the current study was to propose an evaluation approach and provide bench scale data sets that could form the basis for decision making towards selection of the best performing resins and implementation of pilot scale ion exchange process.

4.2 Materials and Methods

4.2.1 Water sources

The following water sources, presented in Table 4.1, were used in this part of the research. Raw river water (RW) from the Mille-Ile River (QC, Canada) was collected at the influent of the Ste. Rose water treatment facility and at the effluent of a granular tri-media filter (without coagulation) only intended to reduce suspended solids. Ultrapure (Milli-Q) water spiked with aquatic NOM from Suwannee River (SRNOM, International Humic Substances Society) served as the reference water source. The pH of synthetic SRNOM water was adjusted to neutral range (pH ~ 7.5) by buffering with NaHCO₃ (40 mg/L), and adding NaOH (0.1 N) and NaCl (1 mg/L).

Table 4.1, Characteristics of the waters used in this study

Water source	Symbol	¹TOC	¹SUVA	¹Turbidity
Raw River	RW	6.0	4.39	5.0
River water filtrate 1	F1	5.8	4.13	1.8
River water filtrate 2	F2	5.7	3.75	1.0
Suwannee River NOM	SRNOM	8.6	4.15	-

¹TOC: mg/L, SUVA: UV₂₅₄/TOC: L.mg⁻¹.cm⁻¹, Turbidity: NTU

4.2.2 Anion exchange resins

From a long list of commercially available resins for organic matter removal, six resins were acquired from different manufacturers (Table 4.2). Resins were selected due to their relevant application, superior performance, characteristics and availability.

Table 4.2, List of ion exchange resins

Resin	Manufacturer	Structure	Basicity	Porosity	¹Capacity - eq/L	¹Bead Size - µm
Amberlite IRA 458	Rohm and Hass	Polyacrylic	SB	Gel	> 1.25	600 - 900
Purolite A860	Purolite	Polyacrylic	SB	MP	0.80	300 - 1200
Ionac Macro-T	Lanxess	Polyacrylic	SB	MP	1.1	470 - 600
Amberlite IRA 67	Rohm and Hass	Polyacrylic	WB	Gel	> 1.60	500 - 750
Purolite A847	Purolite	Polyacrylic	WB	Gel	> 1.60	300 - 1200
Lewatit VPOC 1073	Lanxess	Polyacrylic	WB	Gel	> 1.25	500 - 600

¹ provided by the manufacturer

4.2.3 Kinetic experiments

For the initial screening, resins amounts of 200 – 1000 mg/L (dry) were mixed with SRNOM for up to 8 hrs and their TOC removal performance was compared to select the best two performing resins. Detailed kinetic and adsorption experiments were then conducted using the two shortlisted resins as follows. For the kinetic tests, 7.5 mL (for RW) and or 10 mL (for SRNOM) of resins was mixed with 1L of water for different contact times (up to 24 hrs) using a Jar tester (Phipps and Bird 9900). To construct the adsorption isotherms, 10 to 1000 mg of the two shortlisted resins were carefully weighed and mixed with 1 L of SRNOM (TOC ~ 8.6 mg/L) for 24 hrs (i.e., equilibrium). Resins were filtered from the treated water using a pre-rinsed fast coarse filter (WhatmanTM 113 - 30µm) and samples underwent subsequent water quality analyses.

4.2.4 Resins regeneration

Resins used in the multiple loadings were utilized for the regeneration study. Various ratios of regenerant/resin (g/L, Table 4.3) were mixed using either NaCl (10 % wt.) or NaOH (4 % wt.), and UV₂₅₄ and TOC of the solutions were monitored. Due to operational challenges posed by NaCl and NaOH to the Total Organic Carbon (TOC) analyzer, only a few samples were analyzed for TOC to investigate the correlation between the changes in UV₂₅₄ (given the hydrophobic properties of SRNOM) and TOC of the regenerant.

Table 4.3, Regenerant to resin ratios (mL/mL, g/L, and meq/meq)

	Regenerant:Resin (mL/mL)	Regenerant:Resin (g/L)	Regenerant/Resin (meq:meq)
NaCl (10% wt.)	4/1	450/1	10/1
	40/1	4500/1	100/1
NaOH (4% wt.)	4/1	160/1	5/1
	40/1	1600/1	50/1

4.3 Results and Discussion

4.3.1 Effect of IEX resins on water quality

From the six resins tested at doses of 200 to 1000 mg/L, a TOC removal range of 55 to 75% was observed during the first 2 hrs of contact time with SRNOM. The two Ionac Macro-T and A860 SBR resins and the WBR A847 showed better performance compared to their counterparts while the difference between other resins performances was insignificant (Figure 4.1). Therefore, to select the two best performing resins, they were also rated by their mechanical properties (e.g., attrition, settling velocity) as well as their availability from manufacturer (Monosov et al., 2012). For instance, some degree of attrition was observed for Macro-T and the fastest settling velocity was observed for A860. Given the primary interest in comparing weak and strongly basic resins, Purolite A860 (SBR) and Purolite A847 (WBR) were shortlisted for subsequent experiments.

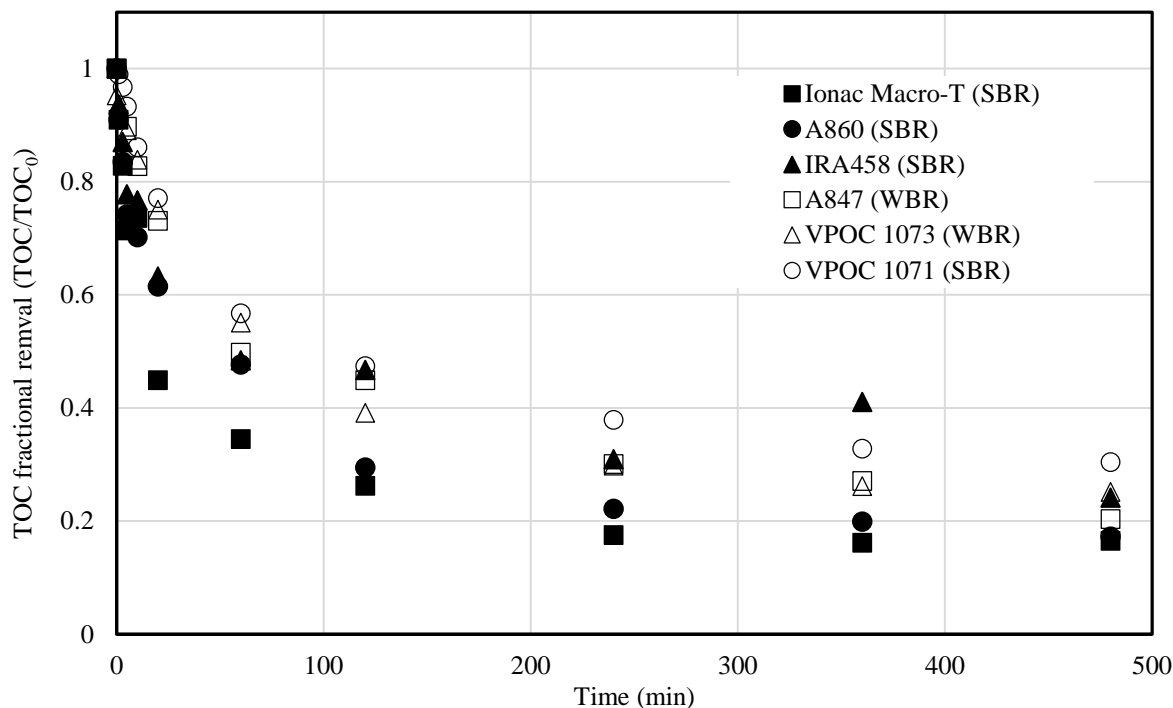


Figure 4.1, TOC Removal performance of various resins—100 mg/L, SRNOM

Figure 4.2.A demonstrates the TOC and UV transmittance (UVT) profiles for SRNOM treated with 10 mL/L of A860 and A847 over 2 hrs. The SBR (i.e., A860) showed a slightly better removal compared to the WBR (i.e., A847); however, the difference after 24 hrs of treatment was insignificant (~ 96 and 93 % removal, respectively). For the first 30 minutes, SUVA (i.e., $100 \times \text{UV}_{254} / \text{TOC}$) did not show a tangible change; however, it dropped rapidly to 30% and 15% of its initial value after 2 hrs and 24 hrs, respectively (data not shown). The reason for this observation is attributed to the preferential removal of smaller low-SUVA molecules in early stages of the treatment, that occupy inner pores and channels, followed by more adsorption of UV_{254} adsorbing compounds (i.e., hydrophobic high molecular weight fractions) (Mergen et al., 2008; Newcombe et al., 1997; Zhang et al., 2014).

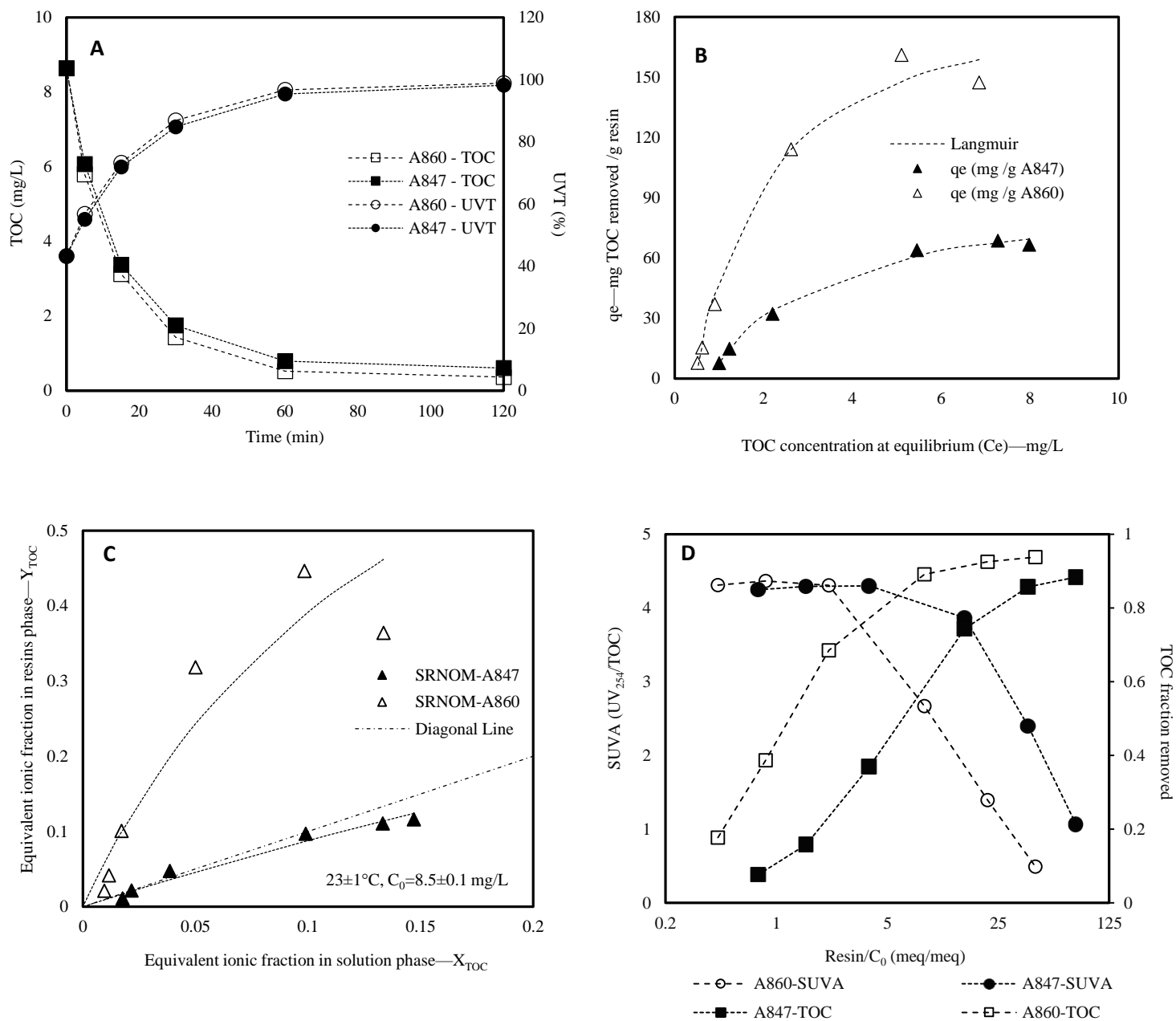


Figure 4.2, Comparison of A860 and A847 in terms of TOC and UVT (A), adsorption isotherms (B), exchange equilibrium (C), and SUVA vs. resin/ C_0 loading (D)

In spite of similar TOC and UV_{254} removal, Dissolved Inorganic Carbon (DIC) was reduced by about 90% under A860 whereas only 30% removal was recorded for A847 after 2 hrs (Figure A.1). As a result of the ion exchange process, A860 (SBR) released ~ 3 times higher Cl^-

compared to A847 (WBR). The correlation between the net Cl^- (meq/L) released versus the net (DOC + DIC) removed (meq/L) was linear with a slope of 1.13 ± 0.03 (p-value < 0.0001, at 95% confidence level) for A860, indicating the dominance of ion exchange mechanism. For A847, on the other hand, the net Cl^- vs. net (DOC+DIC) was nonlinear and all data fell below the diagonal line (i.e., slope <<1) showing a different removal mechanism than ion exchange. It has also been reported in other studies that (acrylic) weakly basic resins (e.g., A847) mainly remove organic acids through sorption rather than ion exchange, even though the acrylic backbone can give the weakly basic resin stronger alkalinity thereby promoting the ion exchange mechanism (Bolto et al., 2002b; Cornelissen et al., 2008; Harland, 1994). Nonetheless, the kinetic test performed did not highlight any significant difference between the resins' kinetics.

Isotherm data obtained for both resins (Figure 4.2.B) showed an upwardly convex trend indicating type I adsorption isotherm which corresponds to monolayer coverage of the resins surface (Brunauer et al., 1940; Qi et al., 2012). Therefore, Langmuir isotherm (equations 1 and 2) were fitted through the data in order to obtain the maximum sorption capacity (q_m), equilibrium constant (K_L). In addition, studies have shown that non-ionic fractions of NOM are not removed under IEX (Bolto et al., 2004; Cornelissen et al., 2010; Huber et al., 2011; Qi et al., 2012). To account for these fractions Qi and co-workers have suggested the following modified Langmuir equation by considering the non-removable fraction of NOM (β) defined as $C_{\text{non-removable}}/C_0$ (Qi et al., 2012).

$$q = \frac{q_m K_L (C_e - C_0 \beta)}{1 + K_L (C_e - C_0 \beta)} \quad (1)$$

$$q = \frac{C_0 - C_e}{M} \quad (2)$$

where C_0 is the initial concentration of TOC (mg/L), C_e is the concentration of TOC at equilibrium (mg/L), $C_{\text{non-removable}}$ is the concentration not removed under IEX (i.e., C_e), and M is the resin weight (g).

Very good agreement between the model and experimental data was obtained under Langmuir equation ($R^2 \sim 0.99$) and the estimated isotherms constants (i.e., q_m , K_L , and β) are shown in Table 4.4. Sorption capacity (q_m) for A860 was more than double the one of A847 despite the reported higher exchange capacity for A847 (see Table 4.2). Higher equilibrium constant (K_L) and lower non-removable fraction of NOM were estimated for A860 compared to A847, showing a more favorable sorption under A860. Values estimated for non-removable NOM (β) were 6-9 % for SRNOM, depending on the resin used, demonstrating the impact of accounting for β on isotherm calculations (i.e., improving the goodness of fit) and also the behavior of removal (Boyer and Singer, 2008b).

Table 4.4, Langmuir isotherm parameters for SRNOM under A860 and A847

Parameter	A860	A847
q_m , Sorption capacity— <i>mg TOC/g resin</i>	198 ± 24	94 ± 8
K_L , Equilibrium constant— <i>L/mg TOC</i>	0.63 ± 0.26	0.40 ± 0.11
β , Non-removable NOM—%	6 ± 0.90	9 ± 1.1
Adjusted R^2	0.979	0.991

Analysis of the ternary equilibrium system containing TOC, HCO_3^- , and Cl^- was performed to assess the affinity of resins for SRNOM, and results are shown in Figure 4.2.C. Using the equation proposed by Li and SenGupta, (2000), $Y_{\text{TOC}} = \frac{\alpha X_{\text{TOC}}}{1 + \alpha X_{\text{TOC}}}$ (where Y_{TOC} is the fraction of NOM in the resin phase (meq/meq) and X_{TOC} is the fraction of NOM in the solution

phase (meq/meq)), the estimated equilibrium constants (α) for SRNOM under A860 and A847 were 6.43 and 0.96, respectively, clearly showing a stronger affinity (~ 6.5 times) of A860 for SRNOM.

To standardize the comparison between the resins, the TOC fraction removed and SUVA were plotted against the amount of the resins used normalized by the initial concentration of organic matter i.e., Resin/ C_0 (meq/meq) (Figure 4.2.D; see section A.1 in Appendices for charge density calculations). Up to the addition of 50 mg/L of resins (A860_{Resin/ C_0} : 2.14 meq/meq, A847_{Resin/ C_0} : 3.85 meq/meq), SUVA value did not change tangibly ($\sim 3\%$), whereas a considerable fraction ($\sim 68\%$, and 40% , respectively) of TOC was removed by resins. Increasing the resin dose resulted in a rapid decline in SUVA profiles and more improvement in TOC removal. The observation in Figure 4.2.D can be explained by preferential removal of smaller molecules (contributing to a smaller DOC fraction) that can easily penetrate through the resin pores and inner channels outperforming the removal of larger high-SUVA molecules, especially at lower resin concentrations. At higher resin concentrations (i.e., more exchange sites and resins pores) this competition becomes less pronounced because of more surface exchange/adsorption of larger molecules (Newcombe et al., 1997; Pelekani and Snoeyink, 1999; Zhang et al., 2014). Also, the higher and sharper decrease of SUVA under A860 showed the preferential removal of aromatic NOM compared to A847. Additional discussion regarding the impact of resins on molecular weight distribution of SRNOM is provided in section A.2 of Appendices.

4.3.2 Multiple loadings test (MLT)

A860 and A847 in both $-\text{HO}^-$ and $-\text{Cl}^-$ forms were used in multiple consecutive batch loading cycles of SRNOM (i.e., 700 BV of water). The form of the resins used (OH^- or Cl^- form) is important since it consequently dictates the type of the solution used for regeneration (NaOH

or NaCl). Results obtained indicated higher pH values of up to 3 units in the waters treated with --HO^- form resins, in particular for A860-OH (data not shown). As the ion exchange became less significant (i.e., less Cl^- release) throughout the cycles, the change in pH was also reduced. Figure 4.3.A demonstrates the difference in TOC profiles for the two resins over 7 cycles. The greatest removal was recorded for the 1st cycle (i.e., fresh resins) where A860-Cl and A847-OH showed ~ 73% and ~ 64% of TOC removal, respectively. The removal efficiency declined over 700 BV to 54% and 41% for A860-Cl and A847-OH, respectively. The average TOC removal over 700 BV was 59, 59, 49, and 46% for A860-Cl, A860-OH, A847-OH, and A847-Cl, respectively. Therefore, strongly basic A860 resin exhibited better removal (by about 10%) compared to its weakly basic counterpart (A847) in both forms after treatment of 700 BV of water. Similar trends and observations were recorded for UV_{254} profile (data not shown). The SUVA profile for all resins indicated an initial drop (6-23 %) after the first cycle; however, SUVA value raised slightly above its initial value (5-12 %) after the 2nd cycle. It is hypothesized that the compounds removed primarily in the initial cycle(s), block the resins pores and inner channels thereby hindering further sorption of other organic molecules into the inner channels. The extent of this phenomenon is however highly dependent on the molecular weight of the organics removed (Mergen et al., 2008; Zhang et al., 2014).

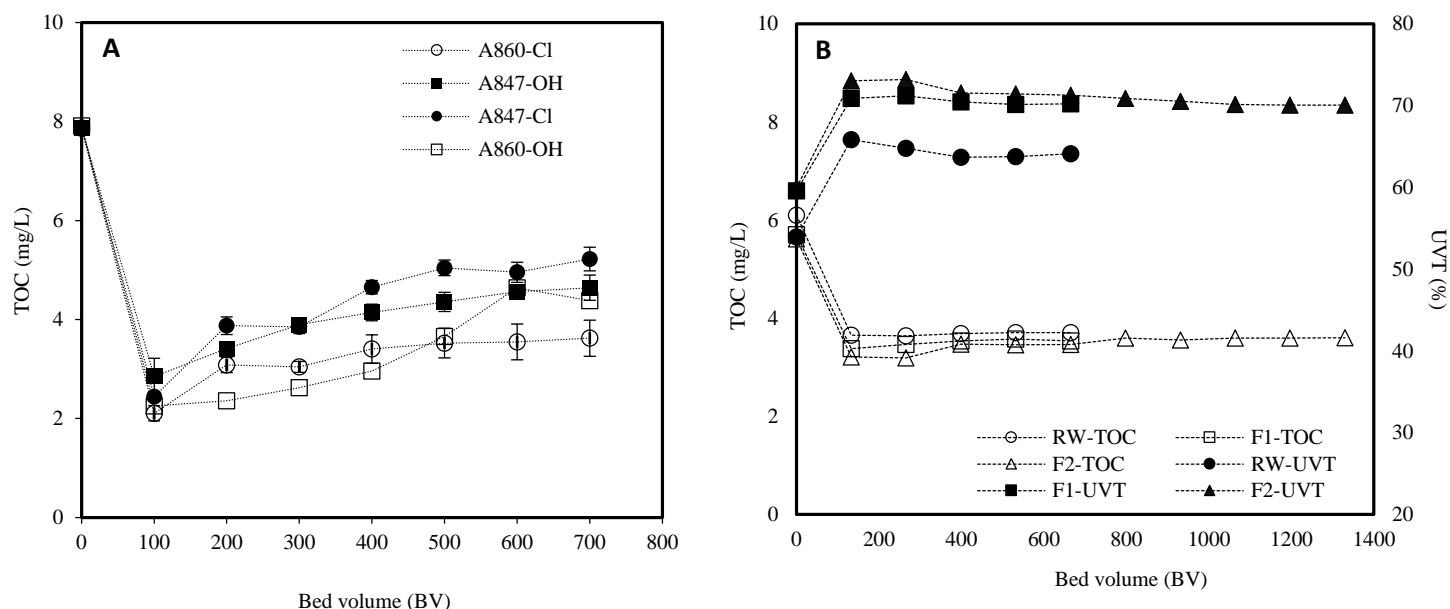


Figure 4.3, Multiple loadings of HO⁻ and Cl⁻ forms of resins (10 mL/L) with SRNOM (A), and A860-Cl (7.5 mL/L) with RW, F1, and F2

Using the raw river water (RW) and its filtrates (F1, F2), 1300 BV of water was treated with A860-Cl and all waters exhibited similar removal of $\sim 40 \pm 5\%$ (Figure 4.3.B). The proximity of the TOC profiles for raw water (5 NTU) and filtered waters (1 NTU) indicated that this level of turbidity had no tangible impact on the efficacy of TOC removal, whereas this can become challenging for column operation of IEX resins (Graf et al., 2014). Interestingly, despite the lower removal observed compared to SRNOM, the efficiency of removal remained constant ($\sim 40\%$) even at higher bed volumes. The LC-OCD analysis of the apparent molecular weight (AMW) of the raw river water (RW) showed the presence of biopolymer, neutral, and low MW acid fractions (Figure A.3) which are reportedly identified as non-removable NOM fraction by IEX (Cornelissen et al., 2010; Huber et al., 2011). Moreover, given the relatively constant performance of resins over multiple loading cycles it is postulated that the removable NOM

in these waters is mainly comprised of small-medium humic molecules that could easily penetrate through the resin pores without blocking the inner channels and or being excluded from diffusion by small pores of the resins (Boyer et al., 2008b; Mergen et al., 2008; Tan and Kilduff, 2007).

4.3.3 Regeneration

Figure 4.4.A exhibits the changes in TOC and UV₂₅₄ of the regeneration solutions used to restore the performance of A860-Cl and A847-OH resins (NaCl 10% wt., and NaOH 4% wt., respectively). The horizontal dashed lines show the cumulative TOC removed over cycles which can be also seen as the 100% regeneration efficiency target. Regeneration efficiency was defined as the ratio of the TOC released (UV₂₅₄ increase) in the regenerant over the cumulative amount of TOC uptake (and or alternatively UV₂₅₄ reduction) during MLT. TOC and UV₂₅₄ profiles for both regenerants (i.e., NaCl and NaOH) followed the same pattern suggesting UV₂₅₄ as a suitable surrogate to gauge the regeneration efficiency. The estimated regeneration efficiency during 2 hrs of mixing for A860-Cl and A847-OH was ~ 95% and ~74%, respectively.

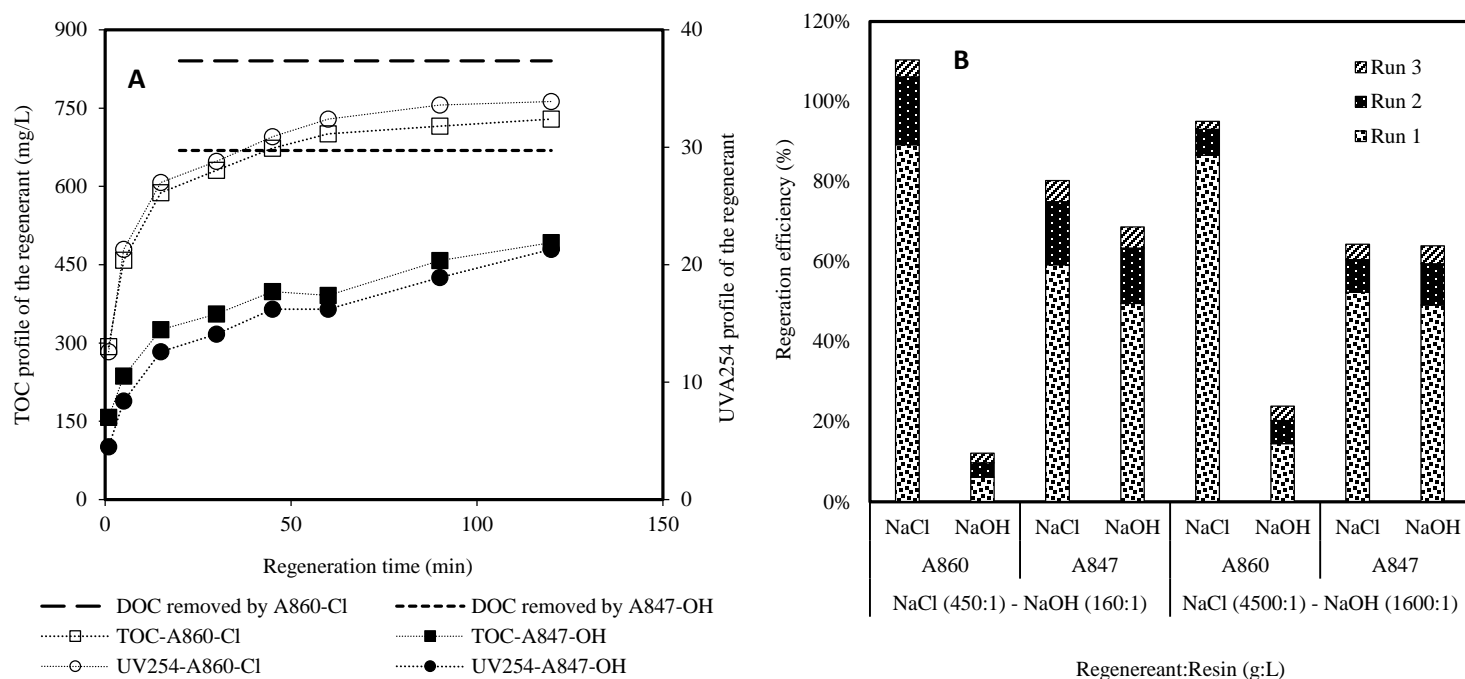


Figure 4.4, Regeneration efficiency of A860-Cl and A847-OH under NaCl and NaOH, respectively, for 2hr (A), and for three consecutive 30 min cycles (B)

The impact of regeneration method was also investigated in this study. Instead of a continuous two-hour mixing, three 30-minute mixings were applied on each resin under brine and caustic solutions at different volumes (i.e., different regenerant—g/resin—L ratios, see Table 4.3) and results are presented in Figure 4.4.B. Interestingly, despite the added benefit of the 2nd and 3rd runs, a substantial fraction (50-85%) of regeneration took place in the 1st cycle. The strongly basic resin (A860) showed greater regeneration efficiency compared to the weakly basic resin (A847) when brine was used, and the use of NaOH was found to be inefficient for A860. On the other hand, both NaCl and NaOH performed well (71-80 %) for A847 with brine resulting in ~ 10% higher regeneration efficiency at lower volumes (i.e., 450:1 g/L). Higher volumes of regenerant did not show any tangible improvement in the regeneration efficiency

(except 12% for the case of A860-NaOH) and values obtained were within the range of the experimental error ($< 10\%$). For the case of A860-Cl regenerated with 450:1 NaCl—g/Resins—L (and also all the 1st runs for lower regenerant ratio) the estimated regeneration efficiency was higher than unity i.e., 110 %, that was attributed to an error in diluting the 1st run sample for UV₂₅₄ measurement. Nonetheless, these preliminary results elucidated the existing difference between the regeneration efficiency of the two resins.

The abovementioned methods of regeneration were compared in terms of their overall efficiency based on $\text{TOC}_{\text{released}}/\text{TOC}_{\text{adsorbed}}$ at the lower regenerant/resin (g/L) ratio. A860 showed 87% and 95% and A847 showed 74% and 74% of regeneration efficiency for two-hour and triple 30-minute mixing, respectively. Therefore, the consecutive approach seemed to be a more efficient method for the regeneration of resins. Moreover, majority of regeneration takes place in the first 30 minutes and from a practical perspective a single 30 minute regeneration can significantly improve the regenerant use and reduce the mixing time. Given the results obtained, A860-Cl clearly exhibited its advantage in regeneration which was $\sim 20\%$ higher than the one of A847-OH. Similar range of regeneration efficiency for A860-Cl (91-99%) was also observed for resins saturated with raw river water and the filtered waters (data not shown).

4.4 Conclusions

Two strongly basic (Purolite A860) and weakly basic (Purolite A847) IEX resins were initially screened and compared in terms of their removal kinetics and regeneration efficiency under batch and simulated commercial conditions. The kinetic experiments did not show any tangible difference in the performance of resins at NOM removal; however, isotherms tests indicated the strongly basic A860 to possess higher capacity and affinity for organic molecules (Figure 4.2). The results of multiple loading tests (i.e., simulating realistic conditions) further

clarified the difference between resins indicating higher TOC removal capacity (~ 10%) for the strongly basic A860 under multiple consecutive batch loadings. Different regeneration scenarios were examined and results indicated that 50-85% of regeneration takes place in the first 30-minutes. Moreover, increasing the regenerant amount (from 450:1 to 4500:1 g-NaCl/L-resins) had no tangible impact on the efficacy of regeneration. Overall, strongly basic A860 resins showed superior TOC removal and regeneration efficiency (~ 20%) compared to weakly basic A847 and hence, was recommended for future studies. The approach undertaken in this study can be used as a holistic decision making scheme to look at various aspects that could influence the performance of IEX process used (for removal of NOM) in drinking water treatment applications.

Supplementary Information

Supplementary information related to this chapter is provided in Appendix A.

Chapter 5: Impact of NOM Properties on the Kinetics of Ion Exchange Process

The strongly basic A860 selected from the previous chapter 4 was utilized to investigate the removal kinetics of four standard natural organic matter (NOM) isolates during batch and consecutive loadings. The objective of this chapter was to carry out a detailed kinetic investigation on the effect of NOM properties (e.g., MW, charge density, and source) on the efficacy of IEX process. Also, empirical and physical models were evaluated for predicting the kinetic behavior (e.g., DOC profile) of the batch systems studied. In general, high levels of DOC removal (80-98 %) were observed; however, some fractions of NOM were not removed even under extensive treatment conditions. Suwannee River (SR) NOM, SR Fulvic Acid (FA) and Pony Lake (PL) FA were greatly removed ($> 90\%$) and highly preferred by resins ($\alpha > 5$, over Cl^- , and HCO_3^-) whereas SR Humic Acid (HA) was the least preferred organic structure among the four isolates studied ($\alpha \approx 1$). Moreover, the removal efficacy of Fulvic acids was consistent over consecutive loadings cycles whereas it decreased for SRNOM and SRHA over the course of operation. The stoichiometric correlation between the chloride released and organic molecules removed indicated that ion exchange was the dominant mechanism. Also, it was found that molecular weight and charge density of NOM played a major role in the efficacy of ion exchange process. Under the operation conditions applied, pore diffusion was found to be the rate-limiting step for the uptake of NOM; hence, it was used as the appropriate model to predict the kinetics of removal. Using this model, free liquid diffusivities and effective pore diffusion coefficients of organic molecules were estimated and findings were corroborated with the existing data in the literature.

5.1 Introduction

Use of strongly basic ion exchange resins (IEX) is an effective tool for simultaneous removal of natural organic matter (NOM) and inorganic anions (e.g., nitrate, sulfate) that are widely present in surface waters (Fearing et al., 2004; Martijn et al., 2010). The dominant NOM removal mechanism for this process has been reported to be ion exchange with possible minor contribution from surface adsorption (Boyer and Singer, 2008b; Fu and Symons, 1990; Li and SenGupta, 2001; Tan and Kilduff, 2007). Some kinetic studies on the sorption of organic molecules have concluded pore diffusion to be the rate-limiting step (Bautista et al., 2000; Boyer et al., 2008a; Chen et al., 2002; Li and SenGupta, 2000; Weaver and Carta, 1996; Wu and Gschwend, 1986); however, film diffusion can become significant at low solute concentration i.e., high resin doses (Boyd et al., 1947; Reichenberg, 1953; Weaver and Carta, 1996; Weber Jr and DiGiano, 1996). Aside from resin properties that could impact the efficacy of the process (Bolto et al., 2002b; Boyer and Singer, 2008b; Cornelissen et al., 2008), NOM properties such as molecular weight (MW), polarity (i.e., hydrophobicity), and charge density could significantly influence the IEX-treated water quality. Studies focusing on the effect of NOM properties are however inconclusive and sometimes contradictory. For instance, Croué et al., (1999) observed an inverse correlation between hydrophobicity of NOM and removal performance while Mergen et al., (2008) and Boyer and Singer, (2008a) reported the hydrophobic-transphilic fractions of NOM as the main targets by IEX. Furthermore, Fu and Symons, (1990), Mergen et al., (2008), and Tan and Kilduff, (2007) have pointed out the importance of MW while Boyer et al., (2008b) reported the charge density of the organic molecules to be the key factor in determining the removal efficiency. In this respect, the motive for this research was to attempt to demystify the impact of NOM properties, in particular molecular weight and charge density, on the kinetics and

performance of the IEX process for drinking water treatment applications. Extensive kinetic experiments were carried out on four standard natural organic matter isolates with different MWs and charge densities (Suwannee River NOM, Suwannee River Fulvic Acid, Suwannee River Humic Acid, and Pony Lake Fulvic Acid) and various mathematical and physical models were employed to investigate the underlying removal mechanism and rate-limiting step for NOM. By utilizing these models, effective pore diffusion coefficient ($D_{p,e}$), film diffusion coefficient (D_f), apparent diffusivity (D_a), and free liquid diffusivity (D_l), for each NOM isolate, were estimated and the rate-limiting step was investigated using the Biot number. The significance of this research is the approach in understanding the major influencing NOM properties as well as underlying kinetics for the removal of standard aquatic NOM isolates and can provide the basis for future studies concerning the application of IEX for organic matter removal in drinking water applications.

5.2 Materials and Methods

5.2.1 Water sources

Each synthetic water sample was prepared by dissolving 20 mg of a standard IHSS isolate (International Humic Substances Society) into 1L of Milli-Q water (Table 5.1). The final pH was adjusted to neutral range (~ 7.5) by buffering with NaHCO_3 (40 mg/L), NaCl (1 mg/L), and adding NaOH (0.1 N).

Table 5.1, Characteristics of the standard isolated used in this study

¹ Water Source	^{2,6} Charge density	⁶ TOC	TOC (meq/L)	⁶ SUVA	⁶ Mw
Suwannee River NOM (SRNOM)	10.157	8.33	0.0846	4.41	³ 1030, ⁵ 2190
Suwannee River Fulvic Acid (SRFA)	10.974	8.85	0.0971	5.23	³ 1070, ⁴ 1910, ⁵ 2310
Suwannee River Humic Acid (SRHA)	8.890	7.40	0.0658	7.92	³ 1520, ⁴ 4390
Pony Lake Fulvic Acid (PLFA)	6.840	8.17	0.0559	3.20	³ 760

¹All waters contained 40 mg/L NaHCO₃ and 1 mg/L NaCl

²Estimated at pH = 7.5 using the equation provided by Ritchie and Perdue (2003), Driver and Perdue (2014), and IHSS website

³ Estimated Mw of humic substances using LC-OCD technique (See Chapter 7). Data obtained are estimates and were used for comparison only.

⁴Becket et al., 1987,

⁵Chin et al., 1994

⁶Charge density: (meq/g-C), TOC: mg/L, SUVA: UV₂₅₄/TOC: L.mg⁻¹.cm⁻¹, MW: g/mol (Da)

5.2.2 Kinetic experiments

Using a Jar tester (Phipps & Bird 9900), a practical resin dose of 10 mL (Boyer and Singer, 2006; Galjaard, 2010; Mergen et al., 2008) was mixed with 1 L of water for various contact times from 5 minutes (min) to 24 hrs. For adsorption isotherms, 10 to 1000 mg of dried resins were carefully weighed and mixed with 1L of water to equilibrium (i.e., 24 hrs). Resins were filtered from the treated water using a pre-rinsed fast coarse filter (Whatman 113- 30 µm) and samples underwent subsequent water quality analyses.

5.3 Results and Discussion

5.3.1 Stoichiometry of NOM removal

Using the charge densities estimated for organic isolates at pH ~ 7.5 as elaborated in Appendix B (Driver and Perdue, 2014; Ritchie and Perdue, 2003), the net chloride released (meq/L) was plotted against the net TOC+DIC uptake (meq/L) for various resin doses at equilibrium (Figure 5.1.A). The slopes obtained for SRNOM, SRFA, SRHA, and PLFA were

1.13±0.03, 1.08±0.01, 1.10±0.01, and 1.11±0.01, respectively (p-values < 0.0001, at 95% confidence level), showing slightly greater (~ 10 %) Cl⁻ release than the theoretical value of 1 (i.e., the diagonal line X=Y). Given the expected very low contribution of hydrophobic interactions (Bolto et al., 2002), the reason for higher slopes was mainly attributed to the detachment of weak resin-Cl⁻ bounds as well as analytical errors in the measurement of DOC, DIC, and Cl⁻. Nonetheless, the data obtained here showed that ion exchange was the dominant mechanism for the removal of organic molecules.

5.3.2 Effect of NOM properties on the removal behavior

The following modified Freundlich and Langmuir isotherms were fitted through the experimental data (Figure B.1) and the unknown parameters for both equations were estimated using nonlinear regression schemes and are demonstrated in Table 5.2.

$$q_e = \frac{C_e - C_0}{M} \quad (1)$$

Freundlich $q = K_F(C_e - C_0\beta)^n \quad (2)$

Langmuir $q = \frac{q_m K_L (C_e - C_0\beta)}{1 + K_L (C_e - C_0\beta)} \quad (3)$

where C₀: initial TOC concentration (mg/L), C_e: concentration at equilibrium (mg/L), M: resin mass (g), q: solid phase concentration (resins loading - mg/g), q_e: resin loading at equilibrium (mg/g), q_m: maximum sorption capacity (mg/g), K_F: Freundlich constant (Lⁿ/gⁿ), K_L: Langmuir equilibrium constant (L/g), n: surrogate for affinity, and β: non-removable fraction of TOC (%).

Results obtained suggested the modified Langmuir isotherm as a slightly better fit (Adjusted R² values > 0.97) compared to the modified Freundlich isotherm (Adjusted R² > 0.92). The highest q_m was observed for PLFA and the one for SRNOM was between the ones of SRFA

and SRHA. The higher q_m (theoretically corresponding to the monolayer coverage of the resins surface) for Fulvic acid isolates is attributed to their lower molecular weight facilitating their access to inner pores and exchange sites (Newcombe et al., 2002; Pelekani and Snoeyink, 1999; Zhang et al., 2014). K_L is related to the energy of adsorption (Snoeyink and Summers, 2011) and it is postulated that the considerably lower K_L value for PLFA corresponds to its lower charge density (and SUVA) compared to the other isolates (i.e., less hydrophobic character). That being said, statistical analysis revealed no significant difference among K_L values at 95% confidence. In spite of its dominant hydrophobic character, SRHA showed the highest estimated non-removable TOC of $\sim 32\%$, while the estimated β was ~ 10 , 6 , and 2.6% for PLFA, SRNOM, and SRFA, respectively. The average relative difference (RD) between the experimental β and the estimated β from modified Langmuir and Freundlich equations was 20 and 3% , respectively. Literature findings have reported that the removal of high MW NOM (e.g., > 10 k Dalton, Da) is largely hindered due to the size exclusion of organic molecules by the resin pores (Fu and Symons, 1990; Tan and Kilduff, 2007; Zhang et al., 2014), and or it can be adversely affected from relatively large organic molecules (5k-10k Da) blocking the pore channels of resins thereby limiting the access of smaller molecules to inner exchange sites (Boyer et al., 2008b; Mergen et al., 2008; Zhang et al., 2014). Hence, this high level of non-removable organic matter for SRHA is explained by the adverse effect of size exclusion of large organic molecules (Croué et al., 1999; Fu and Symons, 1990; Tan and Kilduff, 2007).

Table 5.2, Estimated parameters for modified Langmuir and Freundlich isotherms

modified Langmuir				
Water source	q_m	K_L	β (%)	Adjusted R²
SRNOM	198.14 ±23.77	0.63 ±0.26 (p = 0.0963)	5.75 ±0.92	0.9758
SRFA	239.69 ±28.88	0.48 ±0.19 (p = 0.0880)	2.55 ±0.92	0.9867
SRHA	105.26 ±26.73	0.38 ±0.23 (p = 0.2008)	31.43 ±1.83	0.9710
PLFA	529.05 ±121.61	0.13 ±0.05 (p = 0.0718)	9.74 ±0.94	0.9947
modified Freundlich				
Water source	K_F	n	β (%)	Adjusted R²
SRNOM	71.84 ±12.62	0.45 ±0.11	6.15 ±0.35	0.9255
SRFA	87.87 ±4.67	0.40 ±0.03	4.18 ±0.06	0.9934
SRHA	28.63 ±6.72	0.58 ±0.16	32.31 ±2.25	0.9494
PLFA	65.05 ±6.13	0.73 ±0.06	10.54 ±0.67	0.9941

Li and SenGupta, (2000) have proposed the following equation $Y_i = \frac{\alpha X_i}{1 + \alpha X_i}$ to estimate the equilibrium constant (α) for i compound within a ternary equilibrium (e.g., TOC, HCO₃⁻, and Cl⁻). For TOC, Y_{TOC} is the fraction of TOC in the resin phase (meq/meq) and X_{TOC} is the fraction of TOC in the solution phase (meq/meq). The estimated α for SRNOM, SRFA, SRHA, and PLFA was 6.43, 5.54, 1.09, and 5.18, respectively (Figure 5.1.B). Boyer et al., (2008b) reported that charge density is the main influencing factor in the removal of organic matter under IEX; however, the results obtained here indicate the importance of MW as an additional key factor (see Table 5.1) especially at high molecular weight as also previously demonstrated by Fu and

Symons, (1990). The α values for DIC (i.e., HCO_3^-) in all synthetic waters were close and less than 1, indicating greater preference of resins for organic compounds (Figure B.2).

5.3.3 Effect of resins loading

Figure 5.1.C shows the fraction of TOC removed as a function of resin loading i.e., Resin/ C_0 (meq/meq) (see SI). At equal resin exchange site to initial organic ions concentration (resin/ $C_0 = 1$), the removal was between 20-50 % indicating that not all of the exchange sites are available to organic molecules, likely due to size exclusion, pore blocking, and or simultaneous uptake of bicarbonate (Boyer et al., 2008b; Newcombe et al., 2002; Pelekani and Snoeyink, 1999; Zhang et al., 2014). However, at resin/ $C_0 \sim 3$ the removal for SRNOM, SRFA, SRHA, and PLFA was 68, 70, 36, and 67 %, respectively, while the maximum removal for DIC did not exceed 20% (data not shown) further indicating $\alpha_{\text{TOC}} > \alpha_{\text{DIC}}$. Therefore, the hindering effect of bicarbonate on TOC removal is less likely. Addition of further resins did not show any tangible effect on the removal efficiency beyond Resin/ C_0 of ~ 10 , indicating that certain organic fractions are non-removable via IEX resins.

SUVA was nearly constant (± 5 %) for all four waters up to Resin/ $C_0 \sim 3$ showing equal preference of the resins for low and high-SUVA value fractions (Figure 5.1.D). However, with further increase in Resin/ C_0 , SUVA declined and eventually reached a plateau at higher Resin/ $C_0 \sim 27$. It should be noted that high SUVA is generally attributed to high hydrophobicity and high molecular weight (Croué et al., 1999). Therefore, it is postulated that smaller organic molecules (which contribute to a smaller DOC fraction) are preferentially (initially) removed at lower resin doses (Newcombe et al., 2002, 1997; Pelekani and Snoeyink, 1999) having a small impact on SUVA profile; However, at higher resin concentrations the accessible outer surface area is increased and therefore larger molecules (i.e., higher SUVA) could also attach to the sites

available on the resin surface. This can also explain the low reduction of SUVA value for SRHA even up to resin/ C_0 ratios of ~ 27 .

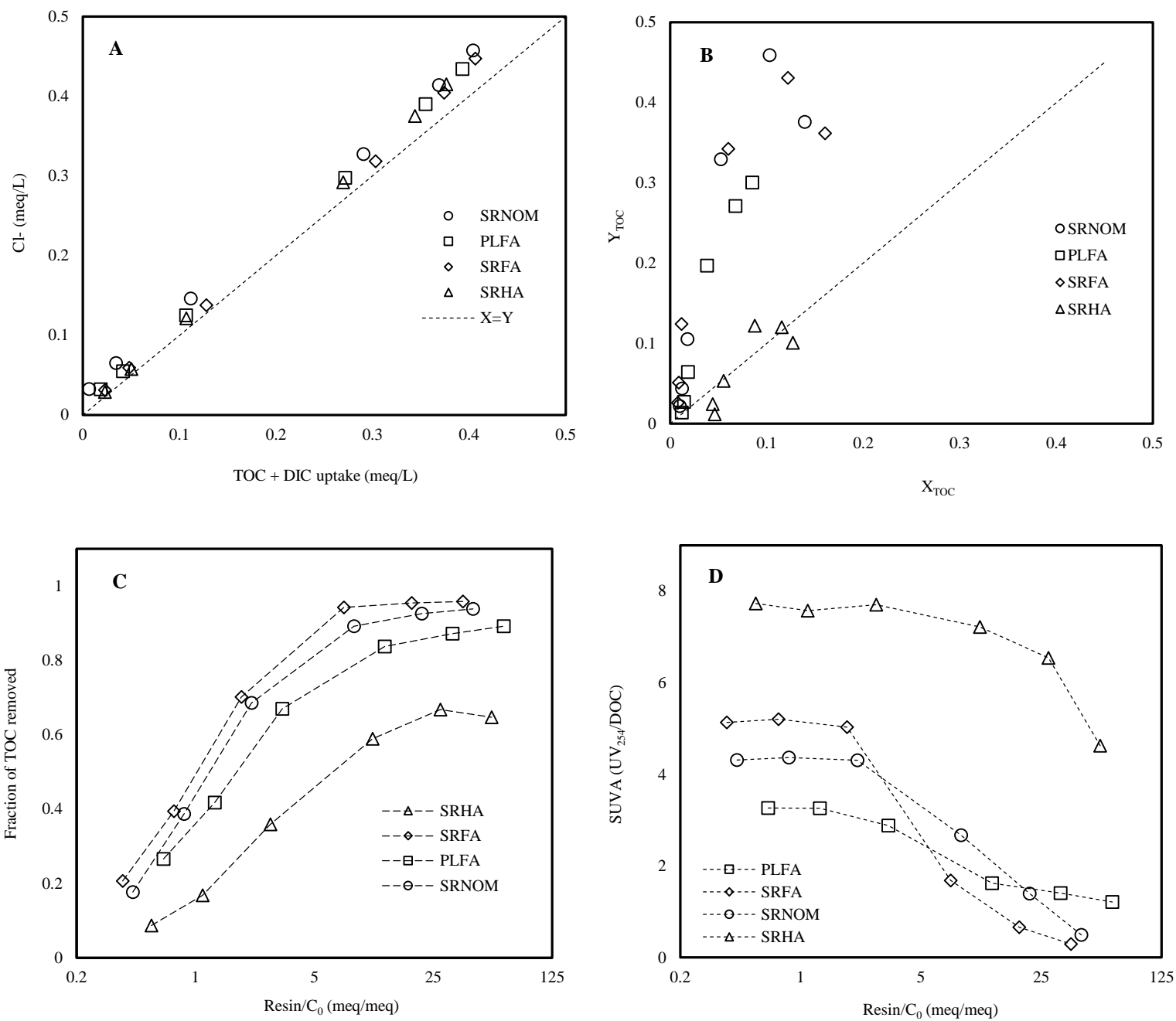


Figure 5.1, Stoichiometry of NOM isolates removal via IEX (A), TOC ternary equilibrium (TOC, HCO_3^- , Cl^-) for NOM isolates (B), fraction of DOC removed vs. resin/ C_0 (meq/meq) (C), SUVA change vs. resin/ C_0 (meq/meq) (D)

5.3.4 Consecutive multiple loadings

The impact of NOM source on the performance of IEX resins over multiple cycles is illustrated in Figure 5.2. SRFA was steadily removed by ~ 85 % over 6 cycles, whereas the removal efficacy was reduced from 80 % to 60 % for SRNOM and from 40 % to 30 % for SRHA. SUVA for SRFA and SRNOM increased after each batch (compared to raw water) with highest increase seen for the first cycle (Figure 5.2.A and Figure 5.2.B). Given the short contact time employed (i.e., 30 min), it is postulated that smaller molecules with lower SUVA predominantly penetrate the resins pores and channels hence leaving the larger ones in the solution. With the reuse of resins, these channels (and pores) become more occupied/blocked resulting in the increased preferential removal of smaller molecules (Newcombe et al., 2002; Pelekani and Snoeyink, 1999; Zhang et al., 2014). That said, SRHA demonstrated an entirely different SUVA profile where it initially decreased in the first two cycles followed by an increase in the subsequent ones (Figure 5.2.C) indicating the initial removal of high SUVA molecules (i.e., high MW) that declined over the subsequent cycles as the exchanges sites (mostly on the surface) became less available. This can be associated to the size exclusion of larger HA molecules by the resin pores and predominant surface adsorption/exchange of SRHA molecules with limited pore adsorption (i.e., penetration) (Zhang et al., 2014). It has been suggested that in addition to ion exchange, SRHA can also be removed via other mechanisms such as NH_3^+ - π bonding between resins and HA and or π - π interaction between dissolved SRHA molecules and adsorbed ones (Shuang et al., 2012; Zhang et al., 2014). The observations here corroborate with the isotherm data showing the lowest q_m (i.e., lowest monolayer coverage) for SRHA and also reports from other researchers showing lower removal for higher MW fractions

of NOM under ion exchange resins (Fu and Symons, 1990; Mergen et al., 2008; Zhang et al., 2014).

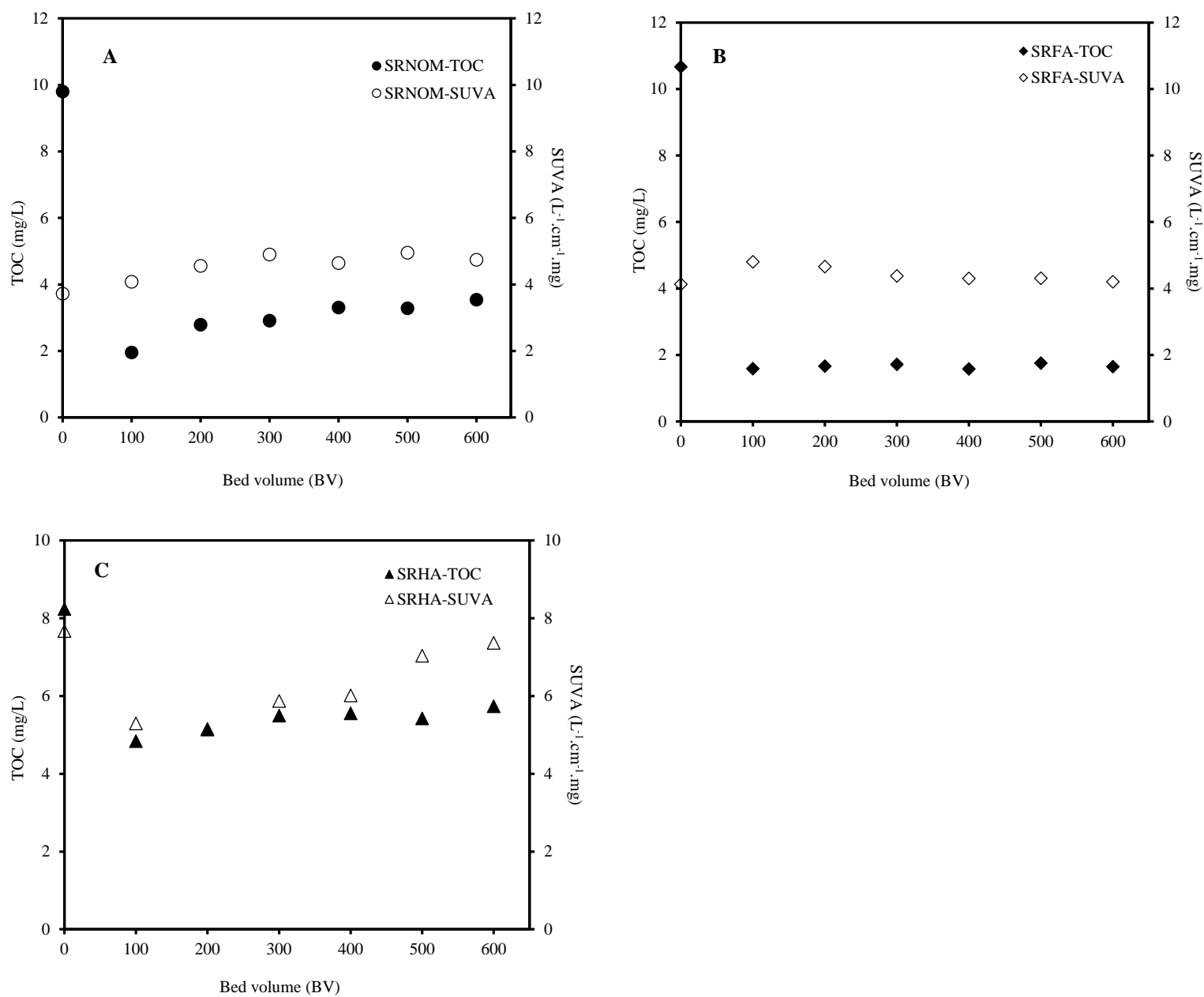


Figure 5.2, TOC and SUVA profiles for SRNOM (A), SRFA (B), and SRHA (C) over consecutive loading cycles

5.3.5 Effect of NOM properties on the removal kinetics

Under the resin dose of 10 mL/L, SRFA, SRNOM, and PLFA showed similar uptake rates, while SRHA removal rate was lower over the course of treatment (Figure 5.3.A). The extent of TOC removal after 2 hrs for SRNOM, SRFA, PLFA, and SRHA was 96, 97, 93, and 81 %, respectively, with the change in the liquid phase concentration being insignificant from 2 hr to 24 hr indicating the equilibrium between the resins and solution. Dissolved inorganic carbon in all water was reduced by 90 % (over 2 hrs) showing a strong removal of bicarbonate compounds. Given the prevalent ion exchange mechanism and also the high resin/ C_0 ratio applied (10 mL/L \approx 82-143 meq/meq), the removal deficiency for SRHA was attributed to the size exclusion of very large molecules by resin pores (Croué et al., 1999; Fu and Symons, 1990; Zhang et al., 2014). SUVA values for SRNOM, SRFA, and PLFA increased initially followed by a sharp drop after 30 min whereas SRHA profile declined slightly (\sim 10%) over the course of treatment (Figure 5.3.B). This observation showed that lower-SUVA value molecules (i.e., less hydrophobic and/or smaller molecules) are preferentially (initially) removed during ion exchange which is in agreement with previously shown isotherm data. However, this was not seen for SRHA since the removal of larger HA molecules is limited by their inability to access the interior resin pore channels. According to the study of Louie et al., (2015) 90 % of SRHA had a MW of 10-50 kDa while this number was 37 % and 21 % for SRNOM and PLFA, respectively. Same study estimated no fraction present in <10 kDa for SRHA while SRNOM, and PLFA had 61 % and 75 % of their respective MW < 10 kDa.

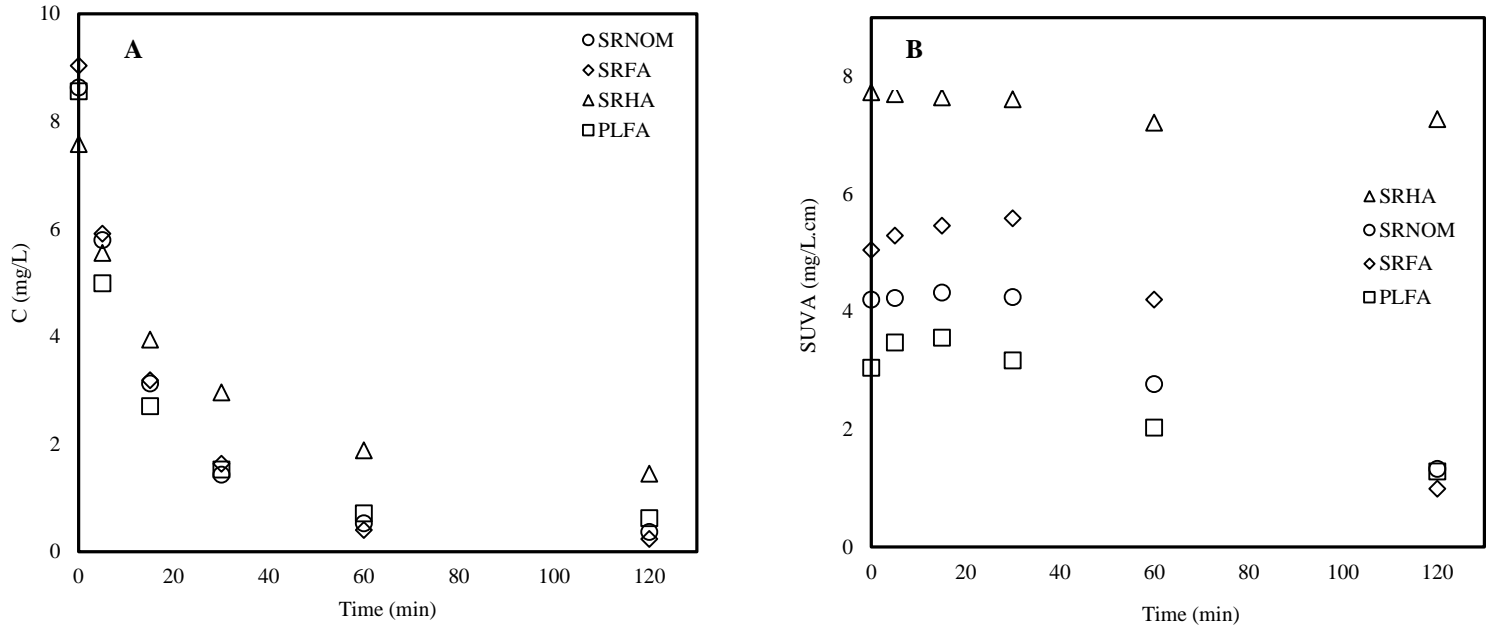


Figure 5.3, Concentration vs. time (A) and SUVA vs. time (B) for the organic isolates (resin dose: 10 mL/L)

5.3.6 Kinetic rates and diffusion coefficients estimation

Kinetic data from Figure 5.3.A were analyzed using a pseudo- first order, pseudo-second order, pore diffusion (PDM), and film diffusion (FDM) models as elaborated in Appendix B, B.2. Parameters were estimated by fitting the equations into the kinetic data using nonlinear optimization schemes. For a completely stirred batch system and single-size resin beads, the analytical solution for intraparticle diffusion (IDM, equations A.3, and A.4) is provided by Crank, (1979):

$$U(t) = \frac{C_0 - C_t}{C_0 - C_e} = \frac{q_t}{q_e} = 1 - \sum_{n=1}^{\infty} \frac{6\omega(\omega + 1)}{9 + 9\omega + \beta_n^2\omega^2} \times \exp\left(-\frac{D_{a,1}\beta_n^2 t}{R_p^2}\right) \quad (4)$$

ω is calculated from:

$$\frac{q_e}{VC_0} = \frac{1}{1 + \omega}$$

β_n are nonzero roots of the following equation:

$$\tan\beta_n = \frac{3\beta_n}{3 + \omega\beta_n^2}$$

where $U(t)$ is the fractional attainment of equilibrium and C_0 , C_t , and C_e are concentration of solute (i.e., TOC, mg/L) at $t = 0$, at time t , and at equilibrium, respectively, and R_p (cm) is the radius of resin beads assuming they are spherical (0.0375 cm), and $D_{a,1}$ is apparent diffusivity (cm^2/s). This set of interrelated equations was solved in Matlab using nonlinear unconstrained optimization schemes.

For the film-diffusion controlled removal, the following equation represents the changes in DOC concentration of solution (Helfferich, 1962):

$$U(t) = 1 - \exp\left(-\frac{3 \cdot D_f \cdot (\bar{V}\bar{C} + VC_0)}{R_p \cdot \delta \cdot \bar{C}V} t\right) \quad (5)$$

where \bar{C} is the resin exchange capacity (meq/L), δ is film thickness $\approx 10^{-3}$ cm (Harland, 1994; Helfferich, 1962), C_0 is initial solute concentration (meq/L), V is solution volume (L), \bar{V} is resin volume (L), and D_f is the film diffusion coefficient (cm^2/s). Unknown parameters $D_{a,1}$ and D_f are assumed to be constant and are estimated from the experimental data using nonlinear optimization schemes.

Pseudo 1st and 2nd order rate constants, k_1 and k_2 (and their pertinent adjusted R^2 values) are shown in Table 5.3 (and Table B.1). Based on the results obtained, assuming the pseudo-first order kinetics led to a higher adjusted R^2 and was a stronger fit for the experimental data. The highest k_1 and k_2 were estimated for PLFA, followed by SRNOM, and SRFA. SRHA showed a distinctively smaller k_1 and k_2 (almost half of the one for PLFA) suggesting the MW as an influential parameter on the rate of removal. It should be noted that all the curve fittings are based on the fractional attainment of equilibrium, i.e., $U(t)$, which is normalized for the non-

removable TOC fractions. Boyd et al., (1947) found that the pseudo first order equation can be used to explain both film diffusion and chemical reaction controlled under dilute solute concentrations (i.e., $CV \ll \bar{C}\bar{V}$). The relative concentrations of the isolates to the exchange sites available (i.e., $CV/\bar{C}\bar{V}$ ratio) in this work were between 1/82 and 1/143. Therefore, it was plausible to assume that *dilute condition* was valid for the experiments performed.

$D_{a,1}$ and D_f were estimated using equations 4 and 5 (with 95 % confidence) and the respective values and predicted $U(t)$ profiles for each organic isolate are demonstrated in Table 5.3, and Figure 5.4.A, and Figure 5.4.B. The curve fitted for D_f agreed well with the experimental data ($0.9748 < R^2 < 0.9973$), where the ineffectiveness of the fit for pore diffusion (equation 4) was evident ($0.6798 < R^2 < 0.9477$). The shortcoming of equation 4 could be attributed to: i) assuming D to be constant and independent of C , ii) dilute condition of the experiment ($0.007 < CV/\bar{C}\bar{V} < 0.012$), and iii) film diffusion acting parallel to pore diffusion. In this regard, individual $D_{a,1}$ values for each concentration were estimated using equation 4, and variations of $D_{a,1}$ vs. C during the treatment is demonstrated in Figure 5.4.C. $D_{a,1}$ values for SRNOM, SRFA, and PLFA changed considerably (~ 3 orders of magnitude) during 2 hrs of contact time where $D_{a,1}$ for SRHA only changed about an order of magnitude. These changes introduce a huge error into the optimization scheme used for fitting equation 4 into the experimental data. Under dilute condition assumption, the analytical solution for equations A.3 and A.4 will be (Helfferich, 1962):

$$U(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \times \exp\left(-\frac{D_{a,2}\pi^2 n^2 t}{R_p^2}\right) \quad (6)$$

$$\cong \text{Vermeulen's estimation} \left[1 - \exp\left(-\frac{D_{a,2} \cdot t \cdot \pi^2}{R_p^2}\right) \right]^{\frac{1}{2}}$$

$D_{a,2}$ was estimated by fitting equation 6 into the experimental data and the results are presented in Table 3 and Figure 5.4.D. The quality of the fit was greatly improved ($0.9853 < R^2 < 0.9985$) for the pore diffusion model under the dilute condition assumption highlighting the importance of resin/ions concentration ratio.

5.3.7 Determination of the rate-limiting step

The rate-controlling step was determined using the dimensionless Biot number which is the ratio of internal mass transfer (i.e., pore diffusion) to external mass transfer (i.e., film diffusion) resistances, and is defined as (Ko et al., 2001):

$$Bi = \frac{k_f \cdot R_p}{D_{p,e}} \quad (7)$$

where k_f is the external mass transfer coefficient ($k_f : D_f/\delta$) and $D_{p,e}$ is effective pore diffusion coefficient (see Appendix B, B.3). The $Bi \gg 1$ shows the pore diffusion to be the rate-controlling step where $Bi \ll 1$ indicates the film resistance as the rate limiting step (Chen et al., 2001; Ko et al., 2001). As demonstrated in Table 5.3 all Biot numbers were greater than 1, suggesting pore diffusion to be the rate-limiting step. The average R_p of 375 μm was assumed throughout all estimations; nonetheless, for the resins size range reported by the manufacturer ($R_p : 150 - 600 \mu\text{m}$) the Biot number for all waters will be still greater than 1. That is, the changes in Bi number would be between 40-160 % (for $R_p : 150 - 600 \mu\text{m}$) assuming other parameters remaining constant. Furthermore the values for film thickness (δ) can also vary

between 5×10^{-2} - 10^{-3} (cm) (Harland, 1994; Helfferich, 1962) and hence it can influence the estimated Bi numbers between 0-100 %, yet resulting in higher Bi numbers. In addition, it should be noted that the D_f and $D_{p,e}$ used in equation 7 to estimate Bi were estimated with 95 % confidence and Bi values estimated are only representative of the ratio of internal mass transfer resistance to external one. The rate-limiting step for the removal of organic compounds (under macroporous resins) is reported to be mainly controlled by intraparticle (i.e., pore) diffusion (Boyer et al., 2008a; Chen et al., 2002; Weaver and Carta, 1996; Wu and Gschwend, 1986); however, the effect of film diffusion can become significant at low solute concentrations i.e., high resin dosages (Boyd et al., 1947; Helfferich, 1962; Reichenberg, 1953). It should be noted that D_f is function of R_p and resin/solute concentration, therefore, smaller particles sizes and lower concentrations of solute can shift the rate limiting step from pore diffusion to film diffusion controlled. Free liquid diffusivity (D_l) values were calculated from equation A.5 and were compared with the values available in the literature (Table 5.3). As shown, very good agreement exists between the values obtained in this work and the ranges reported in the literature. Also, the estimated $D_{p,e}$ and D_l were in the same order and showed the highest value for PLFA and the lowest value for SRHA, suggesting the molecular weight of the organic isolates as an influential factor in diffusion coefficients. However, the effect of MW on D_l was limited to about an order of magnitude ($2E-5$ to $3E-6$) despite the large differences between the average MW of organic isolates used in this study (Table 5.1). According to the literature, D_l has an inverse correlation with MW (i.e., $D \propto 1/MW^\gamma$) with γ ranging between 0.333 and 0.5 (Wu and Gschwend, 1986; Sano and Yamamoto, 1993; Egeberg et al., 2002; Beckett et al., 1987; Fettig, 1999). Aside from the effect of MW, to explain the difference in removal rate one has to

also consider the effect of retardation factor (Appendix B, B.3) which combines the impact of resins properties (e.g., ϵ , and τ) and resin-solute affinity (K_D) as shown in Table B.2.

Table 5.3, Estimated rate, diffusion, and mass transfer coefficients (k_1 and k_2 : 1/s; k_f : cm/s ; D : cm²/s)

Source Water	k_1	k_2	$D_{a,1}$	$D_{a,2}$	D_f	$D_{p,e}$	k_f	Bi	$D_{l,model}$	$D_{l,Literature}$
SRNOM	0.081	0.044	6.88 E-10	1.02 E-7	1.69 E-6	2.99 E-6	1.69 E-3	21	8.97 E-6	* 4.11-5.23 E-6
SRFA	0.080	0.041	2.81 E-10	9.95 E-8	1.66 E-6	3.22 E-6	1.66 E-3	19	9.65 E-6	† 1.9-4.5 E-6
SRHA	0.050	0.031	3.69 E-9	5.68 E-8	1.04 E-6	1.00 E-6	1.04 E-3	39	3.00 E-6	‡ 1.1-5.84 E-6
PLFA	0.107	0.064	2.88 E-9	1.35 E-7	2.24 E-6	6.68 E-6	2.24 E-3	13	2.01 E-5	Not available

* Moon et al., 2006.

† Becket et al., 1987; Dixon and Larive, 1997; Morris et al., 1999; Lead et al., 2000a, 2000b; Moon et al., 2006.

‡ Becket et al., 1987; Moon et al., 2006; Morris et al., 1999; Lead et al., 2000a; Wang et al., 2001.

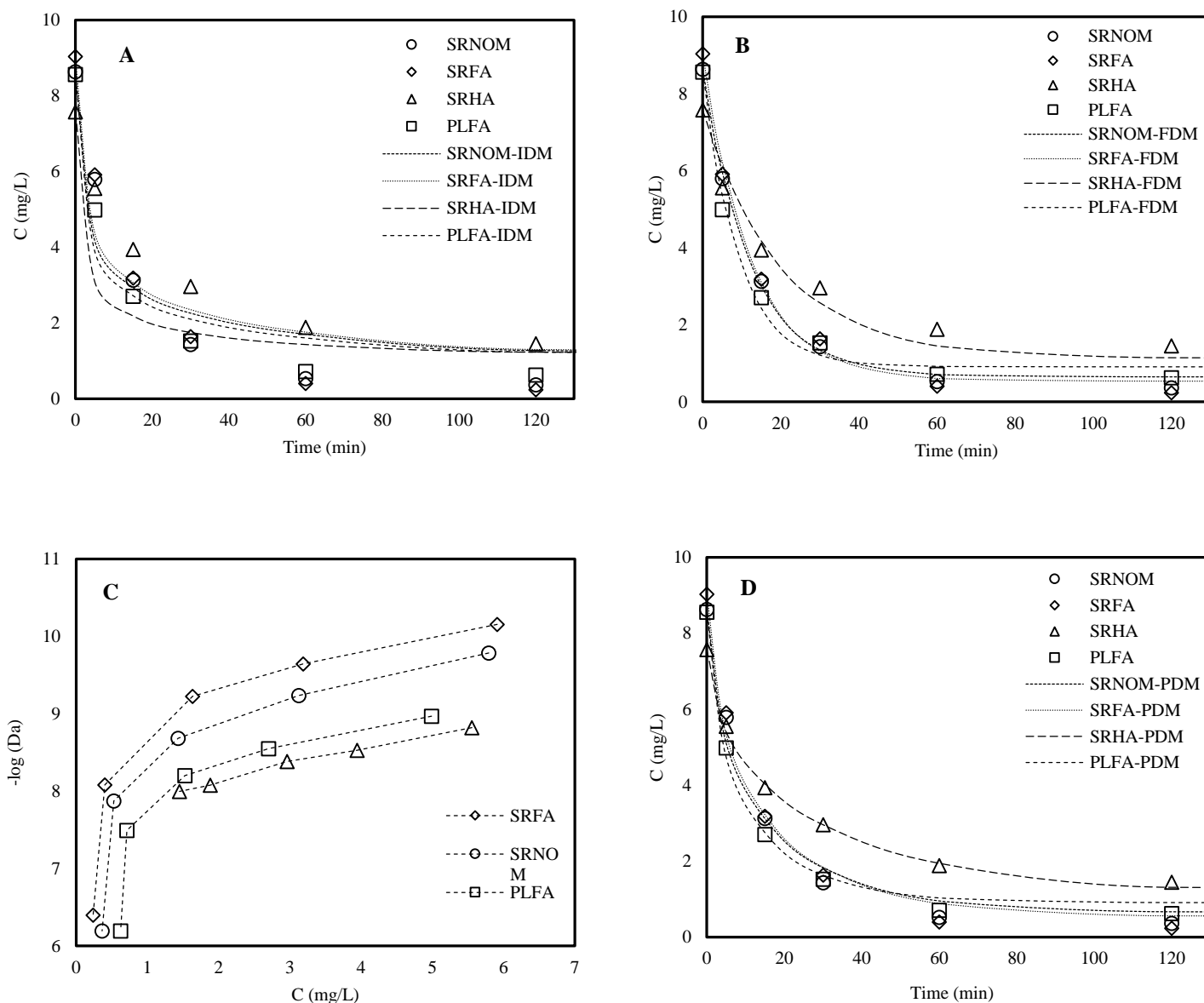


Figure 5.4, Kinetic data fitted with equation 4 (A), equation 5 (B), and equation 6 (D), change of $D_{a,1}$ vs. solution concentration over the treatment (C)

5.4 Conclusions

Extensive kinetic experiments were conducted on four standard organic matter isolates to understand the effect of NOM properties on the efficacy of IEX process for drinking water applications. Ion exchange was identified as the prevalent mechanism for the removal of organic

matter, and both the charge density and molecular weight of organic molecules were found to influence the removal efficacy with low charge density and high MW (i.e., size exclusion) adversely impacting the removal performance. The impact of MW became more pronounced during multiple consecutive batch treatments where the efficiency of removal declined considerably for larger MW organics (SRHA) compared to the smaller MW ones (SRFA). Analysis of the kinetic data suggested the pore diffusion to be the rate-limiting step for the uptake of TOC; however, process parameters such as resin properties and resin/ C_0 ratio can affect this condition. With respect to the removal rates, organic isolates with lower MW showed higher uptake rates compared to the larger HA molecules. Aside from molecular weight of the organic matter, resin properties (e.g., ϵ , τ , R_p) and the affinity of the resin for organic matter (e.g., K_D) were found to impact the apparent diffusivity D_a thereby the overall removal rate during the practice of IEX. The estimated free liquid diffusivities of the organic isolates (D_l) corroborated with the reported data in the literature indicating the validity of the models and assumptions used. This research is one of the very few studies looking at the fundamental kinetics of the removal of standard aquatic NOM isolates and could provide insights for future studies concerning the application of IEX for organic matter removal used in drinking water applications.

Supplementary Information

Supplementary information related to this chapter is provided in Appendix B.

Chapter 6: Impact of Background Water Matrix on the Kinetics of Ion Exchange Process

The effect of NOM properties on the removal behavior of organic matter and IEX efficacy was investigated in the previous chapter 5. To enhance our understanding, the impact of various water matrices (e.g., NOM source, nitrate) and process parameters on the IEX process efficiency for removing NOM from four natural drinking water sources was investigated in this chapter. Various treatment conditions (i.e., contact time and resin dose) were tested and detailed kinetic evaluations were conducted to determine the affinity and removal rate of organic matter as well as nitrate and sulfate, inorganic anions generally present in natural waters. Depending on the treatment condition applied, results obtained showed a range of removal, yet substantial, for organic matter (up to 80 %) and nitrate (up to 80 %), and a superior removal for sulfate (up to 98 %). Pseudo 1st order, pseudo 2nd order, pore diffusion, and film diffusion models were fitted through the experimental data and the highest removal rate was observed for nitrate followed by sulfate and NOM. Using the dimensionless Biot number, the rate-limiting step was suggested to be pore diffusion; however, Biot number was affected by the resin dose/solute concentrations ratio.

6.1 Introduction

The use of strongly basic anionic ion exchange resins (IEX) for the removal of naturally occurring organic matter (i.e., NOM) in surface waters has received significant attention in the past few years (Bolto et al., 2002b; Cornelissen et al., 2008; Croué et al., 1999). Previous studies have pointed out that resin characteristics (Bolto et al., 2002b; Boyer and Singer, 2008b; Cornelissen et al., 2008), NOM properties such as molecular weight (MW), polarity (i.e.,

hydrophobicity), and charge density could significantly influence the efficacy of NOM removal during the IEX treatment (Boyer et al., 2008b; Fu and Symons, 1990; Mergen et al., 2008). Also, some kinetic studies on the removal of organic molecules have reported pore diffusion as being the rate-limiting step (Bautista et al., 2000; Boyer et al., 2008a; Chen et al., 2002; Li and SenGupta, 2000; Weaver and Carta, 1996; Wu and Gschwend, 1986), even though film diffusion can become significant at low concentrations of solute i.e., high resin dosages (Boyd et al., 1947; Reichenberg, 1953; Weaver and Carta, 1996; Weber Jr and DiGiano, 1996). Despite these valuable findings, detailed kinetic evaluation of IEX process for natural water sources is rare in the literature.

Moreover, recent studies focusing on commercial practice of IEX for NOM removal have suggested the use of stirred (a.k.a. suspended) mode operation as opposed to the conventional packed bed columns (Boyer and Singer, 2006; Galjaard, 2010). Given the growing interest on commercialization of the stirred mode operation, it is necessary to understand the robustness and key factors influencing the kinetics (e.g., removal rate) and the performance of IEX process applied. Hence, the drive for this research was to assess the performance of IEX process at removing NOM as well as nitrate and sulfate, which are ubiquitous in natural water sources, under different water matrices and treatment conditions.

Various treatment conditions (i.e., contact time and resin dose) were tested and detailed kinetic evaluations were conducted to determine the affinity and removal rate of organic matter, nitrate and sulfate. Using the data obtained, various mathematical and physical models were employed to investigate the underlying removal mechanism and rate-limiting step. As a result, film diffusion coefficient (D_f), apparent diffusivity (D_a), and the effective pore diffusion coefficient ($D_{p,e}$) for the organic matter (as well as nitrate and sulfate) from different water

sources were estimated and the rate-limiting step was investigated using the Biot number. The significance of this research is in evaluating the performance of IEX process under different water matrices and scrutinizing the underlying kinetics for the removal of aquatic NOM as well as potentially competing anions e.g., NO_3^- and SO_4^{2-} . Findings presented here can provide the basis for future studies concerning the application of IEX for organic matter removal from surface waters sources.

6.2 Materials and Methods

6.2.1 Water sources

All waters used in this study (Table 6.1) were collected from different locations in southwestern Ontario, Canada, during winter-spring of 2013-2014. MAN, RLW, and WEW essentially serve as drinking water sources for treatment plant intakes. Waters collected were filtered (WhatmanTM Membrane Filter, 0.45 μm) within 24 hours (hrs), stored at 4°C in dark, and were used for experiments within less than a month. To assess the performance of the treatment process under different NO_3^- concentrations, FPW and RLW were amended with additional NO_3^- (as NaNO_3) to maximum 26 and 40 mg/L — NO_3^- , respectively.

Table 6.1, Characteristics of the surface waters used in this study

Water Source	¹DOC	¹SUVA	¹NO₃⁻	¹SO₄²⁻	¹DIC
Fanshaw Pond — London, (FPW)	6.4	1.15	1	6	² NA
Ruhl Lake — Hanover, (RLW)	3.9	3.2	15	17	24.4
Grand River — Mannheim, (MAN)	5.4	2.9	20	34	70
Lake Erie — West Elgin, (WEW)	2.1	1	0.8	19	69.4

¹ DOC, DIC, NO_3^- , SO_4^{2-} : mg/L, SUVA: $\text{UV}_{254}/\text{TOC}$: $\text{L.mg}^{-1}.\text{cm}^{-1}$

² Not measured

6.2.2 Kinetic experiments

Using a Jar test apparatus (Phipps & Bird 950), resin amounts from 2.5 – 15 mL/L (wet resin—mL/water—L) were mixed with waters for various time intervals from 5 minutes (min) to 24 hrs. For the adsorption isotherms, various amounts of dried resins (10 to 1000 mg/L) were carefully weighed and mixed with waters for 24 hrs (i.e., equilibrium). After mixing, resins were separated using a pre-rinsed fast coarse filter (Whatman™ 113, 30µm) and samples underwent subsequent water quality analyses.

6.3 Results and Discussion

6.3.1 Effect of IEX treatment on water quality parameters

The impact of various resin doses and treatment times on DOC, sulfate, nitrate, and UV₂₅₄ is summarized in Table 6.2. Under the practical range of 10 mL/L and 30 min contact time (Galjaard et al., 2011; Slunjski et al., 2000), 75-81% of UV₂₅₄, 40-64 % of DOC, 51-72 % of NO₃⁻, and 89-95 % of SO₄²⁻ were removed. Overall, a meaningful difference in terms of efficacy of removal was observed between low (i.e., 2.5, 5 mL/L) and high (i.e., 10, 15 mL/L) resin dosages. That said, increasing the resin dose from 10 to 15 mL/L slightly improved (2-11%) the removal efficacy, and extended contact time (> 45 min) was found to improve the efficiency only by 3-16%. It should be noted that the initial levels of nitrate in raw FPW and WEW were very low (~ 1 ppm) and hence, the results are considerably subject to detection limit range error. FPW and RLW with additional 25 mg/L of NO₃⁻ showed between 63-90 % and 35-80 % removal for NO₃⁻, respectively, under the treatment conditions applied. Also, increasing the nitrate level in FPW and RLW did not show any tangible impact on the efficacy of IEX at DOC removal.

Table 6.2, Summary of the changes in water quality parameters

Resin Dose	Contact Time	ΔUV_{254} %	ΔDOC %	ΔNO_3^- %	ΔSO_4^{2-} %
2.5 mL/L	30 min	32-40	17-32	31-42	54-64
	24 hrs	82-91	41-74	30-48	90-97
5 mL/L	30 min	55-59	28-48	44-58	57-75
	24 hrs	79-93	48-77	46-48	94-98
10 mL/L	30 min	75-81	40-64	51-72	89-95
	24 hrs	82-94	52-80	52-69	94-98
15 mL/L	30 min	84-92	46-75	52-80	93-97
	24 hrs	86-94	56-82	55-78	92-98

6.3.2 Effect of water source on the removal behavior

The modified forms of Freundlich and Langmuir isotherms (equations 1-3) were fitted through the experimental DOC data (Figure 6.1.A, Figure 6.1.B) and the unknown parameters for both equations were estimated using nonlinear regression schemes and are demonstrated in Table 6.3.

$$q_e = \frac{C_e - C_0}{M} \quad (1)$$

Modified Freundlich $q = K_F(C_e - C_0\beta)^n \quad (2)$

Modified Langmuir $q = \frac{q_m K_L (C_e - C_0\beta)}{1 + K_L (C_e - C_0\beta)} \quad (3)$

where C_0 : initial DOC concentration (mg/L), C_e : concentration at equilibrium (mg/L), M : resin mass (g), q : solid phase concentration (resins loading - mg/g), q_e : resin loading at equilibrium (mg/g), q_m : maximum sorption capacity (mg/g), K_F : Freundlich constant (L^n/g^n), K_L : Langmuir equilibrium constant (L/g), n : surrogate for affinity, and β : non-removable fraction of DOC (%).

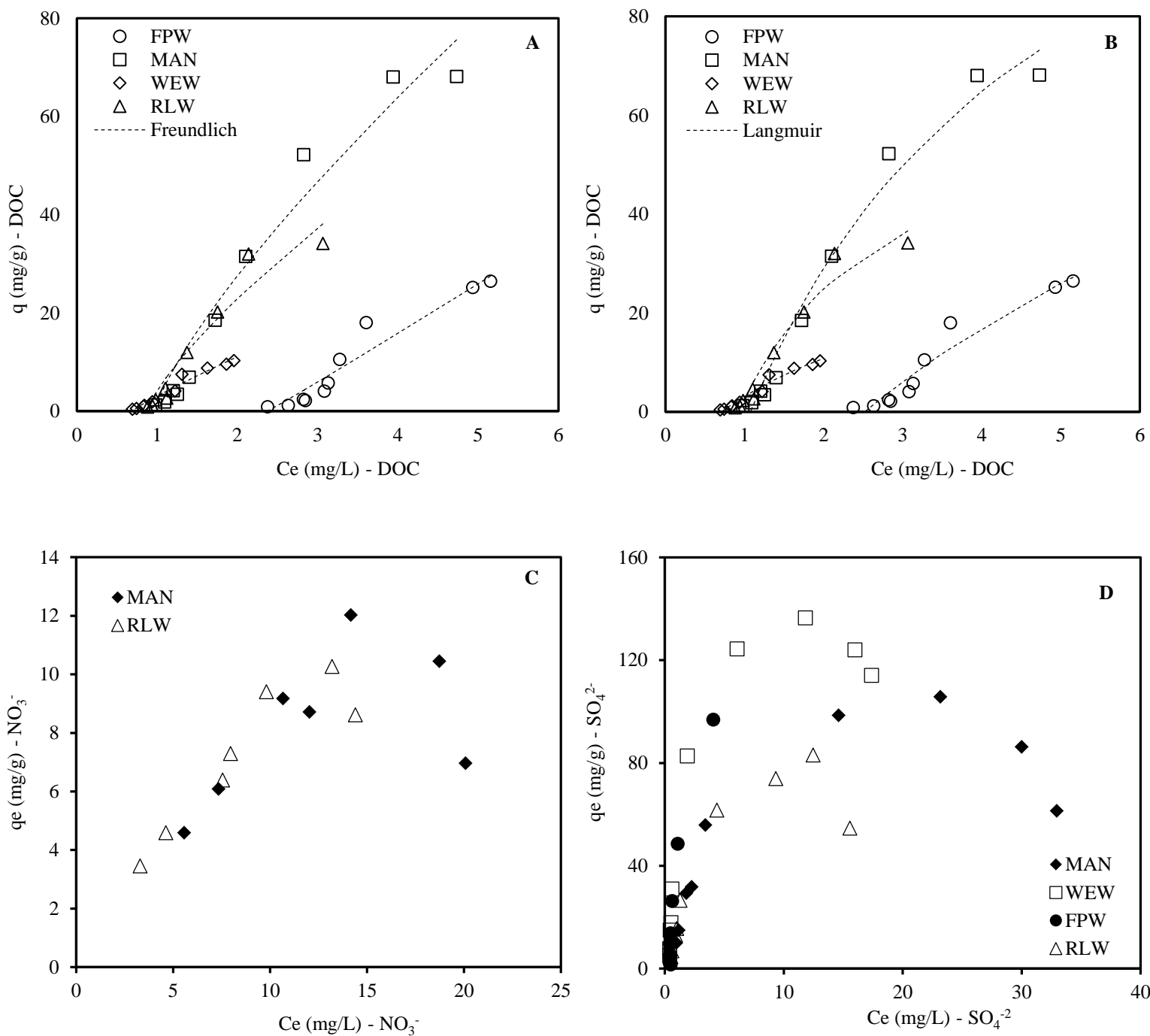


Figure 6.1, Adsorption isotherms for DOC, NO_3^- , SO_4^{2-} in natural waters

Although the adjusted R^2 obtained for the Langmuir equation suggested a slightly better fit but the p-values obtained for q_m and K_L for FPW, WEW and RLW showed the inappropriateness of using Langmuir isotherm for the experimental data (see Table 6.3).

Nonetheless, the use of modified Freundlich equation to study the adsorption isotherms was found to be plausible. K_F is correlated to the adsorption capacity and higher K_F values were observed for the waters with higher SUVA values (i.e., MAN, RLW) indicating higher uptake of more hydrophobic organic matters. The n value is a measure of adsorption strength, that is, the lower the n value the stronger the adsorption. Statistical analysis revealed no significant difference among the estimated n values at 95% confidence.

Figure 6.1.C and Figure 6.1.D also represent the isotherms graphs for NO_3^- and SO_4^{2-} in natural waters in the presence of NOM (see Appendix C, C.1). As can be seen, an irregularity in the isotherm patterns is observed at lower resin dosages (i.e., higher C_e) which can be correlated to the competition among ions for adsorption on the resins. Also, given the higher uptake of DOC at lower resin dosages compared to SO_4^{2-} and NO_3^- , it is postulated that entropy assisted sorption is taking place under this condition (Tan and Kilduff, 2007). Interestingly, a similarity in the isotherm profiles (for NO_3^- and SO_4^{2-}) exists between FPW and WEW as well as between MAN and RLW. This can be attributed to their initial SUVA values (Table 6.1) showing close values between FPW and WEW also for MAN and RLW, indicating similar NOM properties between these pairs.

The estimated non-removable fraction (β) using the modified Freundlich isotherm was compared with the experimental data and an average relative difference of 3.7 % was observed. The range of non-removable DOC fraction varied between 19-43 % of the total DOC which corresponds to 0.7- 2.8 mg/L of dissolved organic carbon (Figure C.1). Biopolymers, neutrals and to some extent building block fractions of NOM which have low-zero UV_{254} absorbing properties and are reportedly not removed via IEX (Cornelissen et al., 2010; Huber et al., 2011). Given the relatively low SUVA value (i.e., high fractions of low UV_{254} absorbing compounds)

for the waters tested it is less likely that size exclusion of large organics is playing a role (Boyer et al., 2008b; Mergen et al., 2008; Zhang et al., 2014). As demonstrated in Figure C.1, SUVA was decreased between 30-70 % at low resin dosages < 0.2 g/L and remained almost constant ($< 10\%$ variation) with further increase in the resins dose i.e., exchange sites. The reason for this observation (along with the high β values) is attributed to presence of the hydrophilic non-ionic fractions.

Table 6.3, Estimated parameters for modified Langmuir and Freundlich equations

modified Langmuir					
Water Source	q _m	K _L	β (%)	Adjusted R ²	
FPW	127.16 ± 153.55 (<i>p</i> = 0.435)	0.103 ± 0.16 (<i>p</i> = 0.531)	0.46 ± 0.02	0.9211	
MAN	152.33 ± 37.60	0.253 ± 0.11	0.20 ± 0.01	0.9740	
RLW	71.60 ± 23.21	0.488 ± 0.27 (<i>p</i> = 0.125)	0.24 ± 0.01	0.9479	
WEW	37.34 ± 26.74 (<i>p</i> = 0.205)	0.314 ± 0.30 (<i>p</i> = 335)	0.34 ± 0.02	0.9584	
modified Freundlich					
Water source	K _F	n	β (%)	β _{Experimental}	Adjusted R ²
FPW	9.62 ± 6.60 (<i>p</i> = 0.188)	1.03 ± 0.50 (<i>p</i> = 0.078)	0.44 ± 0.10	0.43	0.9113
MAN	27.02 ± 7.11	0.78 ± 0.19	0.18 ± 0.04	0.34	0.9461
RLW	20.91 ± 1.94	0.77 ± 0.13	0.23 ± 0.01	0.26	0.9129
WEW	8.70 ± 0.57	0.89 ± 0.15	0.34 ± 0.02	0.19	0.9520

p-values not shown are smaller < 0.05 at 95% confidence level

6.3.3 Effect of NOM properties on the removal kinetics

Further to the observations above, the kinetics of removal for DOC, SO_4^{2-} and NO_3^- were investigated using pseudo 1st (and 2nd order rate for DOC) equations (see Appendix C, C.2) and

the constants k_1 and k_2 at each resins dose are depicted in Figure 6.2. The relative standard error associated with k value estimates varied between 3-10 % with $0.97 < R^2 < 0.99$ and $p < 0.0001$. Based on the results obtained, assuming the pseudo-first order kinetics led to a higher adjusted R^2 and was a stronger fit for the experimental data. k_1 values obtained for DOC, NO_3^- , and SO_4^{2-} were similar at 2.5 and 5 mL/L resin dose and started to show difference at higher resin dose where higher exchange site were available. Overall, the highest k_1 value at each resin dose was estimated for NO_3^- , followed by SO_4^{2-} , and DOC. Previous studies (and also the following data) have demonstrated the pore diffusion to be the rate limiting step during the practice of IEX; hence greater uptake rates for nitrate was attributed to the effect of small size of NO_3^- compared to SO_4^{2-} and DOC. The case of FPW + 25 mg/L NO_3^- that showed lower uptake rate of NO_3^- (compared to MAN, and RLW) is likely influenced by the nature of its NOM competing with nitrate. The relational change of k_1 versus resin dose for all four waters was between 0.6-1 for DOC, 0.2-0.7 for NO_3^- , and 0.7-1 for SO_4^{2-} demonstrating the lowest effect of resin amount on NO_3^- and its highest effect on SO_4^{2-} . This indicates the effect of increasing the resins dose on the kinetics of DOC removal (and NO_3^- and SO_4^{2-}) and further suggests the appropriateness of using pseudo 1st order kinetics for the removal of ions via IEX.

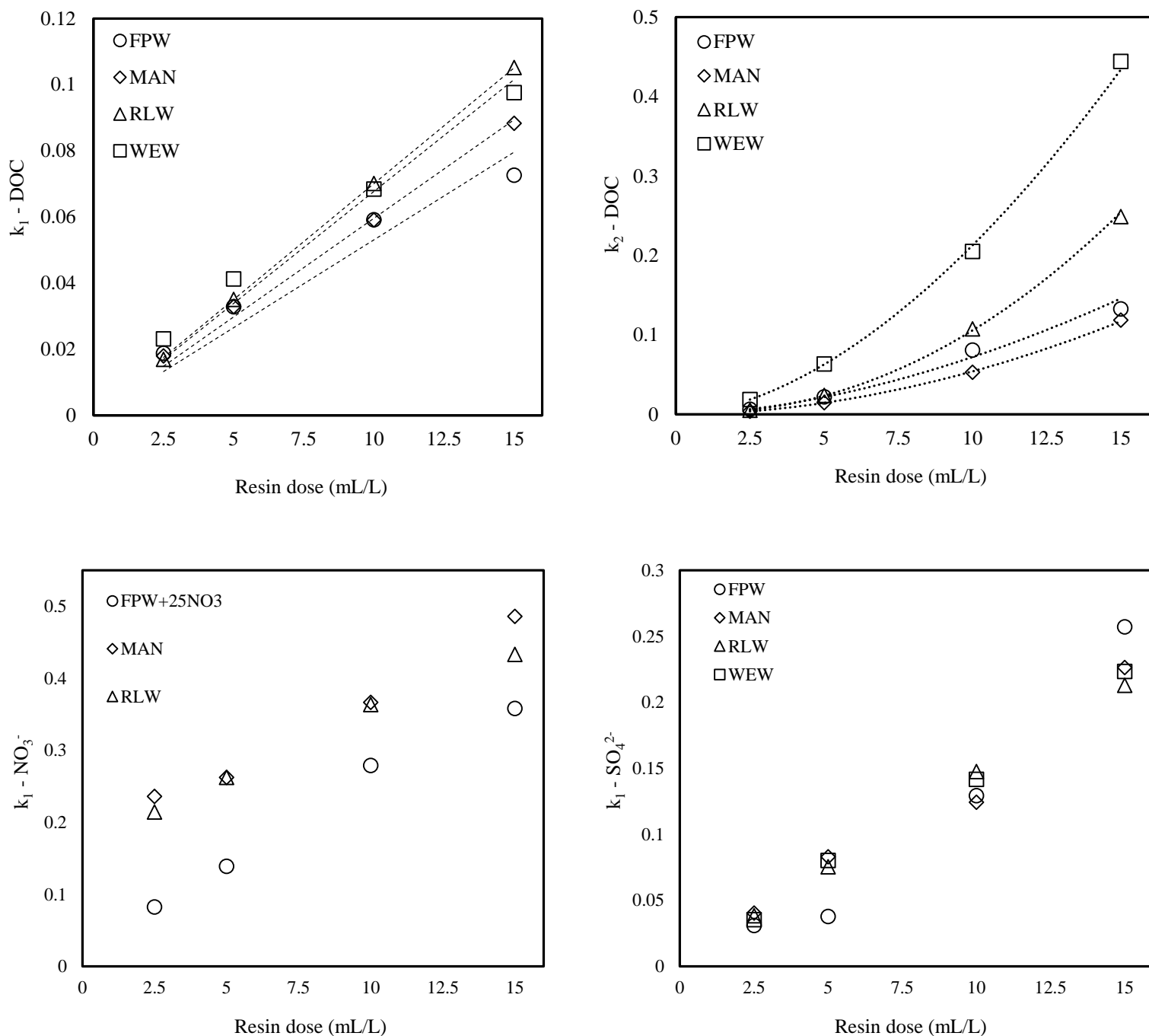


Figure 6.2, Change of k_1 and k_2 for DOC, NO_3^- , and SO_4^{2-} with the resin dose

The impact of additional NO_3^- on DOC removal rate values is demonstrated in Figure 6.3. Addition of 25 mg/L of NO_3^- led to slightly lower k values especially at higher resin dosages i.e., 15 mL/L (12-17 %). The difference in k_2 values were more significant (55-63 %) because of the

2nd order equation used. It should be noted that all of the curve fittings are based on the fractional attainment of equilibrium, i.e., $U(t)$, which is normalized for the non-removable DOC fractions (β). (Boyd et al., 1947) found that the pseudo first order equation can be used to explain both film diffusion and chemical reaction controlled under dilute solute concentrations (or high resin concentrations). Therefore, it was plausible to assume that *dilute condition* was valid for the experiments performed.

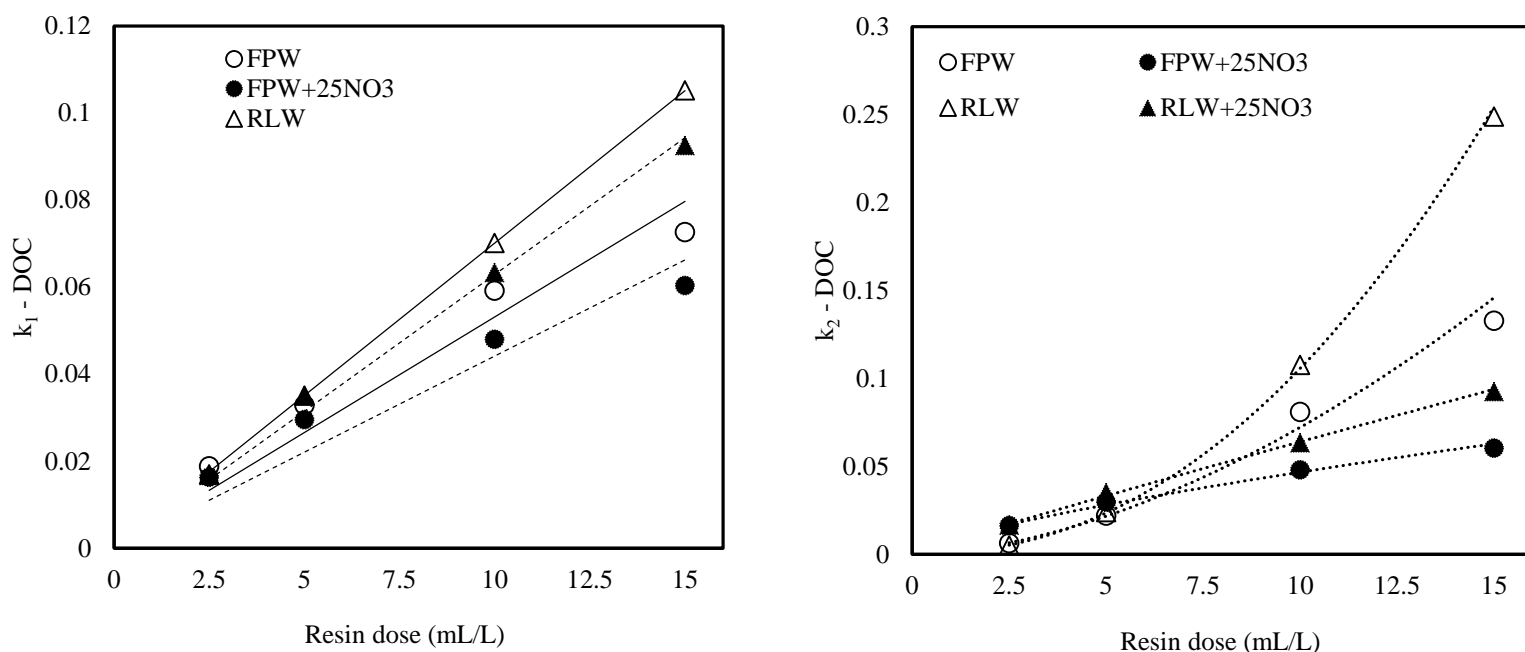


Figure 6.3, Effect of additional NO₃⁻ on k_1 , and k_2 values for DOC

6.3.4 Kinetic rates and diffusion coefficients estimation

Kinetic data were also analyzed using pore diffusion (PDM), and film diffusion (FDM) models as elaborated elsewhere (See Chapter 5). Under dilute condition assumption the analytical solution for PDM for a completely stirred batch system and single size resins will be (Crank, 1979; Helfferich, 1962) :

$$U(t) = \frac{C_t - C_e}{C_0 - C_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \times \exp\left(-\frac{D_a \pi^2 n^2 t}{R_p^2}\right) \quad (4)$$

$$\cong \text{Vermeulen's estimation} \left[1 - \exp\left(-\frac{D_a \cdot t \cdot \pi^2}{R_p^2}\right) \right]^{\frac{1}{2}}$$

where $U(t)$ is the fractional attainment of equilibrium and C_0 , C_t , and C_e are concentration of solute (e.g., DOC - mg/L) at $t = 0$, at time t , and at equilibrium, respectively, and R_p (cm) is the radius of resin beads assuming they are spherical (0.0375 cm), and D_a is apparent diffusivity of the solute molecules (cm^2/s). This form of the equation was used in this study because of dilution conditions discussed above and also based on the previous study presented elsewhere (See Chapter 5).

Also, the following equation represents FDM model to predict the changes in DOC (also NO_3^- , and SO_4^{2-}) concentration of the solution (Helfferich, 1962):

$$U(t) = 1 - \exp\left(-\frac{3 \cdot D_f \cdot (\bar{V}\bar{C} + V C_0)}{R_p \cdot \delta \cdot \bar{C} V} t\right) \quad (5)$$

Where \bar{C} is the resin exchange capacity (mg/L), δ is film thickness $\approx 10^{-3}$ cm (Harland, 1994; Helfferich, 1962), C_0 is initial solute concentration (mg/L), V is solution volume (L), \bar{V} is resin volume (L), and D_f is the film diffusion coefficient of the solute molecules (cm^2/s).

Unknown parameters D_a and D_f for DOC, NO_3^- , and SO_4^{2-} were assumed to be constant and were estimated from the experimental data using nonlinear optimization schemes (Table C.2 and Table C.3). Also, the predicted DOC profiles for all four waters under these models are shown in Figure 6.4 and Figure 6.5. The predicted curves using these models agreed well with the experimental data with the adjusted R^2 ranging from 0.96-0.99 for PDM and 0.97-0.99 for FDM. With the increase in the resin dose, D_f was decreased (0-30 %), while D_a showed an

opposite trend increasing with the increase in resin dose (~ 5-7 times). Overall, the lowest diffusion coefficients (D_a , D_f) were estimated for DOC, followed by SO_4^{2-} and NO_3^- suggesting the effect of molecular size on the rate of removal. According to the literature, D is proportional to the inverse of the MW (i.e., $D \propto 1/\text{MW}^\gamma$) with γ varying between 0.333 and 0.5 (Wu and Gschwend, 1986; Sano and Yamamoto, 1993; Egeberg et al., 2002; Beckett et al., 1987; Fettig, 1999). In addition to the effect of MW, the combined impacts of resins properties (e.g., ϵ , and τ) and resin-solute affinity (K_D), as reflected in the retardation factor (see Appendix C, C.3, Table C.1), have to be taken into account to explain the differences in the overall uptake rate.

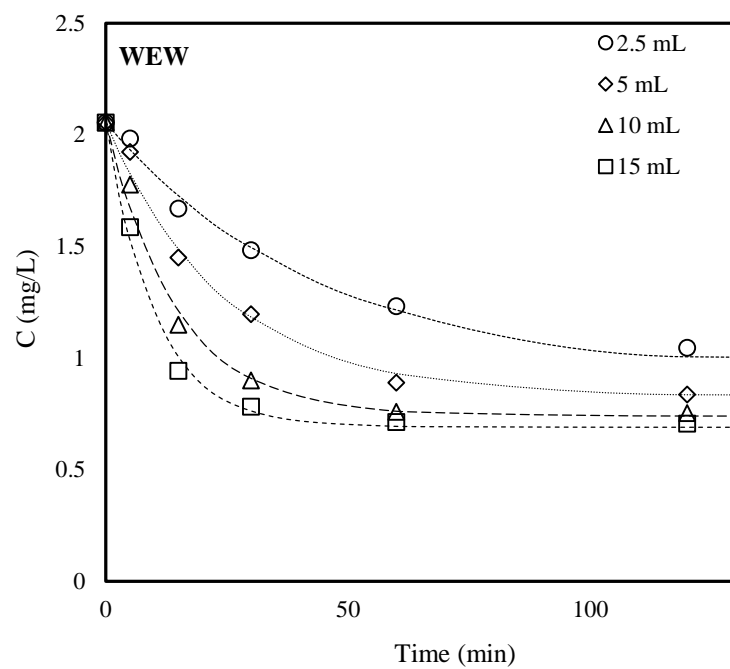
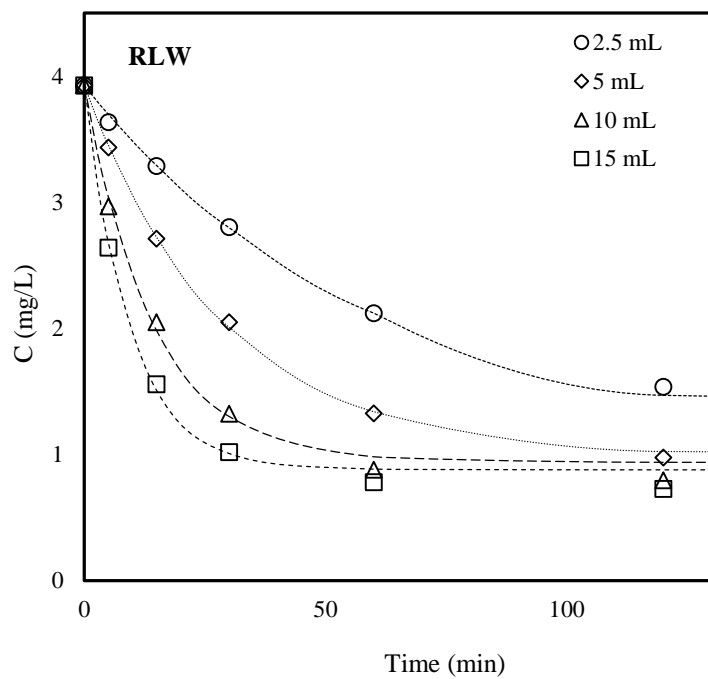
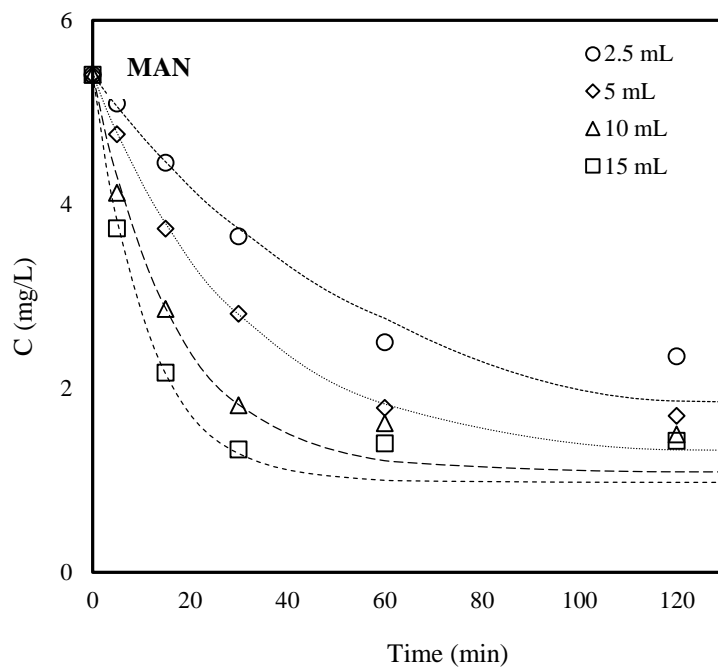
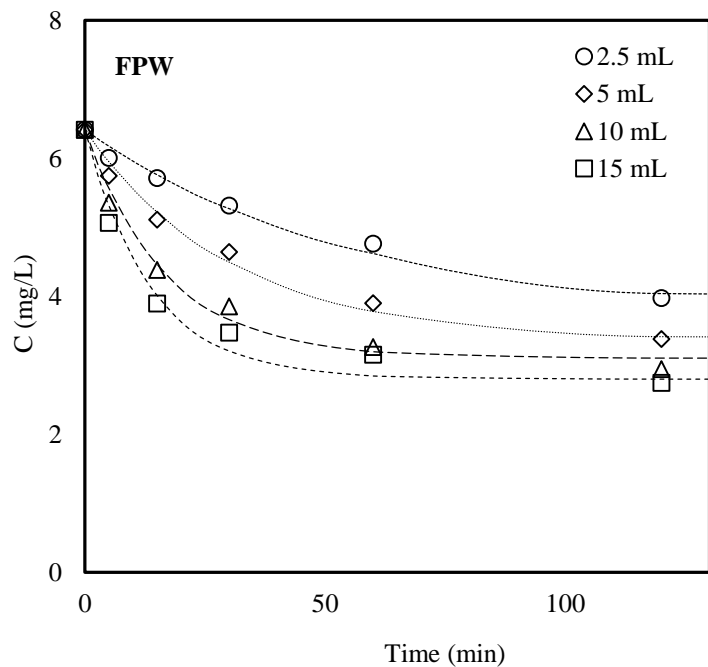


Figure 6.4, Kinetic data fitted with film diffusion model (FDM), dashed lines are predicted data

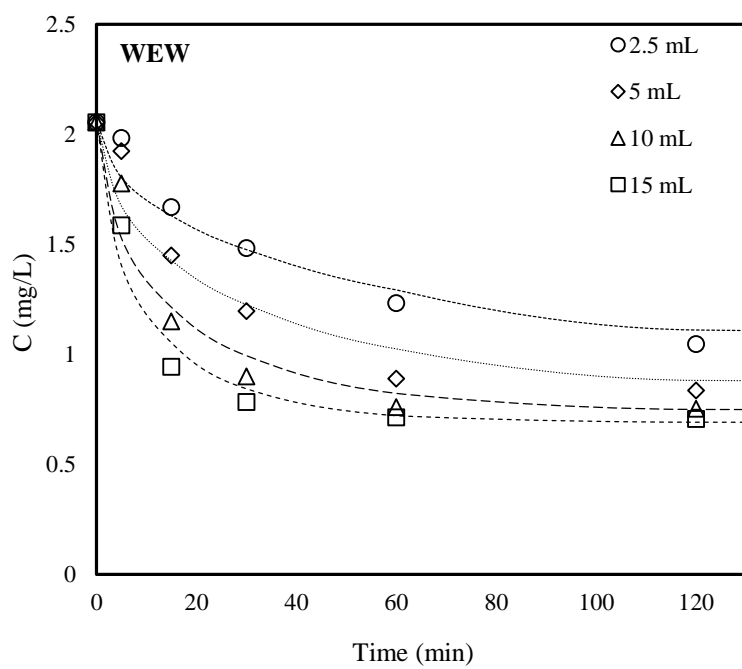
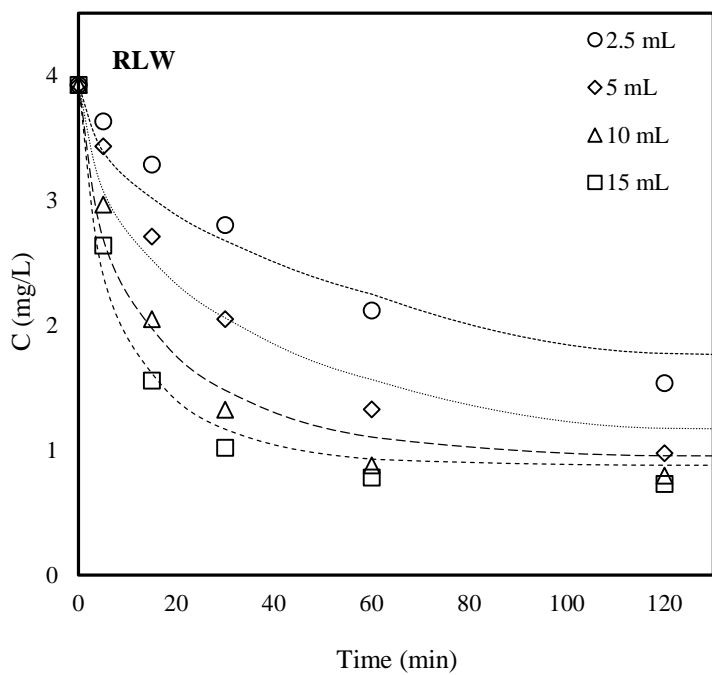
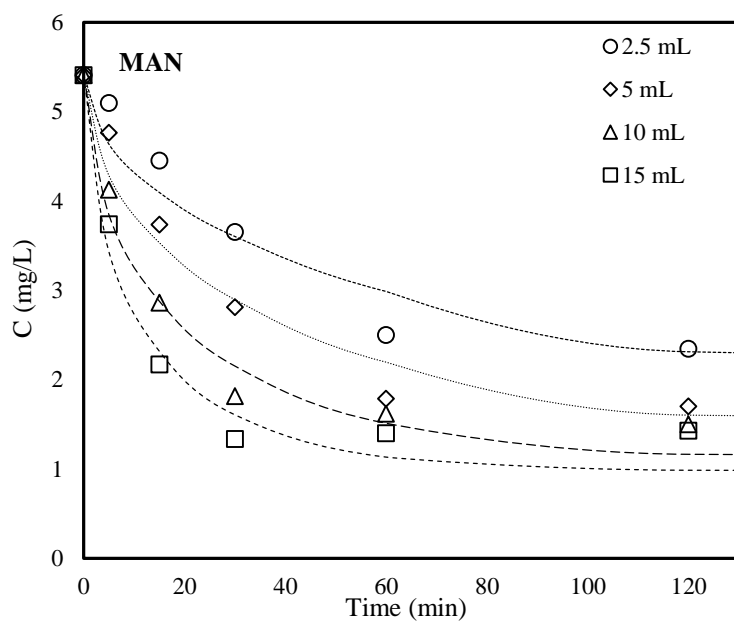
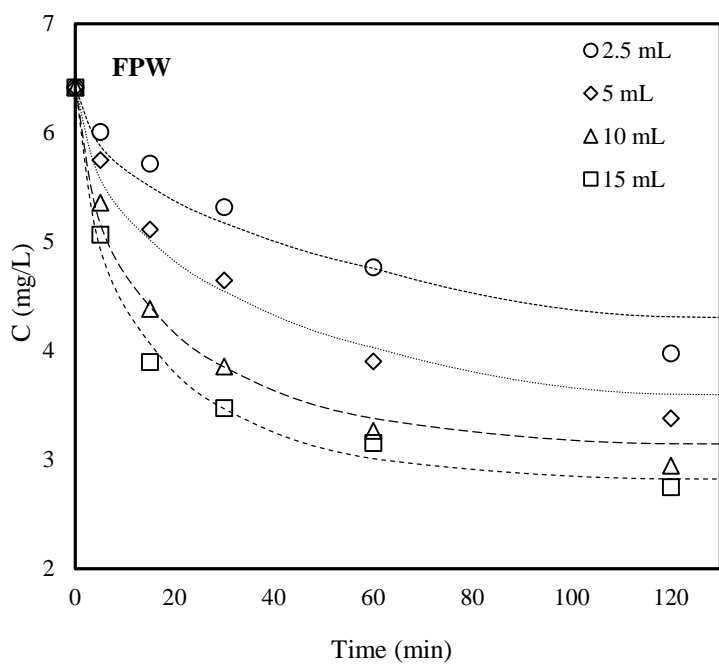


Figure 6.5, Kinetic data fitted with pore diffusion model (PDM), dashed lines are predicted data

6.3.5 Determination of the rate-limiting step

By using the dimensionless Biot number representing the ratio of internal mass transfer (i.e., pore diffusion) to external mass transfer (i.e., film diffusion) impedances, the rate-controlling step was determined using the following equation (Ko et al., 2001):

$$Bi = \frac{k_f \cdot R_p}{D_{p,e}} \quad (7)$$

where k_f is the external mass transfer coefficient ($k_f : D_f/\delta$) and $D_{p,e}$ is effective pore diffusion coefficient (Table C.4). The $Bi \ll 1$ indicates film diffusion as the rate-limiting step where $Bi \gg 1$ shows pore diffusion to be the rate limiting step (Chen et al., 2001; Ko et al., 2001). As demonstrated in Table 6.4, all Biot numbers (for DOC) were greater than 1, indicating that pore diffusion was indeed the rate-limiting step. Similar calculations were carried out for nitrate and sulfate and results are presented in Table C.5. The adsorption isotherms for both NO_3^- and SO_4^{2-} for the resin dosage range of 2.5 mL/L – 15 mL/L were linear and K_D (as well R^2) values are presented in Table C.5. Biot numbers calculated for both anions were greater than 1, also indicating pore diffusion to be the rate limiting step during their removal. Resin beads were assumed to be spherical with an average radius (R_p) of 375 μm ; nonetheless, for the resin size range reported by the manufacturer ($R_p : 150 - 600 \mu\text{m}$) the estimated Biot number for all waters was still greater than 1. The impact of resin dose on the rate-limiting step was evident when with increasing the resin dose the estimated Biot number decreased indicating a shift in the rate limiting step. Under the application of macroporous resins, the rate-limiting step during the removal of organic compounds has been reported to be controlled by pore diffusion (Boyer et al., 2008a; Chen et al., 2002; Weaver and Carta, 1996; Wu and Gschwend, 1986); however, the effect of film diffusion can become significant at low concentrations of solute (Boyd et al., 1947;

Helfferich, 1962; Reichenberg, 1953). It should be noted that D_f is function of R_p and resin/solute concentration (Helfferich, 1962). Therefore, smaller particles sizes and lower solute/resin ratios can shift the rate limiting step from pore diffusion toward film diffusion controlled. In addition, it should be pointed out that the D_f and $D_{p,e}$ used in equation 7 to estimate Bi were estimated with 95 % confidence and Bi values estimated are only representative of the ratio of internal mass transfer resistance to external one

Table 6.4, Biot number for DOC removal under various resin doses and source waters

Bi				
Resin Dose (mL/L)	FPW	MAN	RLW	WEW
2.5	225	124	145	266
5	105	56	62	122
10	48	27	29	58
15	33	17	19	38

6.4 Conclusions

Removal of dissolved organic carbon as well as NO_3^- and SO_4^{2-} from four different natural water sources using IEX process was investigated. Different resin doses and contact times were studied to gauge the performance of the treatment process applied. Overall, resin doses of 10-15 mL/L and 30-45 min of contact time were found to be sufficient to remove up to 80% of the DOC, and NO_3^- and up to 98 % from initial SO_4^{2-} . Nonetheless, a range of 19 % to 43 % of DOC corresponding to 0.7-2.8 mg/L was not removed even under high resin dosages and extended treatment times. Despite its lower uptake, the fastest removal rate was observed for NO_3^- followed by SO_4^{2-} and DOC indicating the effect of molecular size on diffusion coefficients

thereby removal rate. Utilization of pseudo 1st order kinetic model, film diffusion, and pore diffusion models were found to be plausible to predict the experimental data very well ($R^2 > 0.96$). That said, by utilizing the Biot number concept, pore diffusion seemed to be the rate-limiting step for the uptake of DOC; however, process parameters such as resin properties and dosage can influence this condition. This research is one of the very few studies looking at the fundamental kinetics and factors that could influence the removal of NOM and inorganic anions from natural water sources and its approach could be considered for future studies concerning the application of IEX for organic matter removal from drinking water sources. Overall, findings of this study suggest the applicability of IEX process as a robust treatment process for drinking water applications by laying down a quantitative approach to evaluate the kinetics of this process under various treatment conditions.

Supplementary Information

Supplementary information related to this chapter is provided in Appendix C.

Chapter 7: Impact of Anionic Ion Exchange Resins on NOM Fractions: Effect on N-DBPs and C-DBPs Precursors

Results presented so far have demonstrated the impact of NOM properties and background water matrix on the efficiency of IEX process for organic matter removal. Moreover, optimum ranges for process parameters (i.e., resin dose and contact time) were evaluated and the use of consecutive multiple loadings was found to be beneficial in mimicking commercial applications. Using the findings from previous chapters 4 to 6, the next stage of this research was to gauge the impact of IEX resins on NOM fractions and subsequent water quality parameters such as disinfection by-product formation potential, biological stability, and HO^\bullet scavenging. The following presents the formation potential of carbonaceous and nitrogenous disinfection by-products (C-DBPs, N-DBPs) after ion exchange treatment (IEX) of three different water types in multiple consecutive loading cycles. Liquid chromatography with organic carbon detector (LC-OCD) was employed to gauge the impact of IEX on different NOM fractions and data obtained were used to correlate these changes to DBPs Formation Potential (FP) under chlorination. Humic (-like) substances fractions of NOM were mainly targeted by ion exchange resins (40-67 % removal), whereas hydrophilic, non-ionic fractions such as neutrals and building blocks were poorly removed during the treatment (12-33 % removal). Application of ion exchange resins removed 13-20 % of total carbonaceous DBPs FP and 3-50% of total nitrogenous DBPs FP. Effect of the inorganic nitrogen (i.e., Nitrate) presence on N-DBPs FP was insignificant while the presence of dissolved organic nitrogen (DON) was found to be a key parameter affecting the formation of N-DBPs. DON especially the portion affiliated with humic substances fraction, was reduced effectively (~ 77 %) as a result of IEX treatment.

7.1 Introduction

NOM is a known precursor for disinfection by-products (DBPs) formation in drinking water sources (Singer, 1994). Recently, higher toxicity of nitrogenous DBPs (N-DBPs) compared to carbonaceous-DBPs (C-DBPs) and also the increased use of wastewater influenced water sources for drinking water production have led to more awareness and monitoring of N-DBPs in drinking water (Muellner et al., 2007; Plewa et al., 2004; Shah and Mitch, 2012). Dissolved organic nitrogen (DON) comprising 0.5 – 10% of NOM, could be a source for N-DBPs formation when disinfection and/or oxidation processes are employed (Karanfil et al., 2008; W. Lee et al., 2007; Westerhoff and Mash, 2002). High organic nitrogen content during chlorination/chloramination could lead to higher disinfectant demand, production of haloacetic acids (HAAs) and trihalomethanes (THMs), and more importantly formation of halogenated (i.e., halonitromethanes (HNMs), haloacetonitriles (HANs, cyanogen halides), haloacetamides (HAcAms)), and non-halogenated N-DBPs (i.e., nitrosamines) (Bond et al., 2012, 2011b; Dotson and Westerhoff, 2009; Krasner et al., 2012; W. Lee et al., 2007).

In this respect, the use of strongly basic anionic ion exchange (IEX) resins as an effective tool for the removal of NOM, thereby controlling DBPs formation, has received significant attention (Boyer and Singer, 2006; Fearing et al., 2004; Martijn et al., 2010; Singer et al., 2007). Despite the advantages offered by IEX in controlling DBPs formation potential, some studies have documented N-DBPs and or N-DBPs precursors (e.g., alkylamines) formation in waters treated with strongly basic anion exchange resins, with the extent of formation being dependent upon the water source (Flowers and Singer, 2013; Gan et al., 2013a; Kemper et al., 2009; Kimoto et al., 1980; Najm and Trussell, 2001). For instance, NDMA release from anionic resins was reported as a result of soaking (4 hrs) under distilled water (Najm and Trussell, 2001).

Flowers and Singer (2013) also evaluated a large pool of anionic resins and found that most of nitrosamines were released in the first 50-100 bed volumes (BV) of operation. This is mainly because that the resins received from manufacturer can contain impurities (e.g., dimethylamine, trimethylamine) and/or organic precursors that can be released/detached into the water (Kemper et al., 2009). Also, flow interruption (i.e., soaking resins) and regeneration were found to increase nitrosamines precursors release mainly due to resins swelling (i.e., more open structure) which facilitates the detachment of organic impurities (Flowers and Singer, 2013; Kemper et al., 2009). That said, the formation of N-DBPs (in particular nitrosamines and HNMs) in IEX treated waters is generally attributed to the presence and thereby reaction of reactive disinfectants (i.e., Chlorine, Chloramine, ClO_2) with the amine-containing functional groups of polymeric resins (Flowers and Singer, 2013; Gan et al., 2013b; Kemper et al., 2009; Najm and Trussell, 2001).

Despite the fact that the potentially formed N-DBPs (from IEX process) could be controlled via downstream oxidation processes such as UV/ H_2O_2 (Chu et al., 2014), UV/Persulfate (Chu et al., 2015b), and O_3 /biological activated carbon (BAC) installations (Chu et al., 2015a), the risk associated with their formation due to final disinfection (i.e., disinfectant reaction with DON) could remain in place (Karanfil et al., 2008; Kristiana et al., 2013). Hence, additional research is needed to determine the relative importance and fate of various NOM fractions (DON as well) and subsequent implications on C-DBPs and N-DBPs formation potential during the practice of IEX process.

Furthermore, literature showing NDMA formation as a result of IEX treatment have mainly employed packed bed columns in very extreme conditions (e.g., very long contact time, high resin dose, use of chloramine, etc.) which in turn influences the conclusion. More recent studies have suggested the use of stirred (a.k.a. suspended) mode operation as opposed to the

conventional packed bed columns (Boyer and Singer, 2006; Cornelissen et al., 2009; Drikas et al., 2002; Galjaard, 2010; Gan et al., 2013a; Grefte et al., 2013; Martijn et al., 2010; Slunjski et al., 2000). This is because stirred mode has a lower resin inventory and salt usage and also its performance is not challenged under high turbidity waters (Galjaard, 2010; Slunjski et al., 2000). More importantly, suspended IEX has a significantly lower pressure drop and biofilm formation potential inside the mixing reactor (Flemming, 1987). Given the growing interest on commercialization of the stirred mode operation (Cornelissen et al., 2010; Galjaard, 2010; Martijn et al., 2010), it is necessary to understand the influence of suspended operation on NOM removal and DBPs control. To the best of our knowledge and at the time of this research, there were very limited studies reporting on the effect of ion exchange in the suspended mode on N-DBPs formation potential using practical conditions. As a result, sets of independent experiments using various waters were designed and carried out to address the above mentioned research questions.

7.2 Materials and Methods

7.2.1 Source water and sample preparation

Suwannee River NOM and Pony Lake Fulvic acid were used to represent low N/C (~ 0.02) and high N/C (~ 0.12) content, respectively (Table 7.1). Presence of NO₃ has been suggested to promote nitrosamines formation (Chen and Valentine, 2007; Gerecke and Sedlak, 2003; W. Lee et al., 2007), so PL water was amended with sodium nitrate to investigate this hypothesis. For more consistency in preparation, 20 mg of standard IHSS isolate(s) was dissolved in 1L of phosphate buffer (10 mM, pH ~7.5) on the day of experiment (Table 7.1). Waters prepared were stored in specially prepared glass amber bottles at 4°C in dark.

Table 7.1, Characteristics of the synthetic waters used in this study

Water	TOC (mg/L)	NO₃⁻ (mg/L)	³Charge density (meq/g-C)	⁴MW (g/mol)
¹ Suwannee River NOM (SR)	~ 8.7	-	10.157	1050
¹ Pony Lake Fulvic Acid (PL)	~ 8.7	-	6.840	750
Pony Lake Fulvic Acid + Nitrate (PLN)	~ 8.7	~ 10	6.840	750
² Phosphate Buffer (10 mM, pH:7.5)	-	-	-	-

¹ Standard isolates purchased from IHSS

² Control sample

³ Calculated for pH=7.5 using the equation provided by Ritche and Perdue (2003), Driver and Perdue (2014), and IHSS website

⁴ Estimated Mw of humic substance using LC-OCD, data obtained are estimates and were used for comparison only

7.2.1.1 Disinfection by-products formation potential test

To simulate the performance of resins under realistic suspended operating conditions, consecutive batch treatments of raw water were carried out using 10 mL/L (corresponding to water/resin: 1000 mL/10 mL = 100 bed volumes, BV) of resins and 30 minute contact time. This approach and treatment condition were selected based on the previous evaluations by the authors as well as other researchers (Boyer and Singer, 2006; Drikas et al., 2011; Galjaard, 2010; Gan et al., 2013a; Kitis et al., 2007; Mergen et al., 2008; Monosov et al., 2012; Walker and Boyer, 2011). Resins were filtered out from the treated water after each cycle using a 1.6 µm glass filter (baked at 550°C for 5hrs). Then, resins were reloaded with another liter (i.e., 100 BV) of fresh water and were stirred for 30 minutes (total of 200 BV). This was repeated until 600 BV of water was treated. To save time, number of samples and cost, samples were collected at 100 BV (1st cycle), 300 BV (3rd cycle) and 600 BV (6th cycle) only and underwent subsequent DBPs analysis as follows.

All standard water quality parameter analyses were conducted at Het Waterlaboratorium (HWL), Haarlem, Netherlands. Details of these analyses are presented in the SI section D.3. Samples for DBPs FP test were spiked with sodium hypochlorite and incubated in dark at 25°C for 24 hrs according to the method of Krasner et al. (2004) (see SI, section D.3). Next samples were quenched from chlorine and analyzed for nitrosamines, THMs, aldehydes, haloketones, HANs, HNMs, HAcAms, nitriles and other DBPs. Further details on the analytical methods for DBPs measurement and sample preparations are elaborated in the SI.

7.3 Results and Discussion

7.3.1 Effect of IEX on general water characteristics (TOC, UV₂₅₄, NO₃⁻)

Both PL and PLN waters showed a lower DOC removal (i.e., nearly 20% less) compared to the SR water in the 1st cycle (Figure 7.1.A). However, the DOC removal efficacy for PL and PLN only changed about 6% over the subsequent 3rd and 6th cycles while it decreased rapidly by 43% and 50% for SR water in the 3rd and 6th cycles, respectively (Figure 7.1.A). The higher DOC removal of the SR water in the 1st cycle is attributed to the higher charge density of SR compared to PL fulvic acid as also depicted in Table 7.1 (Driver and Perdue, 2014; Ritchie and Perdue, 2003). However deeper insight into the molecular structure and weight distribution of organic isolates is required to explain their DOC profiles over consecutive loading cycles.

The lower aromaticity of PL compared to SR (SUVA_{PL} ~ 2.9, SUVA_{SR} ~ 4.6), indicated a more hydrophilic and neutral molecular structure for PL that in turn has lower affinity towards ion exchange resins (Mergen et al., 2008; Tan and Kilduff, 2007). Using LC-OCD, changes in MW distribution of NOM fractions during IEX were assessed and are depicted in Figure 7.1.B. SR had a relatively higher humic substances (~ 73 %), whereas PL (and PLN) had higher building blocks (~ 20 %), neutral fractions (~ 20 %), and biopolymers. Humic (-like) substances were mainly targeted by IEX resins (~ 40-67 %) while lower removal of building blocks (20-33 %) and neutrals (12-13%) were observed for an estimated average over 600 BV of treated water (Table D.4). Small and uncertain changes of biopolymers that were present at significantly lower levels (~ 30-90 µg/L) were also observed for all three waters. Results obtained here further illustrate that ion exchange resins mainly target ionic hydrophobic molecules and the removal efficiency of NOM declines with the increase in the non-ionic constituents of NOM (Croué et al., 1999).

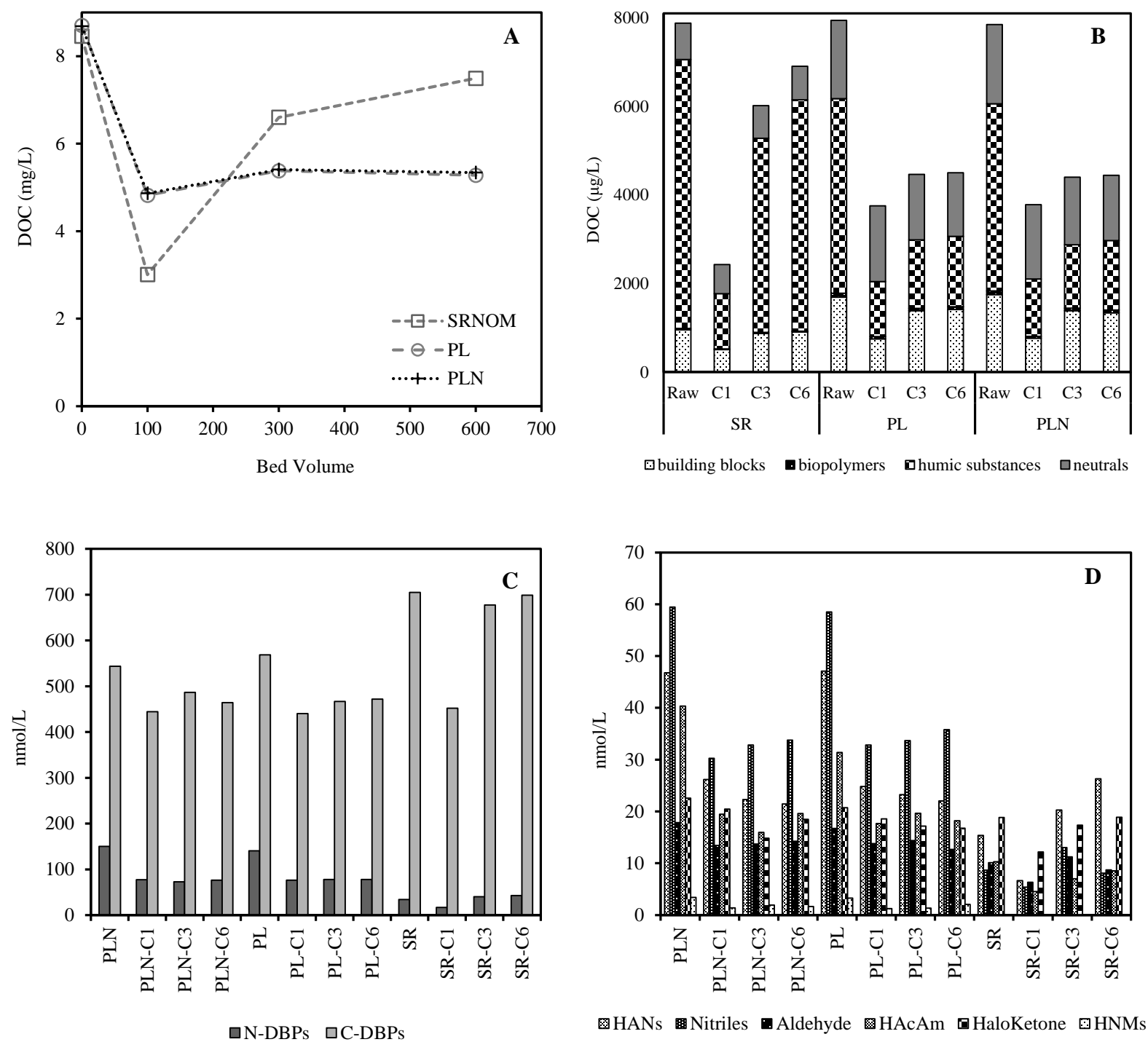


Figure 7.1, DOC profile (A), NOM distribution (B), DBPs formation (C), and specific DBPs formation (D) during consecutive multiple cycles

Using the estimated charge densities for SR, PL, and PLN and also the exchange capacity of the resins (0.8 meq/mL reported by the manufacturer), the resins sites occupied after the 6th cycles for SR, PL, and PLN were estimated to be 1.8%, 2.7%, and 4% of the total resin exchange capacity, respectively. Figure 7.1.B also depicts that a major fraction of humic (-like) fractions for SR are excluded from adsorption at the 3rd and 6th cycles. Given the higher estimated MW for SR isolates (Table 7.1), the change in removal efficiency (for SR) can be attributed to the blocking of resins exchange sites by previously adsorbed SR (i.e., larger molecules) thereby limiting the access of other organic molecules (Fu and Symons, 1990; Mergen et al., 2008; Tan and Kilduff, 2007; Zhang et al., 2014). It should be noted that the profile of SR water over multiple consecutive loadings is different from the ones shown in chapters 4 and 5 (Figure 4.3.A and Figure 5.2.A). That is because the synthetic SR water here was made in phosphate buffer (instead of bicarbonate) and this is postulated to be the cause of the difference in the removal patterns observed in Figure 7.1.A versus chapters 4 and 5. That said, this does not influence the following findings as the focus of this chapter was to correlate the changes in NOM fractions to DBPs FP of the IEX treated water. Profiles of NO₃⁻, UV₂₅₄, and DON for the treated waters showed similar trends and are demonstrated in Table D.4 and discussed in section D.4 of SI.

7.3.2 Effect of IEX on N-DBPs and C-DBPs formation potential

Table D.3 demonstrates the DBP compounds and their respective categories in the water samples. Although considered as emerging DBPs, Tetrachloromethane, dimethylpropanoyl chloride, tetrachloroethylene, tetrachlorocyclopropene did not belong to any major category in Table D.3 and hence were not categorized (Bull et al., 2011; Hebert et al., 2010; Moudgal et al., 2000; Niri et al., 2008). Nitrosamines, HANs, nitriles, HAcAms, and HNMs were collectively presented as N-DBPs and THMs (only chloroform was detected), haloketones, aldehydes

(although not DBPs), and the compounds listed in the “other DBPs” category were considered as C-DBPs. The highest nitrosamines formation was expected in raw and or the first 100 bed volume i.e., C1 samples (Flowers and Singer, 2013). However, no nitrosamines and or nitrosamine precursors were detected in either raw or IEX treated waters. The differences between the results of this study and those of others who reported NDMA (or other N-DBPs) formation can be explained as follows. Most of the studies conducted did not regenerate and rinse resins prior to testing for nitrosamines and their precursors release. This is believed to greatly influence the outcome as manufacturing contaminations (e.g., dimethylamine, trimethylamine) can play a significant role as precursors (Kemper et al., 2009; Westerhoff and Mash, 2002). Second, resin dosage used in here (10 mL/L) was much lower than the ones used (e.g., 200 mL/L) in similar studies (Flowers and Singer, 2013; Kemper et al., 2009; Najm and Trussell, 2001). Third, a short but practical contact time (30 minute) was used in this study, whereas 1h-4h of contact time was reported in others (Najm and Trussell, 2001). Finally, studies have reported chlorination to have lower potential to cause nitrosamines formation compared to chloramine ($\text{Cl}_2 + \text{NH}_3$) (Krasner et al., 2012; Kristiana et al., 2013; W. Lee et al., 2007; Mitch and Schreiber, 2008; Westerhoff and Mash, 2002; Yang et al., 2010). Flowers and Singer (2013) also studied the same resins (A860E, different bead size) with “no prior cleaning” and found insignificant NDMA release ($< 5 \text{ ng/L}$) but some release of NDMA precursors ($> 2000 \text{ ng/L}$) during the first 10 BV of operation (Resin BV = 200 mL); however, no NDMA was detected after 100 BV of column operation.

The average reductions of DOC and DON over 6 consecutive batch loadings (i.e., 600 BV) were 33-41% and 76-77%, respectively. Consequently, the average reduction in C-DBPs and N-DBPs were 14-19% and 3-50% (Table S.5), respectively, with the highest reductions

observed in the 1st cycle (18-36% for C-DBPs and 40-45% for N-DBPs) as shown in Figure 7.1.C. Both N-DBPs and C-DBPs remained unchanged throughout C1 to C6 for PL and PLN, while N-DBPs and C-DBPs formation potentials for SR increased to levels close and even beyond the ones of the raw water. The reason for this observation is mainly attributed to the DOC content which remained constant (6 % change) for PL, and PLN waters (during C1-C6), but increased through the 3rd to 6th cycles for the case of SR (see Figure 7.1.A). The increase in N-DBPs FP for SR-C3 and SR-C6 was mainly due to the increase in HANs (see Figure 7.1.D), and to a lower extend increase of aldehydes and nitriles (Figure 7.1.D). Minor release/detachment of amine groups from the resins and or experimental and analytical error associated with the measurement could explain this observation. Further experiments with more replicates could lead to more conclusive results on this subject.

Considerably higher N-DBPs FP was observed for PL, PLN samples in which also higher organic nitrogen ($\sim 620 \mu\text{g/L}$ compared to ~ 0) was present (Figure 7.1.C, and section 7.2.1). On the other hand, SR showed greater values for C-DBPs FP which is mainly attributed to its higher SUVA value i.e., more hydrophobic composition (Krasner et al., 2006). Contrary to the actual “nmol/L” data (Figure 7.1.C), the normalized data to their corresponding DOC (i.e., nmol/mg DOC) showed inverse trends. That is, the concentration of DBPs per mg/L DOC increased for the IEX-treated waters (Figure D.1). According to the LC-OCD data presented earlier (Figure 7.1.B), IEX mainly targets high charge density/high polarity organic fractions such as humic (-like) substances and is less effective at removing building blocks, neutral, and biopolymer fractions, an observation also reported by others (Bond et al., 2010; Cornelissen et al., 2010; Grefte, 2013; Huber et al., 2011). The building blocks and neutral fractions remaining in the treated waters can potentially promote higher DBP formation, in particular nitrogenous

compounds because of a large pool of amino acids and N-containing compounds, in the event of exposure to chlorine (Grefte et al., 2013; Naidu et al., 2013; Peter, 2010; Yang et al., 2010). In this regard, Ates et al. (2007) also reported on the importance of low or non-UV absorbing compounds in DBPs formation under chlorination. Moreover, as the treatment cycles continued, the “nmol/mg DOC” started to decline as a result of increasing humic substances in the IEX treated water. This demonstrated higher scavenging of chlorine by humic substances diminishing Cl_2 and hydrophilic compounds interactions leading to lower nmol- DBPs/mg-DOC (Vasyukova et al., 2013).

To better correlate the obtained DBPs FP data with other water quality parameters, different parameter combinations were assessed using step wise multiple linear regressions (and ANOVA) and the best correlation was found to be between N-DBPs/C-DBP-s (mol/mol) and DOC/DON ($\text{mg.L}^{-1}/\text{mg.L}^{-1}$) (Table D.6). The mass of nitrogen and carbon in all DBPs were calculated and compared to the original dissolved organic nitrogen (% N/DON) and dissolved organic carbon (% C/DOC), respectively (Figure D.2). Results obtained showed only a small percentage of DON (< 2%) and DOC (< 0.3 %) contributed to DBPs FP. The contribution of dissolved N to DBPs was significantly higher than that of dissolved C (~ 7 times higher), indicating higher reactivity of DON toward chlorine. Moreover, the mass fraction of N in DBPs (mg/mg) increased as a result of IEX treatment. This can further support the earlier statement that IEX removes components (i.e., humic substances) with higher scavenging capability for chlorine (i.e., higher chlorine demand) compared to org-N bound fractions. As a result of IEX treatment, those fractions are removed and more hydrophilic org-N containing fractions become prone to react with chlorine. The (total N)/(total C) ($\mu\text{g}/\mu\text{g}$) in DBPs was found to have a statistically significant inverse correlation with DOC/DON (95% confidence, adjusted $R^2=0.97$,

significance $F=3.21E-9$). The use of statistical t-test revealed no difference ($p\text{-value} = 0.79$, at 95% confidence level) between the data ruling out the hypothesis of NO_3^- promoting more N-DBPs formation. However, this observation is based on use of the limited data associated to a certain type of water and treatment conditions (i.e., treated with IEX resins and dosed with chlorine). Therefore, further research using different waters undergoing different treatments would promote and enhance the knowledge on the impact of NO_3^- .

7.3.3 Impact of IEX treatment on different categories of DBPs

Among all DBPs formed, chloroform was by far the most prevalent compound produced almost 10 times greater than the second most abundant one (Figure 7.2, and Figure D.3). After chloroform, 1,1,1-trichloroacetone, dichloroacetonitrile, 2,2,2-trichloroacetamide, and acetonitrile were largely detected in all samples (Figure 7.2). The amount of the 1,1,1-trichloroacetone formed was significantly higher (20-30 times) than the one of dichloroacetone. HANs were formed as dichloroacetonitrile and trichloroacetonitrile mainly as a result of PL and PLN chlorination. Also, the amount of dichloroacetonitrile was 5-10 times higher than trichloroacetonitrile. Notably, levels of 2,2,2-tri chloroacetamide were 3-5 times higher than the 2,2-dichloroacetamide formed in raw and treated waters. Also, dichloronitropropane, and 1,1-dichloro-1-nitro-ethane (HNMs) were only detected in high organic nitrogen containing waters, i.e., PL and PLN. Overall, aldehydes, nitriles, HANs, and HAcAms were found in all the waters, yet at greater levels in samples with higher levels of DON (i.e., PL, PLN). Under the applications of IEX carbonaceous-DBPs (mainly chloroform, aldehydes, and haloketones) showed lower reductions (13-23 %), whereas a considerable reduction (41-53 %) was observed for nitrogenous DBPs (such as HANs, nitriles, HAcAms, and HNMs in Table D.3). Extended discussion regarding the role of different NOM fractions on DBPs FP is provided in the following.

Aldehydes can be formed from amino acids and primary amines reaction with chlorine (and or chloramine) (Bond et al., 2012; Joo and Mitch, 2007). Mitch and Schreiber, (2008) reported immediate formation of aldehydes from tertiary alkylamines as result of reaction with hypochlorite. Aldehyde formed as a result of chlorination can later be transformed to nitrile (in the presence of more chlorine i.e., 2 molar equivalents compared to amines) through the “decarboxylation pathway” (Joo and Mitch, 2007; Mitch and Schreiber, 2008). In fact, nitriles are major and aldehydes are minor products of amino acids chlorination via “oxidative decarboxylation” because of the higher molar equivalent of chlorine that is generally added (Westerhoff and Mash, 2002).

HANs and haloketones are reported to be the major (after THMs) by-products of chlorination of humic materials (Reckhow et al., 1990) and formation of HANs was reported to be mostly due to the presence of hydrophilic basic fraction of NOM (Chen and Westerhoff, 2010; Westerhoff and Mash, 2002). The higher level of di-chloroacetonitrile (5-10 times) compared to tri-chloroacetonitrile indicates the presence of α -amino acids (e.g., aspartic acids) and humic acid fractions which can react with chlorine to form HANs (Bond et al., 2011b; Dotson et al., 2009; Westerhoff and Mash, 2002). These compounds can later be transformed into HAcAms and haloacetic acids (HAAs) (through base-catalyzed decomposition), depending on the chlorine contact time and pH (Chu et al., 2010a, 2010b). Formation of HAcAms is generally attributed to the hydrophilic acid fraction of NOM (Bond et al., 2012; Chu et al., 2010a, 2010b). This matches with the fact that PL is a highly hydrophilic, nitrogen enriched isolate from a microbial source (Brown et al., 2004; D’Andrilli et al., 2013; Mao et al., 2007).

Generation of halonitroalkanes, in particular HNMs, is reported at lower yields compared to THMs, nitriles, and aldehydes as a result of chlorination/chloramination of NOM (mainly

hydrophilic) (Bond et al., 2012, 2011b; Joo and Mitch, 2007; Song et al., 2010). However, higher toxicity of these compounds could be problematic and concerning even at low levels (Plewa et al., 2004; Shah and Mitch, 2012). Similar to this research, HNMs were slightly reduced (i.e., 10-15%) in wastewater impacted streams treated by MIEX (Gan et al., 2013). HNMs occurrence is generally promoted as a result of ozonation and Medium Pressure UV disinfection and is affected by the downstream disinfection process (Bond et al., 2012; Shah and Mitch, 2012; Singer, 1994).

Using the Pearson's coefficient, all the by-products categories, except THMs (i.e., chloroform) and haloketones, were found to have a meaningful strong correlation with DOC/DON (Table 7.2, ρ close to 1). On the other hand, they all found not to have a significant correlation with SUVA₂₅₄ ($\rho \ll 1$). The absence/weakness of correlation between DBPs and SUVA₂₅₄, especially for low SUVA waters, was also reported by other researchers (Ates et al., 2007; Tan et al., 2005).

Table 7.2, Pearson's coefficient for DBPs and water quality parameters

	UV ₂₅₄	DOC	DON	SUVA	DOC/DON
THM	0.94	0.69	-0.04	0.94	0.57
HANs	0.29	0.68	0.93	-0.12	-0.73
Aldehyde	-0.15	0.34	0.87	-0.55	-0.95
Nitriles	-0.08	0.40	0.77	-0.52	-0.94
HAcAm	0.01	0.47	0.91	-0.41	-0.87
HaloKetone	0.45	0.73	0.68	0.05	-0.55
HNMs	-0.15	0.32	0.86	-0.54	-0.92

Interestingly, there is a higher dependency between SUVA and DBPs FP (and lower dependency between DOC/DON and DBPs FP), in particular N-DBPs, when percentage removal is monitored (Table D.5) as opposed to what was observed in Table 7.2 between actual N-DBPs levels and SUVA values. That said, one has to note that comprehensive stepwise F-test is required to be performed on the dependency of each parameter and Pearson's coefficient is only to provide a preliminary insight. Also, uncertainties and small amount of some species would require further work to verify above findings. For instance, Chen and Westerhoff, (2010) developed and proposed a model to predict THMs, HAAs, HANs, and NMDA over the analysis of over 200 samples covering a wide range of characteristics using DOC, UV₂₅₄, Br, and DON as water quality parameters. Their findings indicated that inclusion of DON had a positive impact improving the predictions.

7.4 Conclusions

As a result of IEX treatment, humic (-like) substances of NOM were mainly targeted (40-67 % removal) whereas hydrophilic, non-ionic fractions such as biopolymers, neutrals, and building blocks were poorly removed (12-33 %). Charge density and MW of NOM were found to play a key role in removal performance especially at long-term operation. Findings here pointed to the key role and importance of hydrophilic, non-ionic fractions of NOM when DBPs (especially N-DBPs) are concerned. Hence, using isolation methods and/or preparative columns to make up and test these fractions is of great value and can further shed light on this subject. Regeneration and rinsing of IEX resins is believed to play an important role in mitigating the potential formation of N-DBPs and their precursors (e.g., NDMA). Findings here demonstrated the efficacy of strongly basic ion exchange resins in removing portions of total C-DBPs FP (13-23 %) and total N-DBPs FP (41-53 %) over 600 BV of treated water. The greatest reduction in DOC, and DBPs was observed in the first cycle i.e., 1st 100BV and was reduced as treatment continued. The presence of dissolved organic nitrogen (DON) was found to be a key parameter affecting the formation of N-DBPs. DON, especially the portion affiliated with humic substances fraction, was reduced effectively (average ~ 77 %) as a result of IEX treatment.

Supplementary Information

Supplementary information related to this chapter is provided in Appendix D.

Chapter 8: Impact of Anionic Ion Exchange Resins on NOM Fractions: Effect on AOC and Biostability

Further to understanding the impact of IEX treatment on different NOM fractions and its subsequent effect on water quality, the change in biostability of IEX-treated water was studied throughout Assimilable Organic Carbon (AOC) measurement. The AOC level in finished water and distribution system is important since it can promote bacterial regrowth and biofilm formation. This is even more important for countries such as Netherlands and Switzerland where no residual chlorine is added to the distribution system. Five different waters underwent ion exchange treatment (Resin Dose: 10 mL/L) in short (30 min) and extended (24 hrs) contact times. Liquid chromatography with organic carbon detector (LC-OCD) was employed to gauge the impact of IEX on different NOM fractions and data obtained were used to correlate these changes to AOC. Humic substances fractions of NOM were mainly targeted by ion exchange resins in all the waters tested (85-100 %) whereas neutrals (36-58 %), building blocks (31-72 %), and biopolymers (~ 11%) showed lower efficiency during 24 hr of treatment. The practice of ion exchange treatment did not adversely affect the AOC formation of the treated waters; rather application of IEX reduced AOC levels by 30-40%. Despite the contribution of humic substances fractions to AOC (40-60 %), the remaining hydrophilic fractions (i.e., biopolymers, neutrals and building blocks) were found to show a considerably higher tendency/fraction (i.e., higher AOC/TOC) to be assimilated by microorganisms and contribute to AOC.

8.1 Introduction

The use of strongly basic IEX resins as an efficient treatment for NOM (i.e., DOC) as well as inorganic anions (e.g., nitrate, sulfate) has received considerable attention (Bolto et al., 2002b; Fearing et al., 2004; Martijn et al., 2010; Mergen et al., 2008; Tan and Kilduff, 2007). Easier operation, no blockage and or bacterial growth (Flemming, 1987), shorter mixing time (< 30 minutes) along with high efficiency (even at high flow rates) are amongst the positive points that has incentivized the increase in IEX installations for the past few years (Boyer and Singer, 2006; Martijn et al., 2010; Mergen et al., 2008; Singer et al., 2007). After thorough research and assessment, PWN Technologies, Netherlands has decided to substitute its conventional coagulation-sand filtration process (CSF) with combined suspended ion exchange i.e., SIX[®] - CeraMac[®] (i.e., IEX - MF) processes at Andijk water treatment plant. The treatment train at Andijk consist of SIX[®] (i.e., IEX), CeraMac[®] (i.e., MF), UV/H₂O₂, GAC, and ClO₂ processes supplied by Ijssel Lake as the source water (DOC_{avg} ~ 5.7 mg-C/L; DON_{avg} ~ 1.2 mg-N/L; NO₃⁻_{avg} ~ 8.8 mg-NO₃⁻/L).

Assimilable Organic Carbon (AOC) is a key standard in Dutch water quality routinely monitored by water utilities in Netherlands (Smeets et al., 2009; van der Kooij et al., 1999). AOC levels higher than 10 µg/L acetate-C (measured by conventional AOC bioassay) could deteriorate biological stability of water leading to bacterial regrowth and biofilm formation within the distribution system (Van der Kooij, 2002, 1992, 1987). Also, IEX resins are reported to preferentially remove hydrophobic-transphilic NOM with low-medium molecular weights (Boyer et al., 2008b; Drikas et al., 2003) and therefore, one can expect to see a reduction in AOC after IEX treatment (Bazri et al., 2012; Bazri and Mohseni, 2016). That said, the extent of reduction and contribution of various NOM fractions to AOC is not well documented and also

very limited data was available in the literature concerning the effect of IEX treatment on AOC of waters. Historical data and other observations available to PWN-T suggested that IEX removes larger portion of non-biodegradable NOM fractions (e.g., humic substances) compared to the biodegradable ones (e.g., biopolymers). To ensure producing superior water quality, it was of great importance for PWN-T to investigate the impact of ion exchange resins on AOC of several waters. As a result, experiments were designed and carried out to investigate the impact of different NOM sources (i.e., NOM fractions) on AOC under IEX treatment applications.

8.2 Materials and Methods

8.2.1 Water sources

The properties of the waters used in this study are shown in Table 8.1. LC-OCD was used to estimate SUVA (i.e., UV_{254}/TOC) and molecular weight (MW) of NOM in the waters studied. Synthetic waters were made by dissolving 20 mg/L of dry IHSS isolate in 1L of phosphate buffer (10 mM, pH ~7.5, in Milli-Q water) on the day of experiment. Waters prepared/collected were stored in amber AOC-free glass bottles at 4°C in dark.

Table 8.1, Characteristics of waters used in this study

Water	Symbol	³ TOC3	³ NO ₃ ⁻	⁴ SUVA	⁴ MW
¹ Suwannee River NOM	SRNOM	~ 8.7	-	~ 4.4	~ 1030
¹ Suwannee River Fulvic Acid	SRFA	~ 9.9	-	~ 5.2	~ 1070
¹ Suwannee River Humic Acid	SRHA	~ 9.4	-	~ 7.9	~ 1520
Ijssel Lake Water	IL	~ 5.9	~ 5	~ 2	~ 760
² Scheveningen Water	PSC	-	-	-	-

1 Standard isolates purchased from International Humic Substances Society (IHSS)

2 Scheveningen water was used as a control, therefore its TOC and NO₃⁻ was not measured

3 TOC and NO₃⁻ : mg/L, SUVA: UV_{254}/TOC : L.mg⁻¹.cm⁻¹, MW: g/mol

4 MW: Molecular Weight, estimated using LC-OCD data

8.2.2 Assimilable organic carbon (AOC) bioassay

Separate batches of 10 mL/L of the resins were mixed with raw waters for 30 min and 24 hr. Contact times of 30 minutes and 24 hours were selected to simulate practical and isotherm (i.e., extended) conditions, respectively. Resins were separated from the water using a 1.6 μm glass filter (baked at 550° C for 5hr) and water samples underwent further AOC analysis.

AOC measurement performed was slightly different from the conventional AOC bioassay (Van der Kooij et al., 1982). All samples were initially inoculated with P17 strain and allowed to reach stationary phase (AOC-P17). Then, NOX strain was added (AOC-NOX) and the total AOC was calculated as AOC-P17 + AOC-NOX. For SRNOM and IL waters, NOX and P17 were also added separately to assess the AOC promoting compounds that can be assimilated by NOX (i.e., amino acids, carbohydrates) and or P17 (i.e., carboxylic acids and carbohydrates) (Van der Kooij, 2002; Van der Kooij et al., 1982). For each experiment, AOC analysis was conducted in duplicates. All water quality analyses were carried out at Het Waterlaboratorium (HWL), Netherlands.

8.3 Results and Discussion

8.3.1 Effect of IEX treatment on physiochemical water properties

Relative reductions in UV₂₅₄, TOC, and SUVA for different waters as a result of ion exchange treatment are shown in Table 8.2. Among the IHSS standard isolates, the highest and lowest reductions in UV₂₅₄, TOC, and SUVA for 30 min and 24 hr was observed for SRFA and SRHA, respectively. The data of SRNOM was between those of SRHA and SRFA, even though it was closer to that of the SRFA. Despite the substantial TOC removal observed for SRHA after 24 hrs it is evident that the remainder 20% of TOC contributes to 75% of its SUVA value, indicating a high molecular weight character that could not be removed via IEX. More

interesting, IL water showed a better removal than SRHA despite its lower SUVA. Despite the more hydrophilic-like nature of the NOM in IL (i.e., low SUVA), it showed a similar SUVA removal as SRNOM and SRFA, and a greater removal than SRHA. In fact, the UV₂₅₄ absorbing fraction of IL NOM (i.e., TOC) was removed to a greater extent than that of SRHA. Had (initial) SUVA been the only factor affecting the IEX removal, one would have expected to obtain the highest removal for SRHA and the lowest for IL water. On the other hand, if molecular weight (i.e., MW) had been the main parameter influencing the removal, the highest and lowest removal should have been observed for IL and SRHA, respectively. These observations suggest that a combination of SUVA (i.e., hydrophobicity of organic matter) and molecular weight was influencing the removal during ion exchange treatment.

Table 8.2, Relative reduction of UVA, TOC, and SUVA over 30M and 24H treatment

Time	30 minutes			24 hours		
Water	UV/UV₀	TOC/TOC₀	SUVA/SUVA₀	UV/UV₀	TOC/TOC₀	SUVA/SUVA₀
SRFA	0.233	0.284	0.821	0.037	0.122	0.307
SRNOM	0.355	0.429	0.828	0.058	0.167	0.346
SRHA	0.606	0.659	0.920	0.152	0.202	0.753
IL	0.349	0.581	0.600	0.126	0.388	0.325

Boyer and Singer (2008b) and Mergen et al. (2009) reported that charge density and SUVA would be the best two parameters for predicting ion exchange removal performance. The charge density for SRFA, SRNOM, and SRHA at pH~7.5 was estimated to be 10.94, 9.62 and 8.85 (meq/g-C) (Ritchie and Perdue, 2003). However, the charge density of IL NOM was not determined due to the limitations in carrying out the potentiometric titration (Ritchie and Perdue,

2003). Hence, the exact role of charge density and the extent of its impact on ion exchange performance were not established conclusively. That said, the data obtained here and also from other studies highly suggest that molecular weight of organics, along with the SUVA, plays an influential role when higher molecular weights (> 5000 Da) are subjected to IEX treatment (Allpike et al., 2005; Croué et al., 1999; Fu and Symons, 1990; Mergen et al., 2008; Tan and Kilduff, 2007). Additionally, LC-OCD results indicated that the average MW of the remaining organics (after IEX treatment) was about ~ 10 % (after 30 min) and 10-20 times (after 24 hr) higher than those of the raw water. This in turn supports the key impact of molecular weight, even though it must be further assessed and confirmed through examining wider range of water qualities. Hence, the lower removal of SRHA (MW : ~ 1520 Da) can be explained by the phenomenon of resin pores becoming blocked, limiting the access of other organic molecules (Fu and Symons, 1990; Mergen et al., 2008; Tan and Kilduff, 2007). Further data and discussion has already been provided in chapter 5.

8.3.2 Effect of IEX treatment on NOM fractions

For a more detailed understanding of interaction between resins and different fractions of NOM, samples were analyzed using LC-OCD according to the method of Huber et al., (2011). Figure 8.1 depicts the affinity of ion exchange resins towards various NOM fractions i.e., humic substances (HS), building blocks (BBs), biopolymers (BP), and neutrals (NEU) during the course of treatment. The original LC-OCD chromatograms are presented in Appendix E . As depicted in Figure 8.1, all IHSS organic isolates were mainly consisted of HS (or HS-like), and to a lower extend of BBs (i.e., LMW HS fractions), NEU, and Hydrophobic Organic Carbon (HOC, not shown). IL water was a natural water source and presence of biopolymer fraction, that was absent in the IHSS isolates, was observed in its LC-OCD chromatograms. Biopolymers are

generally hydrophilic, high molecular weight, saturated (non-UV absorbing) organics with varying levels of dissolved organic nitrogen (DON) (Huber et al., 2011; Leenheer and Croué, 2003). All NOM fractions showed reduction over the course of treatment with HS showing the greatest decrease followed by BBs, NEU, BP respectively (Table E.1). The significantly lower reduction of BP (~ 10 %) and NEU (36-58 %) fractions can be explained by their non-ionic structure. Results obtained were consistent with the findings of other researchers who reported low reduction of neutral and the biopolymer fractions under ion exchange application (Cornelissen et al., 2010; Huber et al., 2011).

In contrary to SRFA and SRNOM, a portion of HS fraction of SRHA was not removed via ion exchange even under extended treatment time. Further LC-OCD analyses showed an increase in the average MW of the HS fraction in SRHA [$MW_0 \sim 1500$ Da, $MW_{24hr} \sim 2200$ Da] indicating that lower MW organics from SRHA were removed via IEX leaving the larger molecules in water. These data support the earlier statement that molecular weight of organic molecules also influences the quality of IEX treated water.

For the case of IL water, the biopolymers, BBs, and NEU were considerable in amount compared to HS fraction after the 30 min and 24 hrs of IEX treatment (Figure 8.1). After 24hr of treatment biopolymers were affected very slightly (< 10% removal) and NEU and BBs were also poorly removed (< 35%), and the highest removal was still associated with HS compounds (~ 100%). Therefore, IEX preferentially targets high charge density/high polarity organic fractions such as humic substances and is less effective at removing building blocks, neutral fractions and biopolymers (Bond et al., 2010; Croué et al., 1999; Grefte, 2013). The significant biopolymer and NEU fractions remaining in the treated water can potentially deteriorate the biological stability of water (a large pool of polysaccharides, amino sugars). Also, it can promote higher

DBPs formation potential, in particular nitrogenous compounds due to a large pool of amino acids and N-containing compounds present in biopolymers (Grefte, 2013; Grefte et al., 2013; Naidu et al., 2013; Peter, 2010; Yang et al., 2010).

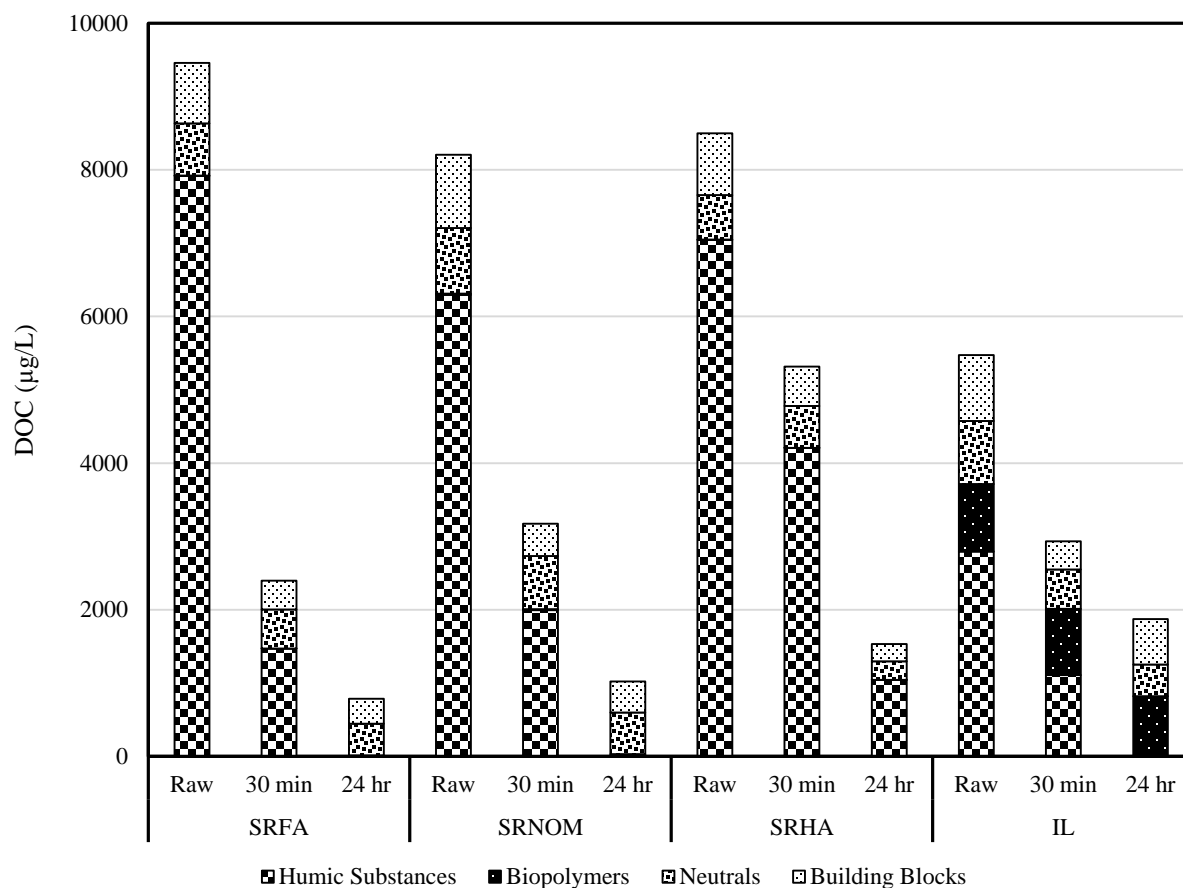


Figure 8.1, Effect of IEX treatment on NOM fractions of various organic isolates

8.3.3 Effect of IEX on assimilable organic carbon (AOC)

Prior to assessing the effect of ion exchange treatment on AOC, the possibility of fresh ion exchange resins releasing AOC promoting compounds was investigated. A local water (PSC) long tested at HWL and known for low AOC content (3-4 µg/L) was used as blank for this study. Control experiments were conducted under identical conditions as those for 30 min and 24 hr

and results obtained showed no significant effect of resins on AOC after mixing. This was attributed to the fact that IEX resins were regenerated (NaCl 10%) and triple-rinsed (Milli-Q) when received from the manufacturer and therefore, any possible manufacturer contamination was washed away.

Table 8.3 demonstrates the results for individual and combined AOC measurements of SRNOM and IL waters (see Appendix E). When NOX was inoculated only, larger AOC-NOX was measured compared to the one that was inoculated after P17 growth (e.g., SRNOM: 51.5 > 10.43). Higher individual AOC-NOX demonstrates the utilization of some carbohydrate (i.e., saccharides) structures that are also digestible by P17 strain. The data in Table 8.3 showed that the sum of individual AOCs of P17 and NOX is greater than when NOX is added after P17 growth (i.e., total).

Table 8.3, Individual and combined AOC (µg/L) of SRNOM and IL waters

Water	TOC (mg/L)	AOC-P17	AOC-NOX	¹Total AOC (P17 + NOX)
SRNOM	8.7	45.5	51.5	57.43 (P17 : 47 + NOX : 10.43)
IL	5.9	17.5	7.65	19.25 (P17 : 15.5 + NOX : 3.75)

¹P17 strain was first inoculated and NOX was added after P17 reached it stationary phase

Data measured for AOC-P17 showed higher levels (and higher standard deviation) compared to the ones of AOC-NOX, indicating the dominant contribution of “carbohydrates + carboxylic acids” to AOC in the waters tested (Figure 8.2). Experiments for SRFA samples were only conducted once (due to sample limitation) whereas each treatment condition was duplicated for SRHA, SRNOM, and IL. Overall the average coefficient of variation (CV %) for the AOC data was < 15 % indicating the repeatability of the AOC experiments (Figure 8.2). AOC was

reduced (for both AOC-P17 and AOC-NOX) as a result of IEX treatment for all the water samples and the fractional change from the original AOC is also shown in Figure 8.2. SRFA and IL showed the highest reductions followed by SRHA and SRNOM. The use of student t-test revealed no statistical difference between 30 min and 24 hr treatments for SRHA and IL samples ($\alpha = 0.05$ & 0.1). Hence, further experiments with more replications could improve the quality of the results assisting in better interpretations. Taking into account all the data available, the average AOC removed in each treatment (ΔAOC) was found to have a statistically significant positive correlation with the average TOC removed in that treatment (ΔTOC): $\Delta\text{AOC} (\mu\text{g/L}) = (0.0031 \pm 0.0003) \times \Delta\text{TOC} (\mu\text{g/L})$, (adjusted $R^2 = 0.92$, p-value = $5.8 \text{ E-}7$ at 95% confidence level).

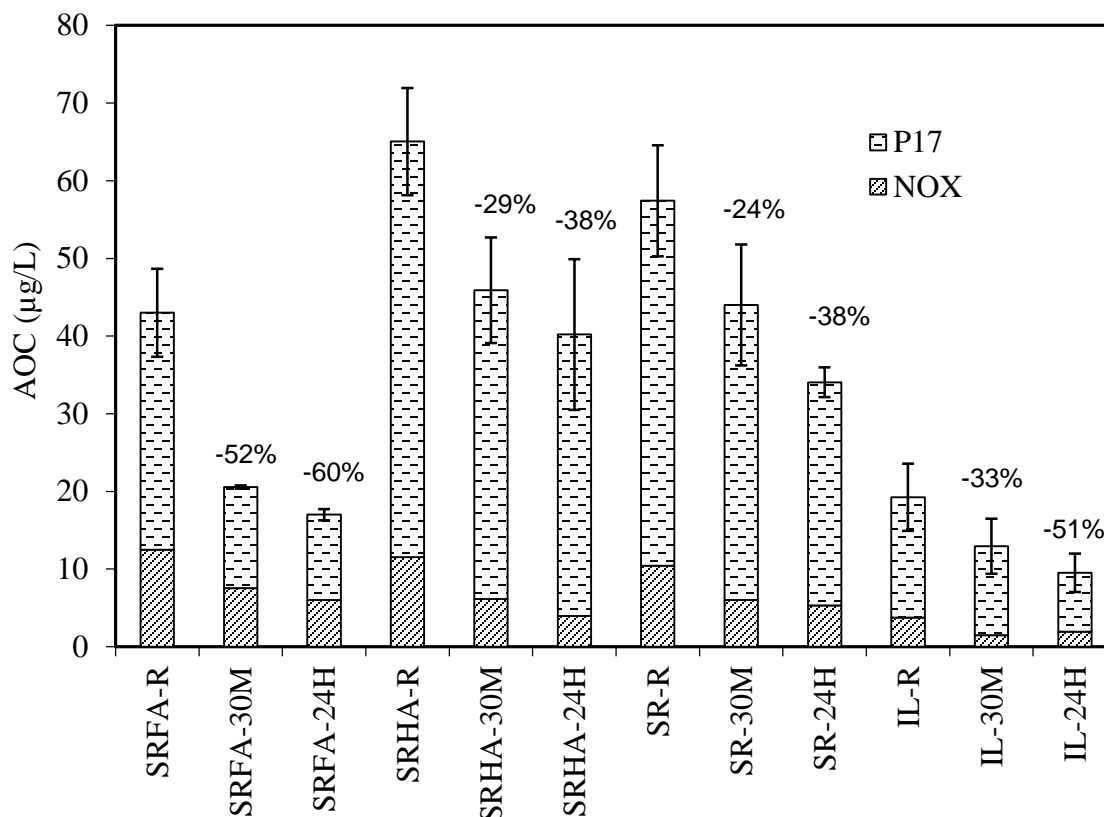


Figure 8.2, AOC (P17+ NOX) of waters treated by IEX after 30 min and 24 hrs

To better compare the AOC data, AOC values were normalized against their corresponding TOC (Figure 8.3). Similar to the results of absolute AOC values observed in Figure 8.2, the highest AOC/TOC ratio (for raw sample) was observed for SRHA followed by SRNOM, SRFA, and IL. Interestingly, the AOC/TOC ratio increased over the course of treatment for all water samples and it was more significant after 24 hrs of treatment compared to 30 min. That is, TOC was removed at a higher rate than AOC in all the samples. This indicates that a larger fraction of the remaining NOM after IEX treatment contributes to AOC. Previously shown LC-OCD results for IHSS isolates (Figure 8.1) indicated BB's and NEU to be the major (i.e., dominant) remaining fractions after 24 hr treatment. Therefore, it is postulated that these

non-removable fractions of BB's and NEU (after 24 hr of treatment) are contributing to AOC. Combining Figure 8.1 and Figure 8.2 shows that the remaining BBs and NEU fractions after 24 hr of treatment approximately contributed to 40-60% of the total AOC. Others have also found that charged hydrophilic and neutral hydrophilic fractions of NOM are more easily assimilable by microorganisms (Buchanan et al., 2004; Chong Soh et al., 2008). That said, it should be noted that in all the IHSS isolates AOC was reduced mainly as a result of humic substances elimination (i.e., high molecular weight, hydrophobic, double conjugated bound). Therefore, all fractions of NOM contribute to AOC, even though to different extents, depending on their amount and biodegradability.

Interestingly IL water with higher levels of biopolymer, neutrals, and building blocks fractions in raw, and IEX treated samples showed the lowest AOC/TOC values. Given the reported higher biodegradability of biopolymers and neutral fractions, one would expect to see a higher AOC/TOC for IEX treated IL water (Grefte, 2013; Naidu et al., 2013). Having said that, the change in AOC/TOC between raw and IEX treated samples were not as significant as in IHSS samples (15-27 % compared to 78-250 %), indicating poor removal of AOC-contributing fractions despite the removal of TOC. The reason for this observation is unclear and has to be determined; however, it is hypothesized that the difference in NOM source could be an influential factor (Bolto et al., 2002a; Mergen et al., 2008). IHSS isolates are organic matters with aquatic source of NOM, whereas IL water NOM consists of organic molecules from microbial, terrestrial, and aquatic sources.

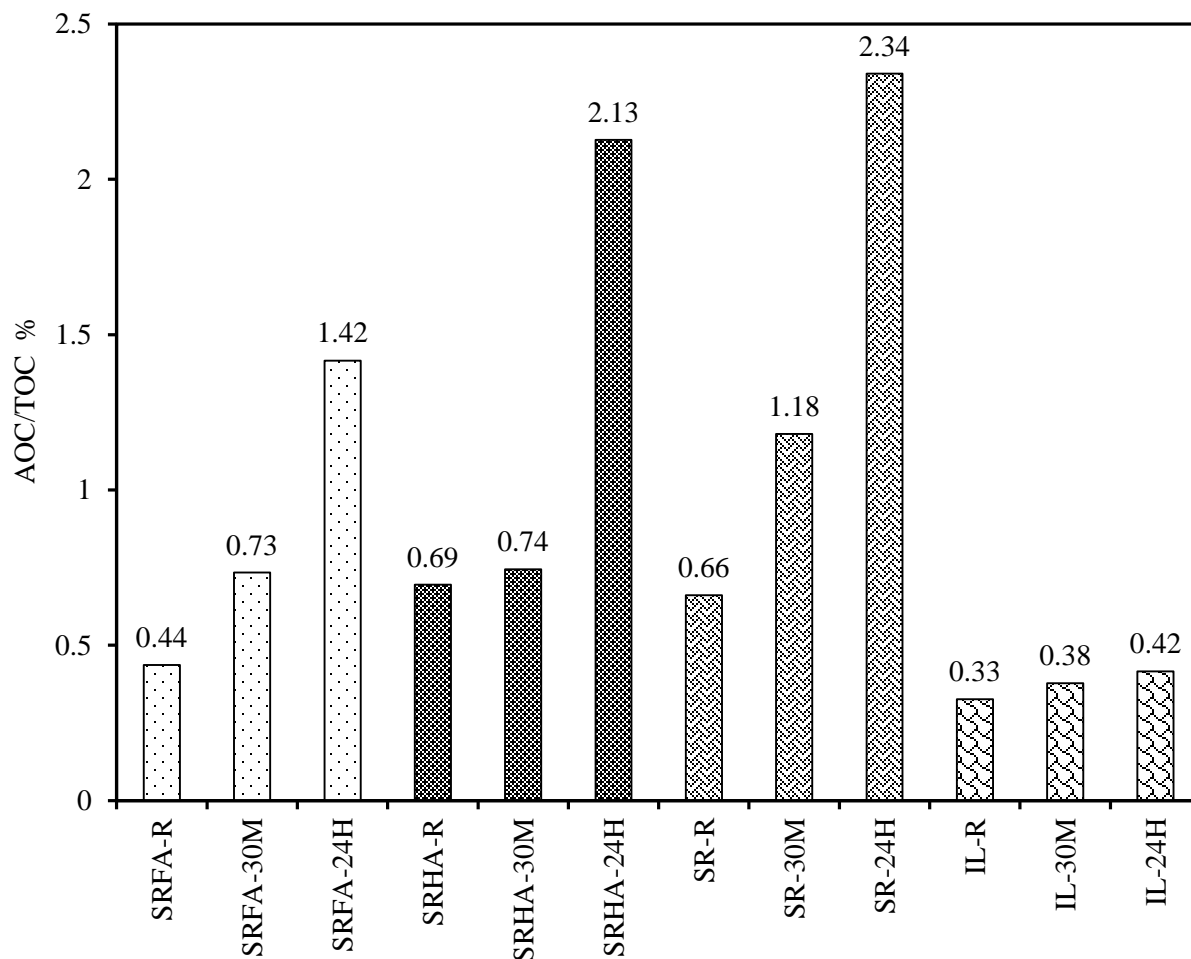


Figure 8.3, AOC/TOC of waters treated by IEX after 30 min and 24 hrs

The biopolymer and HS fractions of IL water showed to have DON of approximately 180 and 60 ($\mu\text{g/L-N}$), respectively, making the total DON estimate to be ~ 240 ($\mu\text{g/L-N}$). DON content of the HS (HS-like) fraction was reduced by 60% after 30 min and was below detection after 24 hr, whereas the DON content of the biopolymer fractions remained unchanged showing the strong attachment to large/hydrophilic organic molecules (Westerhoff and Mash, 2002). Conducting a separate-AOC bioassay using NOX strain only was found to be incapable of producing meaningful information about the DON content. Greater AOC-NOX values were observed for SRNOM, SRFA, and SRHA isolates in which insignificant amount of DON was

present. Petrone et al., (2008) investigated the bioavailability of DOC and DON from 10 different catchments using a BDOC-like method (Seitzinger et al., 2002). DON was reported to show a greater decomposition compared to DOC. Interestingly, DOC decomposition rate was correlated with hydrophobic content whereas DON decomposition was correlated with the hydrophilic content.

Moreover, data obtained for AOC/TOC indicated a similarity between the trends observed for DBPs/TOC for IEX treated water after 30 minutes (chapter 7). Therefore, one can hypothesize that the organic fractions less affected by IEX treatment are more biodegradable and susceptible to react with chlorine thereby producing higher DBPs. LC-OCD data obtained suggest these fractions to be mainly the neutrals, biopolymers and building blocks (i.e., hydrophilic fractions). Therefore, given a certain DOC level one could expect to see higher AOC and DBPs (and N-DBPs) levels for a natural water with a more hydrophilic NOM structure. Also, the observations here are in line with those reported by (Westerhoff and Mash, 2002) who suggested that dissolved organic nitrogen (found in low SUVA, hydrophilic waters) could potentially deteriorate biological stability of water. In fact the considerable levels of DON could be linked to higher levels of amino acids, amino sugars, and eventually proteins which can be readily assimilate by microorganisms. Further data obtained through the assessment of N-DBPs formed during the chlorination of N-enriched waters (i.e., PLFA, and IL) indicated the presence of reactive amino acids that are reported to be highly biodegradable (Bond et al., 2012).

8.4 Conclusions

Five different waters were used to study the impact of ion exchange treatment on different NOM fractions and subsequent water quality in terms of biostability i.e., AOC. Humic substances fractions of NOM were mainly targeted by ion exchange resins (85-100 % removal)

whereas as neutrals (36-58 %), building blocks (31-72 %), and biopolymers (~ 11%) showed lower removal efficiency. LC-OCD results showed that the average MW of the remaining organics after IEX treatment increased by about ~ 10 % (after 30 min) and 10-20 times (after 24 hr) as a result of IEX treatment indicating that IEX mainly targets low-medium range molecules. The average AOC removed in each treatment (Δ AOC) was found to have a statistically significant positive correlation with the average TOC removed in that treatment (Δ TOC). Overall, IEX reduced AOC levels by 30-40%, however the remaining fractions (NE, BP, BBs) showed to have a high potency to contribute to AOC (higher AOC/TOC). That said, all fractions of NOM contributed to AOC even though to different extents depending on their amount and biodegradability. Approaches similar to BDOC method (i.e., using a similar OND-TOC module rather than LC-OND) could be potentially useful and generate accurate results to assess the contribution of DON to biological stability of water.

Supplementary Information

Supplementary information related to this chapter is presented in Appendix E.

Chapter 9: Enhancement of UV/H₂O₂ Efficacy by Removing DOC and NO₃⁻ using Ion Exchange Treatment

Ultraviolet light in combination with hydrogen peroxide (UV/H₂O₂) is increasingly being applied for the removal of trace contaminants from drinking water supplies. However, presence of NOM and nitrate can adversely impact the efficiency of this process also leading to formation of toxic compounds. In this regard, application of IEX process for simultaneous removal of organic matter and nitrate has shown to be promising (Martijn et al., 2010). To further evaluate the feasibility of using IEX upstream of the UV/H₂O₂ process, four different surface drinking water sources underwent IEX (combined with downstream UV/H₂O₂) and the impact on DOC, Nitrate, UV transmittance, and •OH scavenging of the waters was assessed. Results obtained demonstrated a very good efficiency of IEX resins at increasing UVT (up to 75%) and reducing DOC (up to 80%), NO₃⁻ (up to 75%), and SO₄²⁻ (up to 75%) within the IEX conditions applied. Additionally, data confirmed the positive effect of IEX treatment at reducing the •OH scavenging characteristics of the water, especially for high DOC low transmittance waters. Electrical Energy per Order (EEO) for removing a probe compound (i.e., pCBA) was reduced between 20-40 % indicating the improvement in the efficacy of UV/H₂O₂ treatment. Findings of this study demonstrated the potential of utilizing IEX process to improve the quality of the water undergoing UV/H₂O₂ process and its subsequent benefits on the UV/H₂O₂ efficacy and electrical energy consumption.

9.1 Introduction

The combination of ultraviolet (UV) irradiation and hydrogen peroxide (UV/H₂O₂) is increasingly being applied to the removal of trace contaminants from drinking water supplies. Commercial UV/H₂O₂ systems can employ UV reactors with either a monochromatic output at 253.7 nm (low-pressure mercury lamps equipped with doped quartz sleeves), or a polychromatic output from 200-400 nm (medium-pressure mercury lamps with synthetic quartz sleeves).

When UV/H₂O₂ is applied for drinking water treatment of surface water, dissolved organic carbon (DOC) and nitrate play a very important role. Both DOC and nitrate absorb UV irradiation from 200-300 nm, thereby reducing the photons available for hydroxyl radical production resulting in higher operation cost. Moreover, DOC is a major scavenger of hydroxyl radicals, thereby reducing the oxidant available for target contaminant degradation. Meanwhile, the photolysis of nitrate (under the application of medium pressure UV) leads to the formation of nitrite, another strong scavenger of hydroxyl radical, posing further and more serious health concerns. United States Environmental Protection Agency (US EPA) has reported the maximum contaminant levels (MCLs) for nitrate and nitrite to be 10 and 1 mg/L, respectively. Also, there have been reports of increases in Ames II mutagenicity for surface waters containing DOC and nitrate when subjected to polychromatic UV/H₂O₂ treatment (Heringa et al., 2011; Kolkman et al., 2015; Martijn and Kruithof, 2012; Martijn et al., 2015). Having said that, when nitrate was reduced, prior to UV/H₂O₂, a reduction in Ames II mutagenicity response was observed (Martijn et al., 2015). Also, downstream treatment with granular activated carbon has been reported to remediate any possible increase in genotoxicity (Heringa et al., 2011; Martijn and Kruithof, 2012).

While downstream treatment can be effective to ameliorate potential health concerns, it does not have any potential to improve UV/H₂O₂ performance. In this regard, the ion exchange (IEX) treatment process could be utilized as the pre-treatment to UV/H₂O₂ to remove DOC and nitrate simultaneously. Previous studies have suggested the use of strongly basic anionic ion exchange resins (SBR) for the removal of naturally occurring organics (i.e., NOM) in surface waters (Bolto et al., 2002b; Cornelissen et al., 2008; Croué et al., 1999). Furthermore, Martijn et al. (2010) investigated applying ion exchange followed by ultrafiltration upstream of UV/H₂O₂ and reported a 50% improvement in the electrical energy per order (EEO).

In this study four different surface water sources were subjected to IEX treatment conditions (i.e., various resin dose and treatment time). The efficiency of removal was assessed based on the removal of DOC, nitrate, and improvement in UV transmittance (UVT %). Following IEX treatment at selected conditions, three of the surface waters underwent treatment with UV/H₂O₂ and tested for background hydroxyl radical scavenging demand. Finally, the relative savings in EEO between applying UV/H₂O₂ treatment on untreated or IEX treated surface water were calculated using a probe compound (i.e., pCBA).

9.2 Materials and Methods

9.2.1 Source water

All waters used in this study (Table 9.1) were collected from different locations in southwestern Ontario, Canada, during winter-spring of 2013-2014. MAN, RLW, and WEW essentially serve as drinking water sources for treatment plant intakes. Waters collected were filtered (WhatmanTM Membrane Filter, 0.45 µm) within 24 hours (hrs), stored at 4°C in dark, and were used for experiments within less than a month. To assess the performance of the treatment

process under different NO_3^- concentrations, FPW and RLW were amended with additional NO_3^- (as NaNO_3^-) to maximum 26 and 40 mg/L— NO_3^- , respectively.

Table 9.1, Characteristics of the surface waters used in this study

Water Source	¹DOC	¹SUVA	¹NO₃⁻	¹SO₄²⁻	¹DIC
Fanshaw Pond — London, (FPW)	6.4	1.15	1	6	² NA
Ruhl Lake — Hanover, (RLW)	3.9	3.2	15	17	24.4
Grand River — Mannheim, (MAN)	5.4	2.9	20	34	70
Lake Erie — West Elgin, (WEW)	2.1	1	0.8	19	69.4

¹ DOC, DIC, NO_3^- , SO_4^{2-} : mg/L, SUVA: $\text{UV}_{254}/\text{TOC}$: $\text{L.mg}^{-1}.\text{cm}^{-1}$

² Not measured

9.2.2 UV/H₂O₂ experiments

Fifty milliliter water samples (i.e., untreated and IEX-treated) were spiked to approximately 5 mg/L of H_2O_2 (Sigma Aldrich) and ~ 600 $\mu\text{g/L}$ of 4-chlorobenzoic acid (pCBA) (Sigma Aldrich), and irradiated using a collimated beam equipped with a low pressure mercury lamp (Trojan Technologies) for various time intervals i.e., various UV fluences (Bolton and Linden, 2003; Stefan and Bolton, 2005). A calibrated radiometer (IL1700, sensor SED240 for 254 nm, International Light Inc.) was used to determine the UV incident fluence rate (EP°) following the standardized method for UV fluence determination (Bolton and Linden, 2003). The background hydroxyl radical scavenging term (ST, [total $\bullet\text{OH}$ produced] – [$\bullet\text{OH}$ consumed by probe compound]) was calculated following the method described by Rosenfeldt and Linden, (2007). Furthermore, the EEO of the collimated beam reactor, defined as the electrical energy to reduce pCBA by one order of magnitude (90%), was calculated for the different water samples (Rosenfeldt and Linden, 2007).

H_2O_2 concentration was measured before and after each radiation by reaction with iodide catalyzed by molybdate (Klassen et al., 1994). 4-chlorobenzoic acid (pCBA) was detected using

a HPLC equipped with photodiode array detector (Waters 600-MS HPLC equipped with a Waters 996 photodiode array detector, a Waters 717 plus autosampler, and Supelcosil LC-18 column). The eluent consisted of 0.5% H_2PO_4 and acetonitrile, at a ratio of 52%:48%, and was run at a column flowrate of 1.5 mL min⁻¹. The quantification wavelength for pCBA was at 238 nm.

9.3 Results and Discussion

9.3.1 Effect of IEX resins on DOC, UVT, and NO_3^-

A summary of the effect of various resin doses and treatment times on sulfate, nitrate, DOC, and UVT is shown in Table 9.2. Under the practical range of 10 mL_{resin}/L and 30 min contact time (Galjaard et al., 2011; Slunjski et al., 2000), 51-72 % of NO_3^- and 89-95 % of SO_4^{2-} were removed. Under identical conditions, DOC removal and UVT improvement were 40-64 % and 4-31 %, respectively. Overall, a significant difference in terms of efficacy of removal was observed between low (2.5, 5 mL_{resin}/L) and high (10, 15 mL_{resin}/L) resin dosages. However, increasing the resin dose from 10 to 15 mL/L slightly improved (2-11%) the removal efficacy, and longer contact time was found to improve the efficiency only by 3-16%. It should be noted that the initial levels of nitrate in raw FPW and WEW were very low (~ 1 ppm) and hence, the results are considerably subject to detection limit error. Increasing the nitrate levels to 25 and 40 mg/L — NO_3^- in FPW and RLW, respectively, did not show any tangible impact on the efficacy of IEX at DOC removal. Furthermore, FPW and RLW with additional 25 mg/L — NO_3^- showed between 63-90 % and 35-80 % removal (for 2.5-15 mL_{resin}/L) for NO_3^- , respectively.

Table 9.2, Summary of changes in water quality parameters after 30 min and 24 hrs of treatment

Resin Dose	Time	ΔDOC %	ΔUVT %	ΔNO₃⁻ %	ΔSO₄²⁻ %
2.5 mL/L	30 min	17-32	2-12	31-42	54-64
	24 hrs	41-74	4-40	30-48	90-97
5 mL/L	30 min	28-48	3-22	44-58	57-75
	24 hrs	48-77	4-40	46-48	94-98
10 mL/L	30 min	40-64	4-31	51-72	89-95
	24 hrs	52-80	4-40	52-69	94-98
15 mL/L	30 min	46-75	4-36	52-80	93-97
	24 hrs	56-82	4-40	55-78	92-98

The DOC fractional uptake (i.e., fractional attainment as discussed in Chapter 5) profile for different waters treated with 2.5-15 mL/L of resins is shown in Figure 9.1. Fractional uptake was used to normalize the data for non-removable DOC fractions (Qi et al., 2012). Using 10 and 15 mL/L (resin—mL/water—L) resulted in considerably higher DOC removal and 30-45 min of contact time was found to be an optimum range to reach a removal of 80-90%. UVT profiles obtained demonstrated a similar behavior showing greater and faster removal with higher resins doses and longer contact times. Hence, an optimum condition of 10 mL/L and 30 min contact time was selected for subsequent IEX-UV/H₂O₂ experiments.

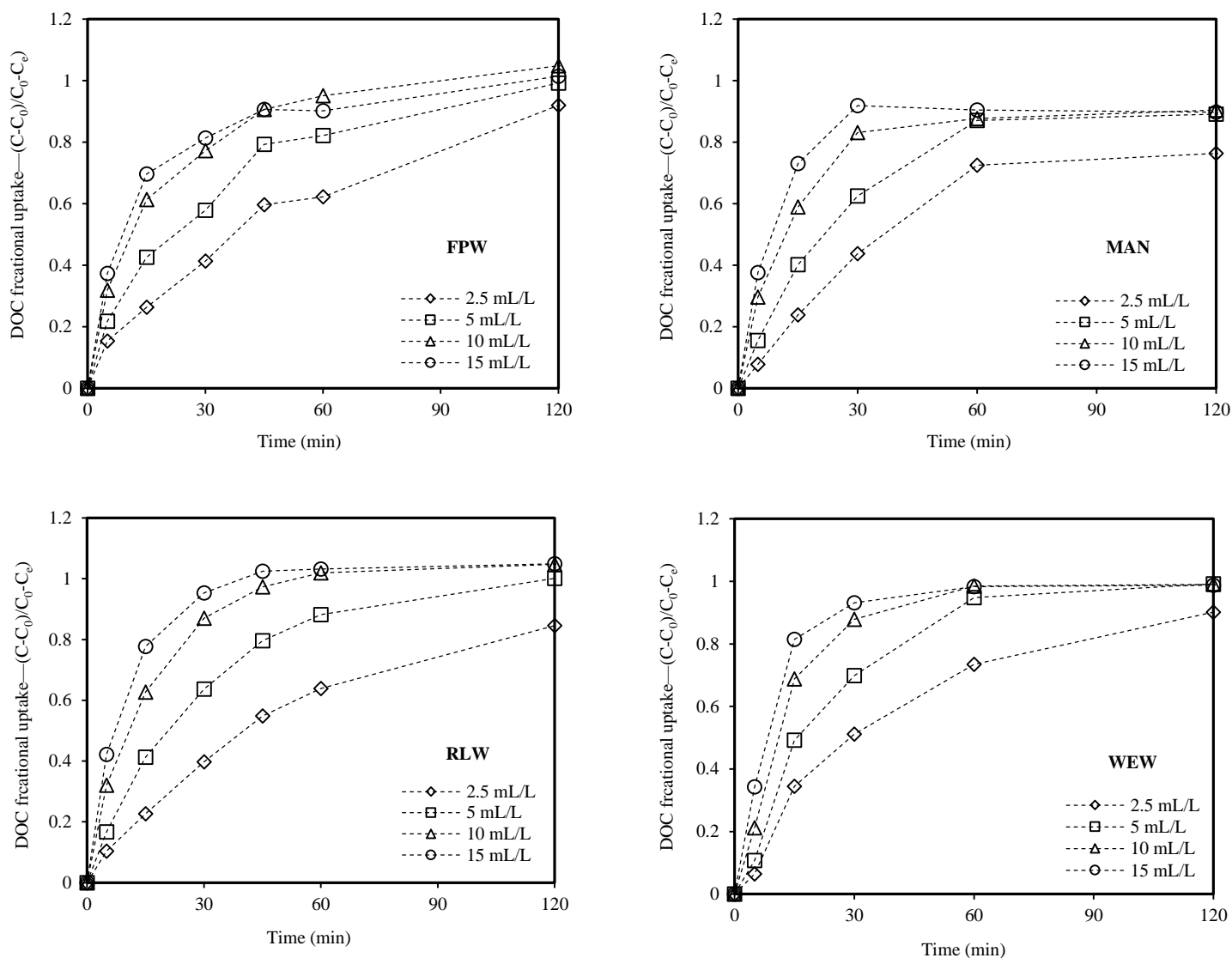


Figure 9.1, DOC fractional uptake under various amounts of A860 resin

The DOC removal rate for all waters under the highest resin dose (15 mL/L) is depicted in Figure 9.2. The kinetic data showed a rapid initial (first 30-45 minutes) decrease in DOC followed by a plateauing slow removal until equilibrium (24 hrs). The UVT improvement observed under 15 mL/L of resins showed 4-27 % increase for the waters treated with IEX. It should be noted that even at high resins dosages and long contact times certain fractions of DOC were not removed. The relative amount of non-removable DOC was 43 %, 34 %, 26 %, and 19

% for FPW, WEW, MAN, and RLW, respectively. The amount for non-removable DOC varied between 1.4 to 4.4 mg/L highlighting the importance and the crucial role that these fractions may play throughout the treatment, e.g., potentially reducing the treatment efficacy by scavenging OH radicals and screening UV. To further investigate this observation, SUVA profile of these waters were also monitored over the course of treatment. FPW, WEW, MAN, and RLW showed 77 %, 59 %, 69 %, and 63 % decrease in SUVA over 24 hrs exposure with 15 mL/L of resins. Therefore, the remainder non-removable DOC was mainly consisted of low-SUVA fractions which can be correlated to the findings of others (Cornelissen *et al.*, 2010; Huber *et al.*, 2011) where the fractions not removed by ion exchange treatment were identified to be biopolymers, building blocks and neutral fractions of NOM. It should be noted that these conclusions are drawn based on the high amount of resins used (15 mL/L) which provided extensive exchange sites for all the ions present in water minimizing their competition.

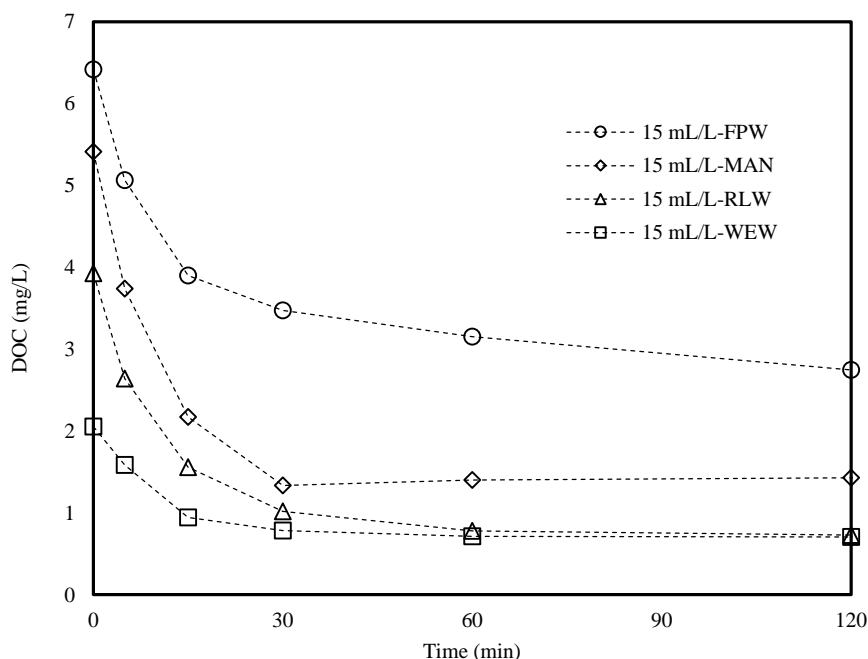


Figure 9.2, DOC profile of waters under 15 mL/L of ion exchange resins

9.3.2 Affinity of IEX resins towards various DOC fractions and anions

Presence of excessive amount of competing ions (e.g., SO_4^{2-}) could reduce the efficacy of IEX resins at removing DOC and NO_3^- . Hence, the relative affinity (i.e., preference) of the resins for DOC, SO_4^{2-} , and NO_3^- at equilibrium was investigated. Figure 9.3 shows the relative affinity of the A860 resin (at equilibrium) for the major anions present in the test waters. At very low resin dosages (e.g., $< 0.2 \text{ g/L} \approx 1 \text{ mL/L}$) the removal for all species was limited by the availability of exchange sites that in turn escalated the competition among ions. At these dosages, relatively higher DOC and SO_4^{2-} were removed compared to NO_3^- . The higher removal of DOC compared to SO_4^{2-} for MAN and RLW (which had higher SUVA) at the lower resin doses could be attributed to the blocking of resin pore channels by DOC molecules, thereby limiting the access of SO_4^{2-} (and NO_3^-) to inner channels (Zhang et al., 2014). At $0.57 \text{ g}_{\text{resin}}/\text{L}$ ($\approx 2 \text{ mL}_{\text{resin}}/\text{L}$), availability of exchange sites exceeds beyond the amount of charged molecules (i.e., SO_4^{2-} , NO_3^- , DIC, and DOC) present in water (for 2 mL/L of resins $\approx 1.6 \text{ meq/L}$, estimated net ions charge in each water: $\sim 1 \text{ meq/L}$). Therefore, both DOC and SO_4^{2-} profiles plateaued quickly and the one of NO_3^- increased further as a result of reduced competition. At $2.2 \text{ g}_{\text{resin}}/\text{L}$ ($\approx 10 \text{ mL}_{\text{resin}}/\text{L}$), which is a typical dose for stirred tank operations, 65, 80, and 97 % removals were recorded for NO_3^- , DOC, and SO_4^{2-} , respectively. The NO_3^- results for FPW and WEW have not been shown due to very low initial concentrations of NO_3^- in these waters.

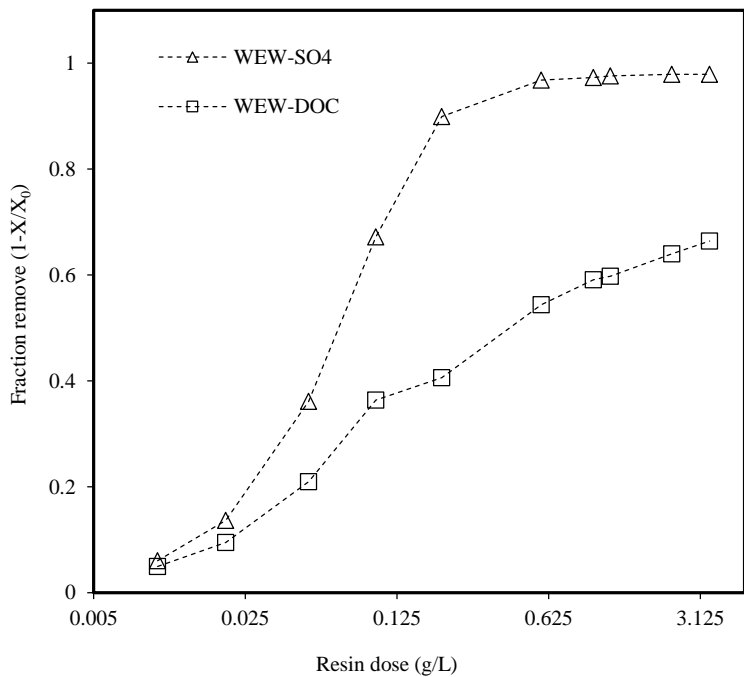
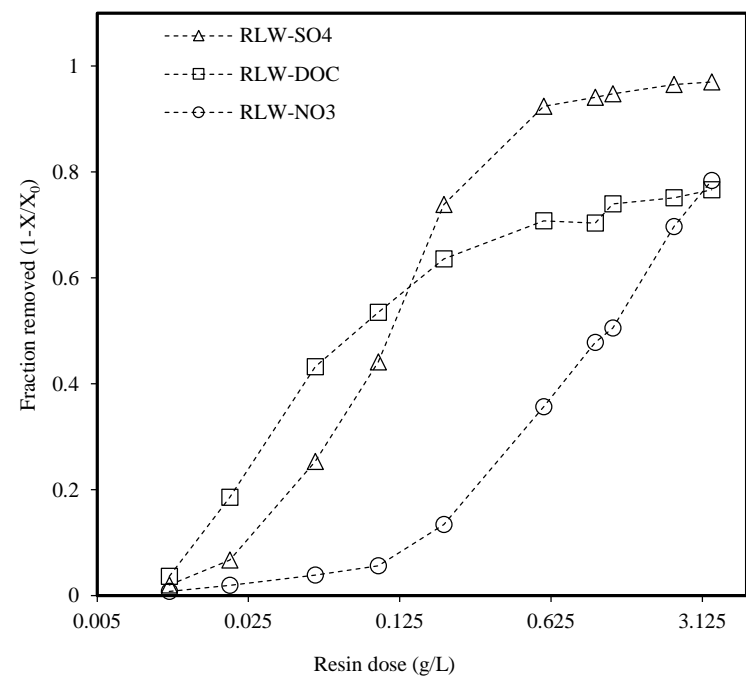
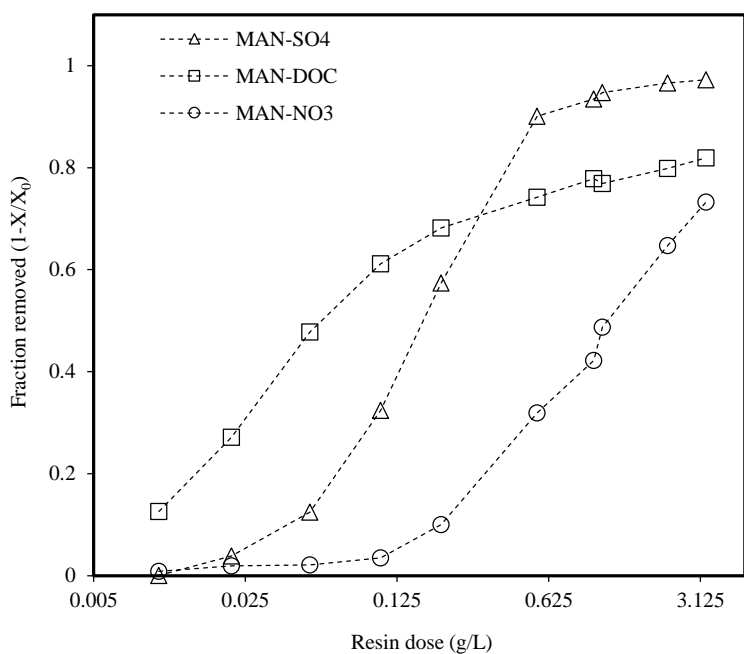
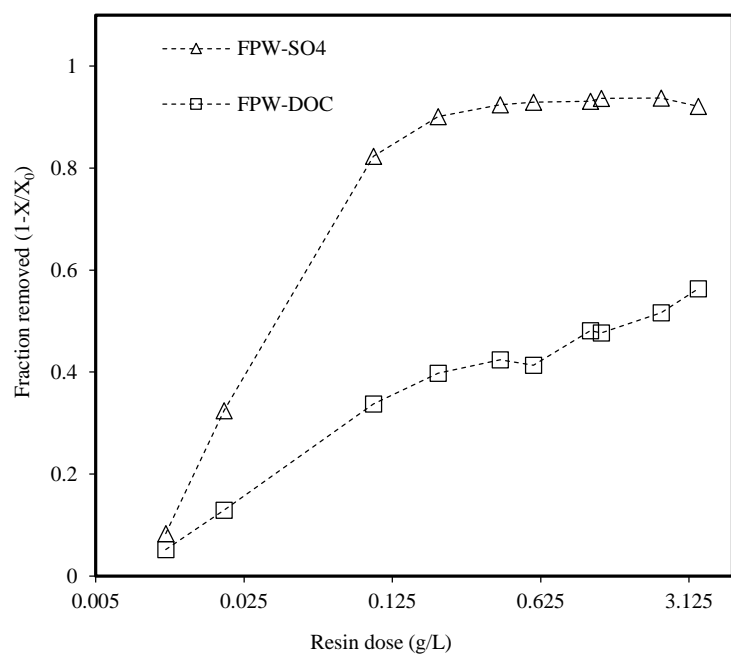


Figure 9.3, Affinity of IEX resin for DOC, SO₄²⁻, and NO₃⁻ in various waters

For all the waters examined, similar trends and extent of removals were observed for both SO_4^{2-} and NO_3^- , whereas the relevant DOC profiles for waters varied depending on the water source indicating the effect of NOM properties on the efficiency and the behavior of removal (Figure 9.4). A substantial fractional uptake was observed for all the waters with increasing the resins amounts up to 0.2 g/L and then profiles started to level off after 0.57 g/L. This further shows that the removal mechanism is dominated by ion exchange for all waters since further increase of exchange sites (from 0.57 to beyond) had minor impact on the removal efficacy. At higher doses of resins where the amount of exchange sites exceeded beyond the charged species, however, the extent of removal was different and yet limited for each water. It is hypothesized that the properties of DOC was a key affecting parameter here. MAN water showed to have the highest removal and affinity followed by RLW, WEW, and FPW. This was correlated to the initial SUVA value of these waters where MAN and RLW had higher values compared to WEW and FPW, indicating higher hydrophobicity. Results obtained for SUVA vs. resins dose also showed a rapid decrease in SUVA value for resin dose < 0.2 g/L followed by a slow change at higher doses. This indicated higher preference of resins for UV_{254} absorbing compounds (i.e., hydrophobic compounds) which were preferentially and rapidly removed even at low resin dosages. This was in agreement with kinetic data indicating that the non-removable portions of DOC were mainly low SUVA, less hydrophobic compounds likely to be biopolymers, building blocks and neutrals. Non-ionic, hydrophilic compounds have been shown to have a lower tendency for removal via ion exchange (Cornelissen et al., 2010; Huber et al., 2011), and also organic molecules with molecular sizes larger than the resins pores could get excluded from penetrating through the resin pores by size exclusion phenomenon (Tan and Kilduff, 2007; Zhang et al., 2014).

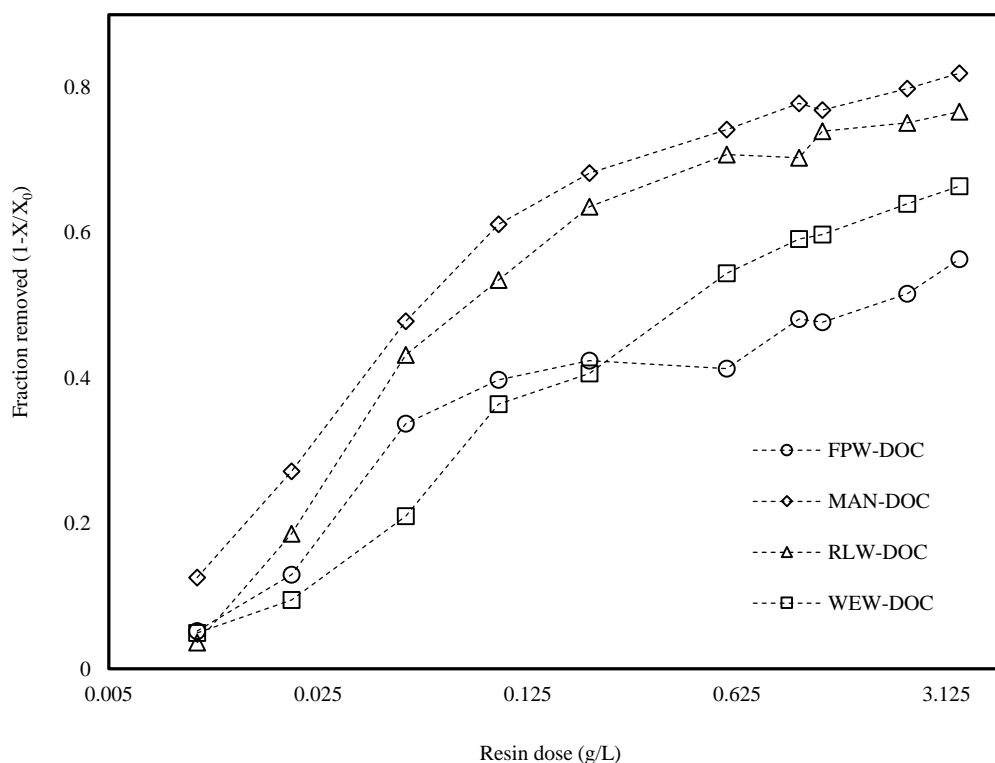


Figure 9.4, Fractional DOC removal under different doses at equilibrium

9.3.3 UV/H₂O₂ treatment

Based on the kinetic data, a condition of 10 mL_{resin}/L and 30 min of contact time was employed to pre-treat RLW, MAN, and WEW waters by IEX prior to UV/H₂O₂ treatment. Table 9.3 demonstrates the change in DOC, NO₃⁻, UVT, scavenging term (ST), and EEO of waters treated with IEX at the stated conditions. Changes in the ST and EEO were calculated according to the method of Rosenfeldt and Linden, (2007). The pCBA degradation data used to calculate the ST are illustrated in Figure 9.5.

Table 9.3, Change in the water parameters as result of IEX treatment (10 mL/L, 30 min)

Water source	ΔDOC—%	ΔNO₃⁻—%	ΔUVT—%	ΔST—%	ΔEEO—%
WEW	- 55	-88	+ 4	- 9	- 12
RLW	- 54	-50	+ 7	- 18	- 21
MAN	- 66	-13	+ 21	- 28	- 38

The two most important water quality parameters that affected EEO for the monochromatic UV reactor employed in these experiments were the UVT and ST. WEW water, a high UVT low DOC water, only exhibited a 4% improvement in UVT and 9% improvement in ST as a result of IEX treatment (Table 9.3). Nonetheless, this resulted in a 12 % improvement in EEO. Results obtained for MAN (UVT₀: 70 %) and RLW (UVT₀: 75 %), however, demonstrated larger improvements showing 21 and 38 % decrease in EEO, respectively. This was mainly attributed to the large increases in UVT (21% and 7%) and reductions in ST (28% and 18%) for MAN and RLW, respectively.

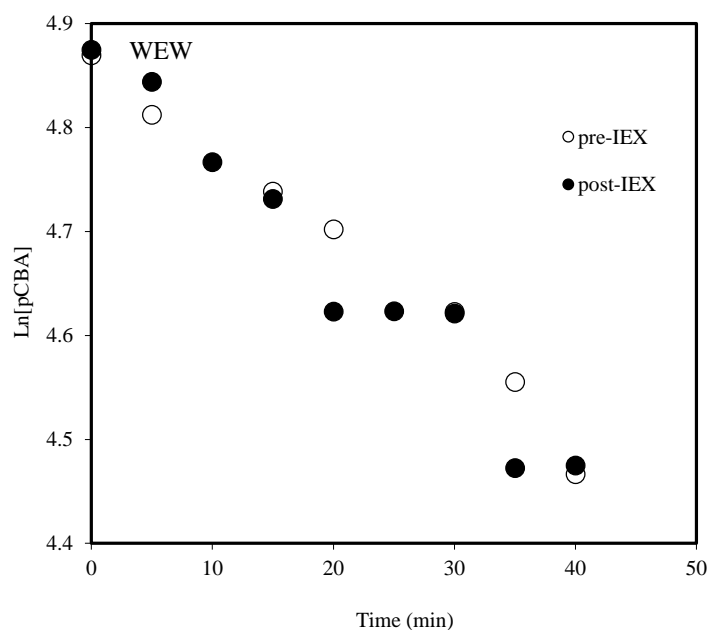
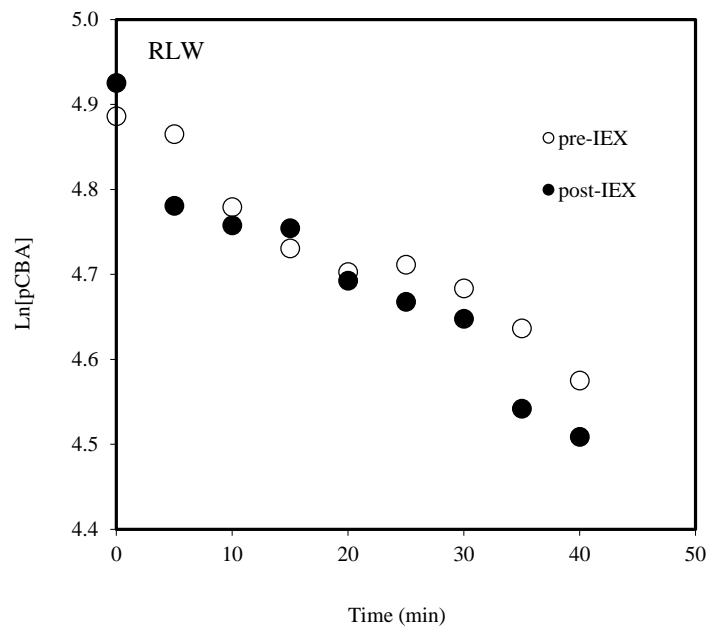
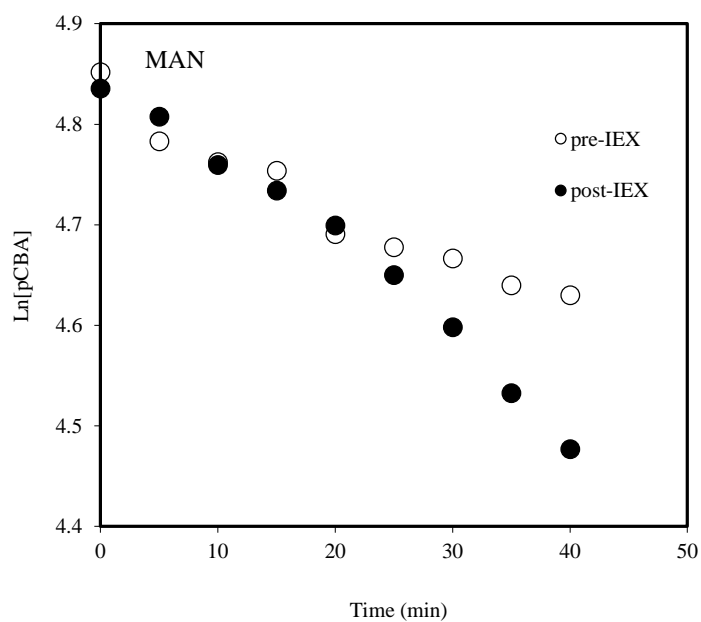


Figure 9.5, Degradation of pCBA during UV/H₂O₂ treatment of pre-IEX and post-IEX treated waters

The bench scale data here (using pCBA as the model compound) clearly pointed out the potential of using ion exchange process as a pretreatment to improve the efficiency of the UV/H₂O₂ process. It should be reinstated that the improvements in EEOs for IEX treated waters were primarily due to the increase in UVT and then due to the reduction in background

scavenging characteristic of the tested waters. Recall that these EEOs were calculated for a bench-scale collimated beam apparatus equipped with a low-pressure mercury amalgam lamp. Greater improvements in EEOs are expected in full-scale reactors given the longer path length available for UV transmission i.e., larger distance travelled by UV photons through water within the UV reactors. Also, since these tests were performed under monochromatic irradiation, the formation of nitrite, from nitrate, was not an issue as opposed to had the tests been done using a polychromatic UV source. For such medium pressure based systems, it is expected that the reduction in nitrate as a result of IEX treatment (4, 7, and 21% reduction of nitrate in WEW, RLW, and MAN, respectively, Table 3) would greatly reduce the formation of nitrite during UV/H₂O₂. Moreover, due to the removal of nitrate and DOC, IEX substantially improved the absorption spectrum between 200-300 nm (Figure 9.6). These reductions would lead to even greater reductions in EEO for polychromatic systems since (i) UVT is improved across the polychromatic irradiation spectrum (200-300 nm) and (ii) background hydroxyl radical scavenging by nitrite is reduced. Further work is required to qualify and quantify these expected benefits, in addition to studying the ability of IEX to mitigate potential increase in genotoxicity that could occur as a result of UV/H₂O₂ treatment.

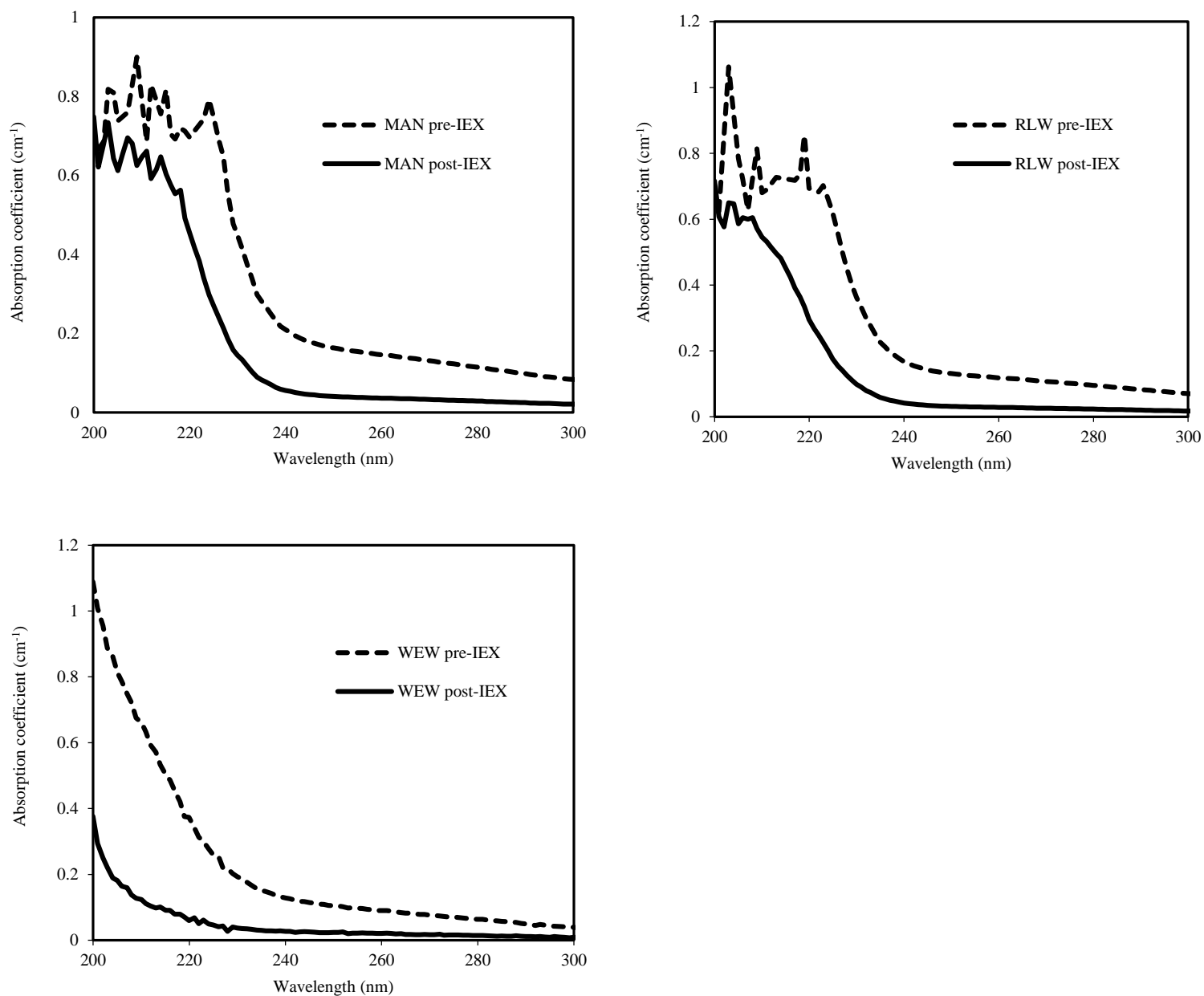


Figure 9.6, Absorption spectra of pre-IEX and post-IEX treated waters

9.3.4 Economics of the IEX process

The economics of using the IEX process could be complicated and highly dependent on the design of the process as well as the influent water quality. The following Table 9.4 demonstrates the economics of the MIEX[®] process for a 30 MGD (mega gallon per day)

treatment plant without taking into account the benefits from reduction in coagulant consumption. The amount of the salt consumed and waste produced can be further reduced to 110-150 lb/MG and 75-100 gal/MG of treated water, respectively, upon the use of EcoRegen™ Ultra low-waste MIEX® regeneration system⁷.

Table 9.4, Economics of MIEX® process for a 30 MGD plant (20 MGD average throughput)^{8,9}

Operating cost per year	0.76 M \$
Capital cost	19 M \$
20 year present worth cost @ 5%	28.5 M \$
Salt consumption	300 lb/MG of treated water (36 kg/ML)
Power consumption	38 kwh/MG of treated water (10 kWh/ML)
Waste produced	250 – 450 gal/MG of treated water

Having said that, Grefte et al., (2013) evaluated the feasibility of using IEX resins (not MIEX®) for the removal of NOM in different locations of a treatment train (i.e., before coagulation, before ozonation, and after slow sand filtration) and estimated the following cost and saving estimations for a treatment plant with the capacity of ~ 22 MGD (Table 9.5):

Table 9.5, Estimated cost and energy expenses for an IEX treatment plant (~ 22 MGD) in Netherlands

Total fixed cost	1224000 € year ~ 1420000 USD year
Energy	900 000 kwh year ~ 30 kwh/ML
Total IEX cost	0.0631 €/m ³ (0.0656-0.0622 €/m ³) ~ 0.0732 USD/m ³

⁷ Orica Watercare, Equipment Brochure, EcoRegen™ Ultra low-waste MIEX® regeneration system

⁸ Orica Watercare, Technical Note V0608, Lifecycle cost comparison of MIEX® vs. GAC

⁹ Orica Watercare, Technical Note V0509, Carbon footprint of MIEX®

The expected savings of using IEX before coagulation and or ozonation was between 0.0129-0.0166 €/m³ (~ 0.015-0.0192 USD/m³) and no advantage was found from using IEX after the slow sand filtration. Also, as a strategy to control DBPs formation (e.g., NDMA), Rosenfeldt et al., (2011) provided a basic present worth analysis (in 2011) of IEX process (process type not specified) for three different plant sizes. For a 50 MGD IEX treatment plant (average flow of 30 MGD), the capital cost and operation and maintenance were 47 M\$ and ~1.5 M\$ (yearly), respectively. Therefore, the type the technology used, location, and presumably the quality of the influent water can influence the economics of the IEX process.

9.4 Conclusions

The feasibility of using strongly basic ion exchange resins as a pretreatment process for UV/H₂O₂ advanced oxidation was investigated in this study. Under practical conditions (e.g., 10 mL/L and 30 min) and depending on the water source, reduction of 46-75 % in DOC, 52-80% in NO₃⁻, and 93-97 % in SO₄²⁻ and increase of 4-36 % in UVT was observed. These findings pointed out the efficiency of IEX at simultaneously removing DOC, SO₄²⁻, and NO₃⁻ at different extents. That said, certain fractions of DOC (i.e., NOM) were found to be non-removable by ion exchange even at high dosages (15 mL/L) and long contact time (24 hrs). These fractions were identified with low SUVA values indicating to be mainly hydrophilic and non-ionic. The effect of ion exchange treatment on the EEO of UV/H₂O₂ process was investigated in bench scale experiments using pCBA as the model compound. Waters treated with ion exchange showed between 12-38 % improvements in EEO under LP UV. These improvements were mainly due to the increase in the UVT and reduction of scavenging species which could be magnified further should polychromatic UV (i., MP UV) reactors are used for treatment. Due to simple installation and easy operation of IEX, this process can be retrofitted into facilities that aim to target micro

pollutants using UV/H₂O₂ advanced oxidation process but face the challenge of having low UVT water requiring a pretreatment process.

Chapter 10: Conclusions and Recommendations

10.1 Conclusions

- Selection of resins

Six different anion exchange resins underwent initial kinetic screening for the removal of natural organic matter. Resins were compared in terms of NOM removal kinetics, capacity, and physical properties (such as attrition) and the best two performing resins (from each category) were selected for subsequent experiments.

The two selected strongly basic (Purolite A860 – acrylic macroporous) and weakly basic (Purolite A847 – acrylic gel) IEX resins were compared in terms of their removal kinetics (i.e., rate) and regeneration efficiency under batch and simulated commercial conditions (i.e., consecutive multiple loadings). The kinetic experiments (performed at 10 mL/L of resins) did not show any tangible difference between the resins in terms of NOM removal; however, isotherms data indicated the strongly basic A860 possessed greater capacity and affinity for organic molecules. The results of consecutive multiple loadings (i.e., simulating realistic conditions) further elucidated the difference between resins suggesting greater long-term capacity (by about 10%) for TOC removal for the strongly basic A860.

Different regeneration scenarios were examined and results indicated that 50-85% of regeneration took place in the first 30-minutes. Moreover, increasing the regenerant amount (from 450:1 to 4500:1 g-NaCl/L-resins) had no tangible impact on the efficacy of regeneration. Overall, strongly basic A860 resins showed superior TOC removal and regeneration efficiency compared to weakly basic A847 (~ 20%) and hence, were recommended for future studies.

- Effect of NOM source on IEX process performance

Extensive kinetic experiments were conducted on four standard organic matter isolates to understand the effect of NOM properties on the kinetics and efficacy of IEX process for drinking water applications. Ion exchange was identified as the prevalent mechanism for the removal of organic matter. Also, charge density and molecular weight of organic molecules were found to influence the removal efficacy, with low charge density and high MW (i.e., size exclusion) adversely impacting the removal performance. The impact of MW became more pronounced during multiple consecutive batch loadings where the efficiency of removal declined considerably for larger MW organics (SRHA) compared to the smaller MW molecules (SRFA).

Pore diffusion was found to be the rate-limiting step during the uptake of organic matters; however, process parameters such as resin properties and resin/ C_0 ratio could affect this condition. With respect to the removal rates, organic isolates with lower MW showed higher uptake rates compared to the larger HA molecules. Aside from molecular weight of the organic matter, resin properties (e.g., ϵ , τ , R_p) and the affinity of the resin for organic matter (e.g., K_D) were found to impact the apparent diffusivity D_a thereby the overall removal rate during the practice of IEX. The estimated free liquid diffusivities of the organic isolates (D_l) corroborated with the reported data in the literature indicating the validity of the models and assumptions used.

- Effect of background water matrix on IEX process performance

Removal of dissolved organic carbon as well as NO_3^- and SO_4^{2-} from four different natural water sources using IEX process was investigated. Different resin doses and contact times were studied to gauge the performance of the treatment process applied. Overall, resin doses of 10-15 mL/L and 30-45 min of contact time were found to be sufficient to remove up to

80% of the DOC, and NO_3^- and up to 98 % from initial SO_4^{2-} . Nonetheless, a range of 19 % to 43 % of DOC corresponding to 0.7-2.8 mg/L was not removed even under high resin dosages and extended treatment times. Despite its lower uptake, the fastest removal rate was observed for NO_3^- followed by SO_4^{2-} and DOC indicating the effect of molecular size on diffusion coefficients thereby removal rate.

Utilization of pseudo 1st order kinetic model, film diffusion, and pore diffusion models were found to fit the experimental data very well ($R^2 > 0.96$). That said, by utilizing the Biot number concept, pore diffusion was found to be the rate-limiting step for the uptake of DOC.

- Effect of IEX on NOM fractions and subsequent water quality parameters
 - Impact on disinfection by-products

The effect of using ion exchange resins on the formation potential of disinfection by-products (DBPs), in particular nitrogenous DBPs, was investigated in this study. Synthetic waters made from standard organic isolates underwent consecutive multiple loadings of IEX resins and the impact of IEX treatment on NOM fractions and DBPs formation potential was studied. As a result of IEX treatment, humic (-like) substances of NOM were mainly targeted (40-67 % removal) whereas hydrophilic, non-ionic fractions such as biopolymers, neutrals, and building blocks were poorly removed (12-33 %). Charge density and MW of organic isolates were found to play a key role in the removal performance especially during consecutive multiple loadings.

Contrary to some studies reporting the increase in nitrogenous DBPs (in particular NDMA) as a result of IEX treatment, no release of nitrogenous DBPs and or their precursors was observed in this research. This is mainly attributed to the regeneration and rinsing the resins prior to their use. Moreover, findings demonstrated the efficacy of strongly basic IEX resins at

removing portions of total carbonous-DBPs FP (13-20 %) and total nitrogenous DBPs FP (3-50 %) throughout the multiple loadings. The greatest reduction in DOC, and DBPs was observed in the first cycle i.e., 1st 100BV and was reduced as treatment continued. The presence of dissolved organic nitrogen (DON) was found to be a key parameter affecting the formation of N-DBPs. DON, especially the portion affiliated with humic substances fraction, was reduced effectively (average ~ 77 %) as a result of IEX treatment.

- Impact on biological stability (i.e., Assimilable Organic Carbon)

Five different waters were used to study the impact of ion exchange treatment on different NOM fractions and subsequent water quality in terms of biostability i.e., AOC. Humic (-like) substances fractions of NOM were mainly targeted by ion exchange resins (85-100 % removal) whereas as neutrals (36-58 %), building blocks (31-72 %), and biopolymers (~ 11%) showed lower removal efficiency. The average MW of the remaining organics after IEX treatment increased by about ~ 10 % (after 30 min) and 10-20 times (after 24 hr) indicating that IEX mainly targets low-medium range molecules.

The average AOC removed in each treatment (Δ AOC) was found to have a statistically significant positive correlation with the average TOC removed in that treatment (Δ TOC). Overall, IEX reduced AOC levels by 30-40%, even though the remaining fractions (NE, BP, and BBs) showed to have a high potential and tendency to contribute to AOC (higher AOC/TOC). Nonetheless, all fractions of NOM contributed to AOC even though to different extents depending on their amount and biodegradability. Approaches similar to BDOC method (i.e., using a similar OND-TOC module rather than LC-OND) could be potentially useful and generate accurate results to assess the contribution of DON to biological stability of water.

- Impact on scavenging properties (i.e., OH radical and UV)

The feasibility of using strongly basic ion exchange resins as a pretreatment process for UV/H₂O₂ advanced oxidation was investigated in this study. Under practical conditions (e.g., 10 mL/L and 30 min) and depending on the water source, reductions of 46-75 % in DOC, 52-80% in NO₃⁻, and 93-97 % in SO₄²⁻, and increase of 4-36 % in UVT was observed. These findings suggest the efficiency of IEX at simultaneously removing DOC, SO₄²⁻, and NO₃⁻ at different extents. That said, certain fractions of DOC (i.e., NOM) were found to be non-removable by ion exchange even at high dosages (15 mL/L) and long contact time (24 hrs). These fractions were identified with low SUVA values representing mainly hydrophilic and non-ionic fractions. Furthermore, the effect of IEX treatment on the EEO of UV/H₂O₂ process was investigated using bench scale experiments with pCBA as the model compound. Waters treated with ion exchange showed 12-38 % improvements in EEO under LP UV. These improvements were mainly due to the increase in the UVT and reduction of scavenging species which could increase even further should polychromatic UV (i., MP UV) reactors be used for treatment. Due to simple installation and easy operation of IEX, this process could be retrofitted into facilities that aim to target micro pollutants using UV/H₂O₂ process but face the challenge of having low UVT water that requires a pretreatment process.

10.2 Significance of This Work

This study has taken a holistic approach to compare and select SBR and WBR resins for NOM removal based on removal kinetics, capacity, and regeneration efficacy. The approach undertaken in this study is suggested as a holistic decision making scheme to look at various

aspects that could influence the performance of IEX process (for NOM removal) in drinking water treatment applications.

Also, this research is one of the few (open) studies looking at the fundamental kinetics of NOM removal using standard aquatic NOM isolates, as well as natural water sources. The attempt made in this research to understand the kinetics and behaviour of IEX process under different treatment conditions, NOM sources, and water matrices is deemed valuable to gauge the robustness of the process applied for various water sources and also to efficiently combine IEX with other processes (e.g., filtration, oxidation processes) within a treatment train. Analyses and interpretations made from the kinetics data obtained could be beneficial to simulate, design, and fabricate efficient reactor set-up configuration in order to maximize NOM removal as well as regeneration efficiency.

Furthermore, this research has investigated the connection(s) between the effect of IEX process on NOM fractions and key water quality parameters such as (N-)DBPs, AOC, and HO• scavenging. Findings on the importance of resins preparation and process operation in eliminating the possibility of NDMA formation/release are potentially noteworthy for those employing IEX process. Also, feasibility of combining IEX with AOPs (i.e., UV/H₂O₂) has been suggested to be promising, thereby it warrants further investigations.

The engineering significance of this study was to demonstrate the practicality of the suspended IEX process for various water sources, develop lab scale protocols to select the best performing resins, and examine the applicability of this process for commercial installations. Findings of this study indicated the importance of optimizing the resin dose and contact time that can further lead to potential savings. Findings here highlighted the key role of the process

configuration (suspended mixing, process parameters) in determining the performance of the treatment process.

Overall, information obtained throughout the course of this study is deemed theoretically and practically valuable, and hence could contribute to the existing knowledge on IEX application and potentially open new opportunities towards efficient utilization of IEX process. Moreover, these findings could provide the basis for future studies concerning the application of IEX for organic matter removal from drinking water sources.

10.3 Recommendations for Future Work

- One of the obstacles throughout this study was the laborious preparation and availability (i.e., cost) of synthetic waters for consecutive multiple loadings. This also hindered the ability to test various regeneration scenarios and investigate the behaviour of resins after few regeneration cycles. Access to natural water sources to truly gauge the behaviour of IEX resins under extensive multiple loadings can further shed light on the performance (and limitations) of this process. It can also allow the use of spent resins for different regeneration scenarios.
- To overcome the challenges of multiple loadings, it is suggested to fabricate and utilize a pilot scale flow-through completely-stirred contactor that can be run for several cycles without the need to separate-reload the resins.
- Evaluation of the IEX process with different natural water sources is also highly encouraged to assess the robustness and performance of IEX under various water matrices. Also, the rate of removal is influenced by diffusivity of organic matter (and other species) which in turn is a function of temperature ($^{\circ}\text{K}$). Therefore, some seasonal

variations in performance might occur over the course of IEX operations. Year-round operation of IEX process (at pilot scale) can be used to address this uncertainty. Overall, this data could contribute to build upon the existing understating and create a wide database of the performance of IEX process versus different water qualities.

- Regeneration of spent resins has long been considered as one of the factors hindering its wide applications. Given the successful example of SIX[®] and MIEX[®] process in receiving considerable commercialization, further research focusing on optimizing the resin operation cycle, regeneration frequency, and process parameters such as resin/regenerant ratio, regenerant concentration, mixing speed, etc., can help and encourage the application of this process.
- Further research on the impact of IEX on N-DBPs, AOC, and HO• scavenging using wider range of water qualities is strongly recommended. Budget, resources, and time limitations did not allow further investigations on these subjects; however, the findings of this study are deemed to be noteworthy and shall guide further and more extensive investigations. Also, results obtained pointed to the key role and importance of hydrophilic, non-ionic fractions of NOM when DBPs (especially N-DBPs) are concerned. Hence, using isolation methods and/or preparative columns to make up and test these fractions is of great value and can further shed light on this subject.
- Conclusions made regarding the potential cost savings (i.e., reduction in EEO) by using IEX as a pre-treatment did not consider for the energy consumption of the IEX process. Hence, a comprehensive study with the aim of investigating the effect of IEX, as pre-treatment to UV/H₂O₂, on the total life cycle cost of IEX-UV/H₂O₂ is highly recommended.

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Appendices

Appendix A

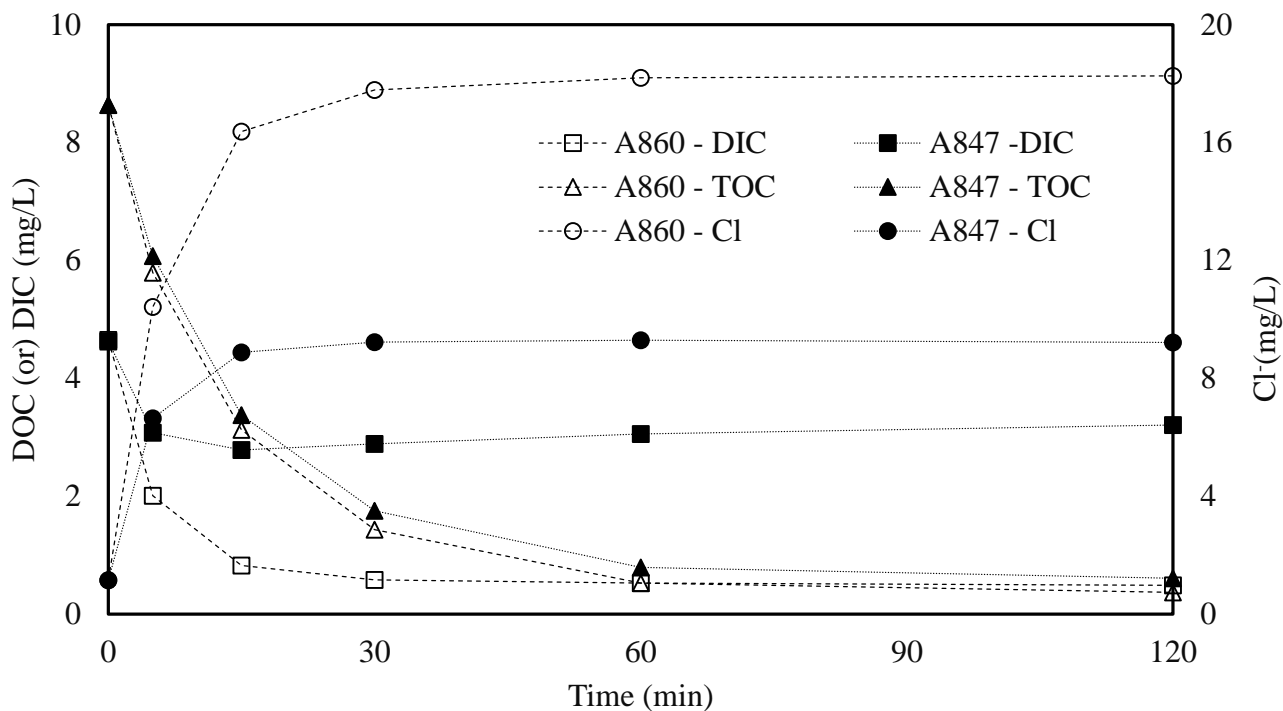


Figure A.1, TOC, DIC, and chloride profiles for A860 and A847 resins during kinetic tests

A.1 Charge Density Estimation

Charge densities for SRNOM isolate at pH~ 7.5 was calculated using the Henderson-Hasselbalch equation (Driver and Perdue, 2014; Ritchie and Perdue, 2003) and DOC concentrations were subsequently converted to meq/L. 1 mL of wet resin was approximately 221 mg after drying in desiccator. Hence the resin doses were also converted to meq/L using the exchange capacities reported in Table 4.2 (assuming all exchanges sites already occupied by Cl⁻).

A.2 Impact of Resins on Molecular Weight Distribution of NOM

The effect of two different resins doses after 24 hrs (i.e., equilibrium) on apparent molecular weight distribution of NOM is depicted in Figure A.2. As shown, 200 mg/L of A860

outperformed identical amount of A847, in terms of removing medium-large molecular weight fractions. However, with the increase of resin dose to 1000 mg/L, the difference between the two resins' performance became less pronounced and both resins removed major (and similar) portions of medium-high molecular weight organics. That said, small late eluting peaks did not show a tangible change under applications of resins. This observation has also been reported by others and is because of the non-ionic/neutral nature of those small molecules (Cornelissen et al., 2008; Huber et al., 2011). Overall, the HPSEC chromatograms were found insufficient to demonstrate a tangible difference between the impacts of resins on molecular weight distribution of NOM.

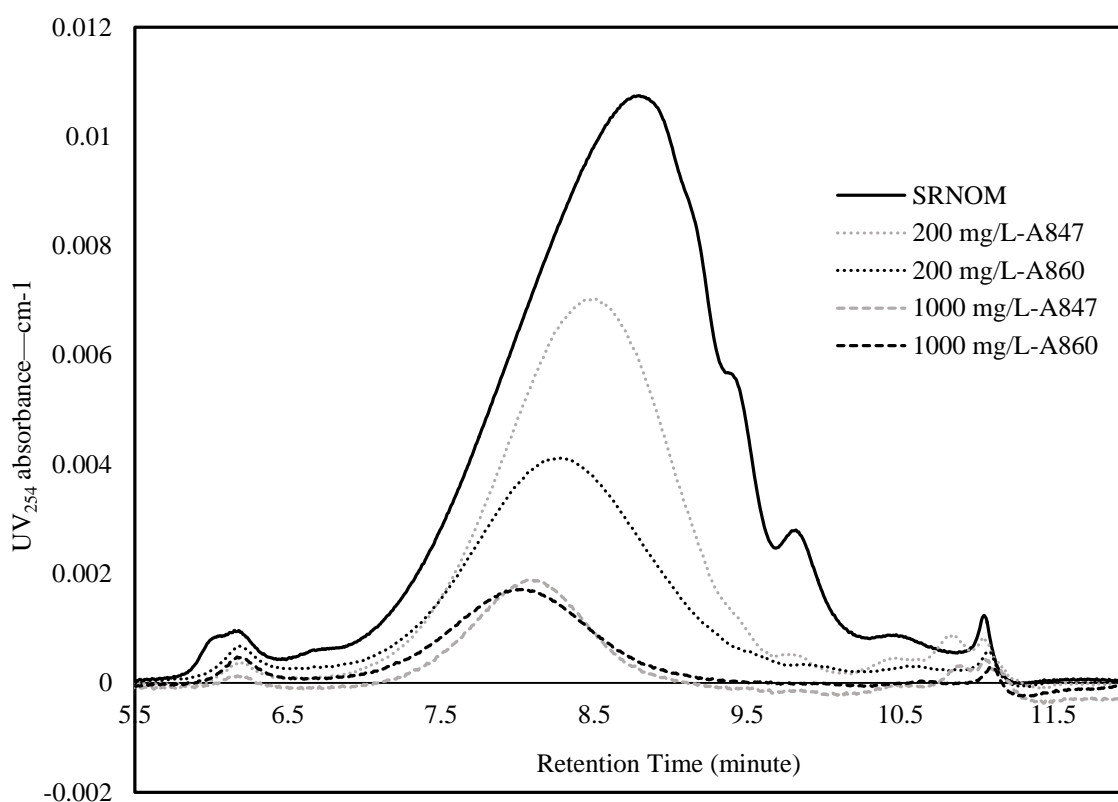


Figure A.2, HPSEC chromatogram of SRNOM for various doses of resins at equilibrium

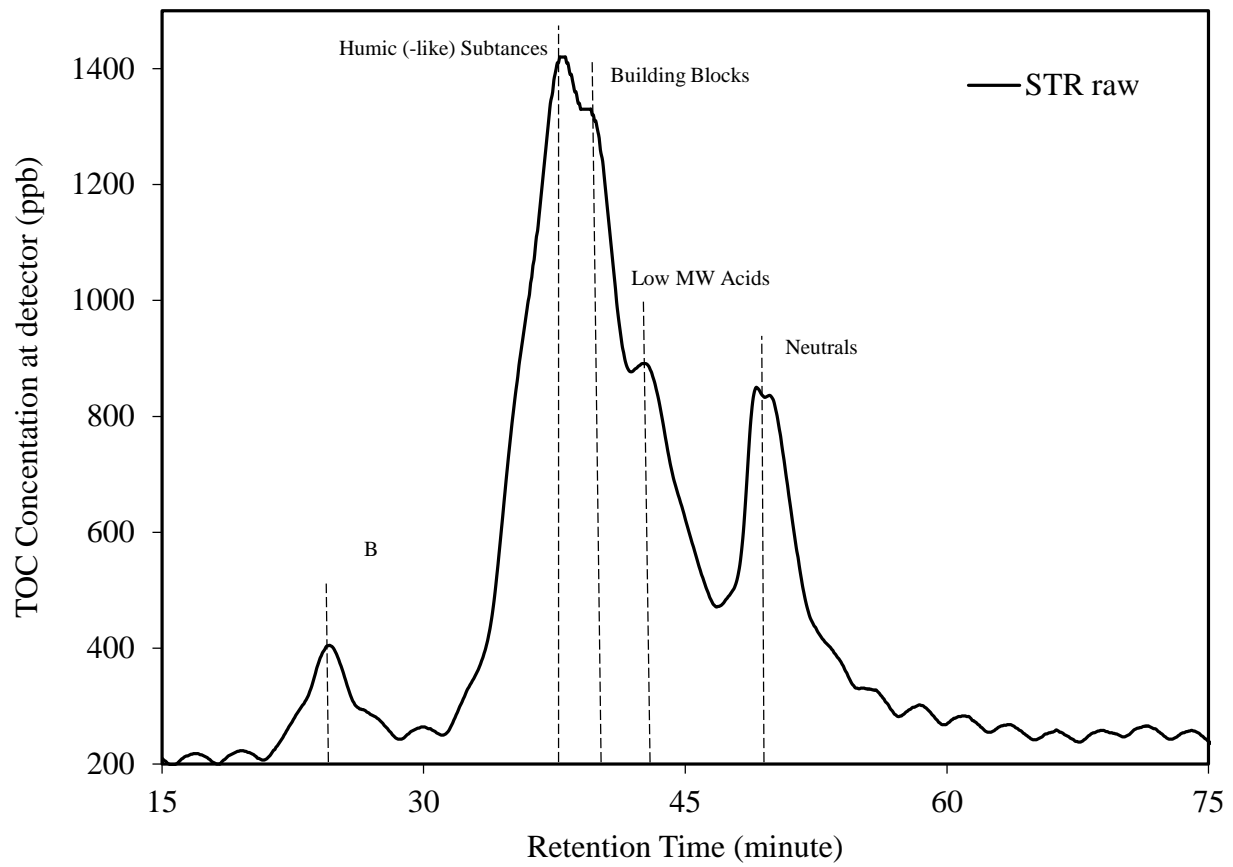


Figure A.3, LC-OCD chromatogram of the Ste-Rose water (RW)

Appendix B

B.1 Charge Density Estimation

Charge densities for all isolates at pH~ 7.55 were calculated using the Henderson-Hasselbalch equation (Driver and Perdue, 2014; Ritchie and Perdue, 2003) and DOC concentrations were subsequently converted to meq/L (Table 5.1). According to the manufacturer, resins exchange capacity was 0.8 meq/mL and 1 mL of wet resin was approximately 221 mg after drying in desiccator. Hence the resin doses were also converted to meq/L (assuming all exchanges sites already occupied by Cl^-) as well. The diagonal line ($X=Y$) demonstrates the ideal ion exchange. To standardize the comparison among different isolates, the TOC fraction removed was plotted against the amount of resins used (meq/L) normalized by the initial TOC concentration (meq/L) i.e., Resin/ C_0 (meq/meq) (Figure 5.1.C)

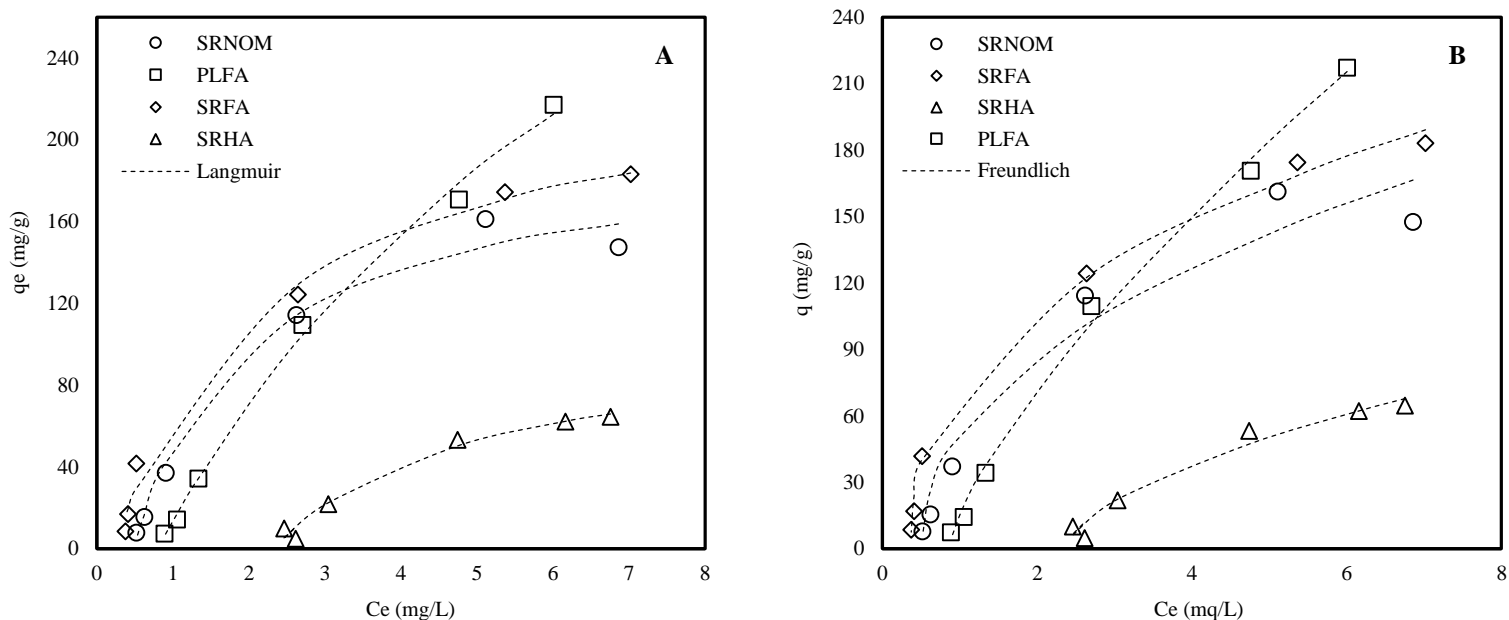


Figure B.1, Isotherm data (markers) fitted by modified Langmuir equation (A) and modified Freundlich equation (B)

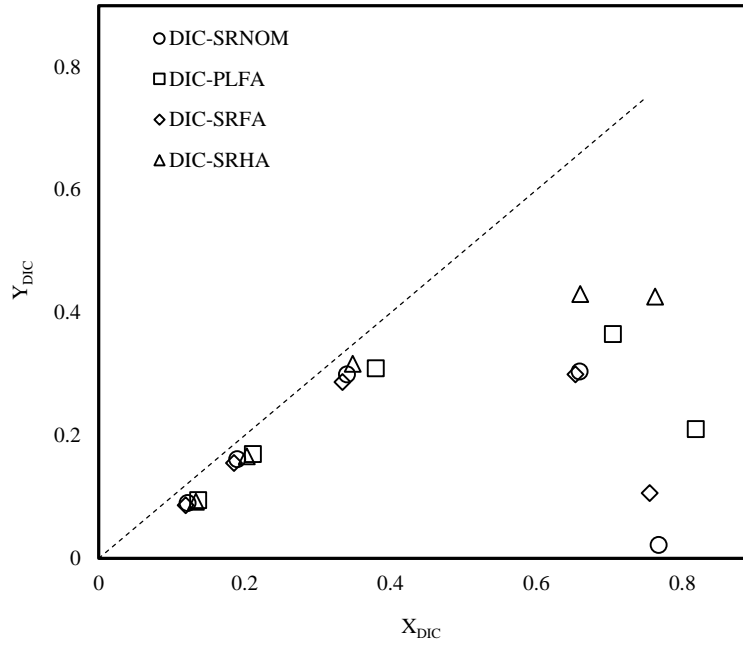


Figure B.2, DIC ternary equilibrium (TOC, HCO_3^- , and Cl^-) for NOM isolates

B.2 Mathematical and Kinetic Models

Pseudo-first order equation (Boyd et al., 1947):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (\text{A.1})$$

Pseudo-second order equation (Ho and McKay, 1999):

$$q_t = \frac{k_2 t q_e^2}{(1 + k_2 t q_e)} \quad (\text{A.2})$$

Intraparticle diffusion model (Boyer et al., 2008a; Chen et al., 2002; Weaver and Carta, 1996; Wu and Gschwend, 1988):

$$\varepsilon \frac{\partial c}{\partial t} + (1 - \varepsilon) \rho_s \frac{\partial q}{\partial t} = \frac{\varepsilon D_{eff}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) \quad (\text{A.3})$$

$$c(t = 0, r) = 0,$$

$$\left. \frac{\partial c}{\partial r} \right|_{r=0} = 0, t > 0$$

$$c(t > 0, r = R) = C$$

$$\frac{dC}{dt} = - \frac{3X_R \rho_a \varepsilon D_{p,e}}{(1 - \varepsilon) \rho_s} \left. \frac{\partial c}{\partial r} \right|_{r=R} \quad (\text{A.4})$$

Where q_t is the resin phase concentration at t (mg/g), q_e is the resin phase concentration at equilibrium (mg/g), q is solid phase concentration (mg/g), k_1 and k_2 are kinetic rate constants, ε is the resin porosity (estimated using Hg-porosimetry ~ 0.46), c is the concentration in the pore fluid (mg/L), C is bulk concentration (mg/L), t is time (s), ρ_s is solid phase density (1.08 g/cm³ according to manufacturer), ρ_a is apparent resin density, $D_{p,e}$ is effective pore diffusion coefficient (cm²/s), and R is the mean radius of resins (cm).

The reported R range for the A860 from the manufacture was 150 – 600 μm and an average value of 375 μm was assumed for all calculations. That said, some researchers have accounted for the resins particle size distribution in their modeling approach (Boyer et al., 2008a; Weaver and Carta, 1996; Wu and Gschwend, 1988).

Table B.1, Kinetic rate constants for pseudo 1st and 2nd order models (95% confidence level)

	k₁	R²	k₂	R²
SRNOM	0.081 \pm 0.003	0.9973	0.044 \pm 0.009	0.9654
SRFA	0.08 \pm 0.005	0.9948	0.041 \pm 0.008	0.9707
SRHA	0.05 \pm 0.005	0.9748	0.031 \pm 0.002	0.9962
PLFA	0.107 \pm 0.008	0.9914	0.064 \pm 0.011	0.9771

B.3 Calculation of D_l and $D_{p,e}$

D_a accounts for free liquid diffusion and sorption to resins resistances, and tortuous diffusion pathway through inside the resins and is correlated to effective pore diffusivity ($D_{p,e}$) and free liquid diffusivity (D_l) as follows (Weber Jr and DiGiano, 1996):

$$D_a = \frac{D_l \cdot \varepsilon / \tau}{[(1 - \varepsilon) \rho_s K_D + \varepsilon]} = \frac{D_{p,e} \cdot \varepsilon}{[(1 - \varepsilon) \rho_s K_D + \varepsilon]} \quad (\text{A.5})$$

Where τ is the tortuosity of the resin and is estimated to be ~ 3 (Li and SenGupta, 2000), and K_D was the linear equilibrium partition coefficient. The term $[(1-\varepsilon) \rho_s K_D + \varepsilon]$ is referred to as retardation factor, by which the liquid diffusivity is reduced due to local microscale partitioning, and ε/τ accounts for reduction in D_l because of the tortuosity of the diffusion path (Weber Jr and DiGiano, 1996; Wu and Gschwend, 1988). Assuming a linear distribution of DOC between the solid and liquid phases was plausible because of the low concentrations of the solute (i.e., ~ 9 mg/L DOC) and high selectivity of the resins for DOC ($\sim \alpha = 5.5\text{-}6$) (Boyer et al., 2008a; Li and SenGupta, 2011). The R^2 values obtained for the linear correlation were between 0.85-98 and are shown in Table B.2.

Table B.2, K_D , and retardation factors for pore diffusion model

	K_D - L/g	R^2	$\tau[(1-\varepsilon) \rho_s K_D + \varepsilon]/\varepsilon$
SRNOM	23.8	0.851	87.79
SRFA	26.4	0.985	97.05
SRHA	14.00	0.939	52.87
PLFA	40.73	0.918	148.10

Appendix C

C.1 Adsorption Isotherm Data for Nitrate and Sulfate

Because of the very low levels of NO_3^- in FPW and WEW ($< 1 \text{ mg/L}$) the NO_3^- isotherms data of these two waters were dismissed. Also, greater preference for SO_4^{2-} and DOC hampered the NO_3^- removal at low resin dosages making the changes in NO_3^- concentration at low dosages (10, 20, and 50 mg/L of resins) within the detection limit of the equipment. As a result, data related to this range were also disregarded. Similarly the SO_4^{2-} data related to 10 mg/L of resin were removed from the graphs.

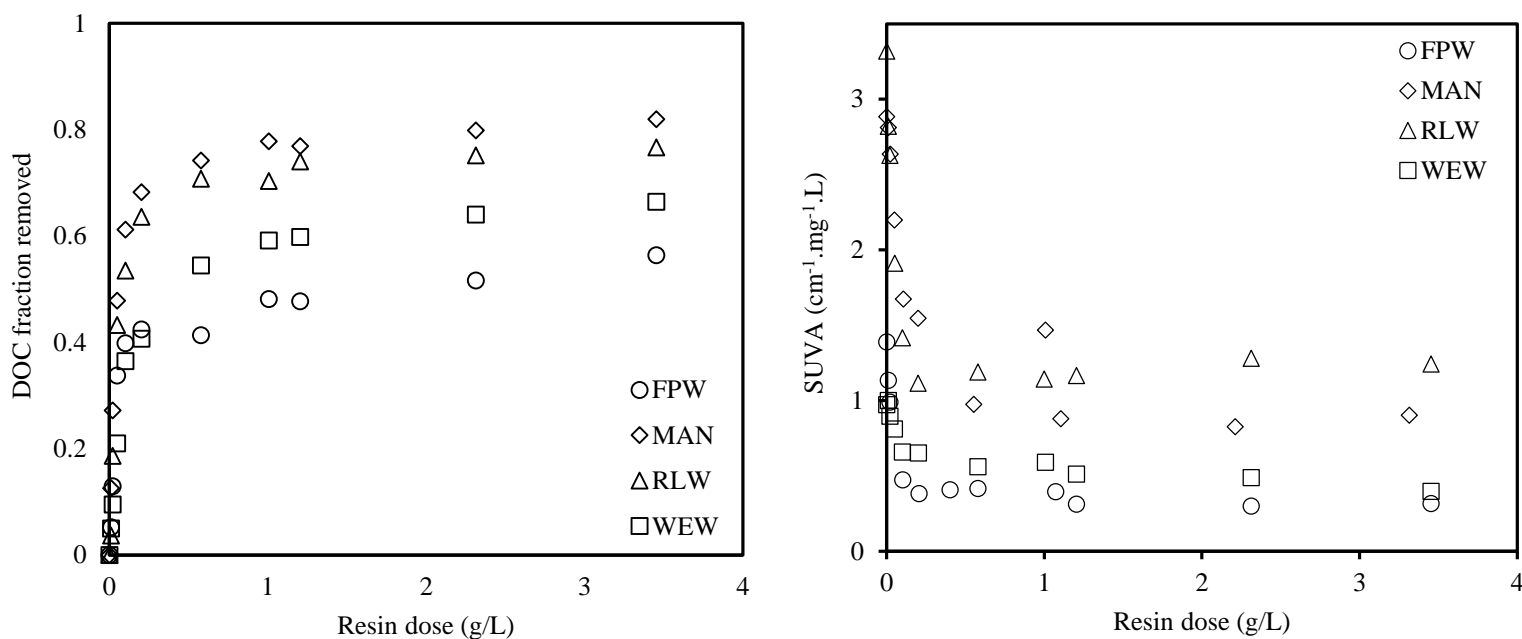


Figure C.1, DOC fraction removed and SUVA vs. resin dose

C.2 Mathematical and Kinetic Models

Pseudo-first order equation (Boyd et al., 1947):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (\text{A.1})$$

Pseudo-second order equation (Ho and McKay, 1999):

$$q_t = \frac{k_2 t q_e^2}{(1 + k_2 t q_e)} \quad (\text{A.2})$$

Where q_t is the resin phase concentration at t (mg/g), q_e is the resin phase concentration at equilibrium (mg/g), q is solid phase concentration (mg/g), and k_1 and k_2 are kinetic rate constants.

The reported R_p range for the A860 from the manufacture was 150 – 600 μm and an average value of 375 μm was assumed for all calculations. That said, some researchers have accounted for the resins particle size distribution in their modeling approach (Boyer et al., 2008a; Weaver and Carta, 1996; Wu and Gschwend, 1988).

C.3 Calculation of Retardation Factor and $D_{p,e}$

D_a accounts for free liquid diffusion (D_l) and sorption to resins resistances, and tortuous diffusion pathway through inside the resins and is correlated to effective pore diffusivity ($D_{p,e}$) as follows (Weber Jr and DiGiano, 1996):

$$D_a = \frac{D_l \cdot \varepsilon / \tau}{[(1 - \varepsilon)\rho_s K_D + \varepsilon]} = \frac{D_{p,e} \cdot \varepsilon}{[(1 - \varepsilon)\rho_s K_D + \varepsilon]} \quad (\text{A.5})$$

Where K_D is the linear equilibrium partition coefficient, ε is the resin porosity (estimated using Hg-porosimetry ~ 0.46), τ is the tortuosity of the resin and is estimated to be ~ 3 (Li and SenGupta, 2000), ρ_s is solid phase density (1.08 g/cm³ according to manufacturer), and $D_{p,e}$ is effective pore diffusion coefficient (cm²/s).

The term $[(1-\epsilon) \rho_s K_D + \epsilon]$ is referred to as retardation factor, by which the liquid diffusivity is reduced due to local microscale partitioning, and ϵ/τ accounts for reduction in D_l because of the tortuosity of the diffusion path (Weber Jr and DiGiano, 1996; Wu and Gschwend, 1988). Assuming a linear distribution of DOC between the solid and liquid phases was plausible because of the low concentrations of the solute (i.e., ~ 2-6 mg/L DOC) and high selectivity of the resins for DOC (Boyer et al., 2008a; Li and SenGupta, 2011). The R^2 values obtained for the linear correlation were between 0.910-0.960.

Table C.1, K_D and R_t values for the waters studied

Source Water	K_D	R^2	R_t
FPW	10.28	0.933	39.62
MAN	20.59	0.944	76.34
RLW	17.60	0.908	65.71
WEW	8.45	0.960	33.09

Table C.2, Estimated D_f values for various treatment conditions and water sources

D_f, DOC						
Resin Dose (mL/L)	FPW	FPW + NO ₃ ⁻	MAN	RLW	RLW + NO ₃ ⁻	WEW
2.5	1.56E-6	1.36E-6	1.50E-6	1.46E-6	1.40E-6	1.93E-6
5	1.37E-6	1.23E-6	1.37E-6	1.46E-6	1.46E-6	1.72E-6
10	1.23E-6	9.99E-7	1.23E-6	1.46E-6	1.32E-6	1.43E-6
15	1.01E-6	8.38E-7	1.23E-6	1.46E-6	1.29E-6	1.36E-6
D_f, NO₃⁻						
Resin Dose (mL/L)	¹ FPW + NO ₃ ⁻	MAN	RLW	RLW + NO ₃ ⁻	¹ WEW	
2.5	6.88E-6	1.97E-5	1.79E-5	1.53E-5	6.86E-6	
5	5.80E-6	1.09E-5	1.09E-5	1.09E-5	5.96E-6	
10	5.82E-6	7.64E-6	7.58E-6	7.61E-6	4.56E-6	
15	4.97E-6	6.75E-6	6.02E-6	6.67E-6	4.13E-6	
D_f, SO₄²⁻						
Resin Dose (mL/L)	² FPW	FPW +25 NO ₃ ⁻	MAN	RLW	RLW + NO ₃ ⁻	WEW
2.5	2.58E-6	2.75E-6	3.36E-6	3.19E-6	3.22E-6	2.95E-6
5	1.58E-6	2.97E-6	3.46E-6	3.14E-6	3.00E-6	3.34E-6
10	2.69E-6	2.46E-6	2.59E-6	3.07E-6	3.04E-6	2.95E-6
15	3.57E-6	2.85E-6	3.15E-6	2.96E-6	3.06E-6	3.10E-6

¹ Nitrate levels in raw FPW and WEW were < 1 mg/L and near the detection limit

² Sulfate level in raw FPW was < 6 mg/L

Table C.3, Estimated D_a values for various treatment conditions and water sources

D _a , DOC						
Resin Dose (mL/L)	FPW	FPW + NO ₃ ⁻	MAN	RLW	RLW + NO ₃ ⁻	WEW
2.5	1.97E-8	1.64E-8	1.79E-8	1.72E-8	1.69E-8	2.47E-8
5	3.70E-8	3.25E-8	3.59E-8	4.05E-8	4.08E-8	4.80E-8
10	7.26E-8	5.54E-8	6.65E-8	8.76E-8	7.74E-8	8.32E-8
15	8.66E-8	7.07E-8	1.05E-7	1.35E-7	1.15E-7	1.23E-7
D _a , NO ₃						
Resin Dose (mL/L)	¹ FPW + NO ₃ ⁻	MAN	RLW	RLW + NO ₃ ⁻	¹ WEW	
2.5	9.98E-8	3.55E-7	3.39E-7	2.72E-7	9.51E-8	
5	1.71E-7	4.03E-7	4.25E-7	4.13E-7	1.84E-7	
10	4.10E-7	5.97E-7	5.94E-7	5.98E-7	3.12E-7	
15	5.60E-7	8.52E-7	7.35E-7	8.39E-7	4.40E-7	
D _a , SO ₄ ²⁻						
Resin Dose (mL/L)	² FPW	FPW + NO ₃ ⁻	MAN	RLW	RLW+ NO ₃ ⁻	WEW
2.5	3.27E-8	3.74E-8	4.64E-8	4.36E-8	4.49E-8	4.05E-8
5	3.97E-8	8.74E-8	1.03E-7	9.35E-8	8.87E-8	9.72E-8
10	1.65E-7	1.54E-7	1.64E-7	1.94E-7	1.93E-7	1.83E-7
15	3.68E-7	2.83E-7	3.17E-7	2.95E-7	3.06E-7	3.07E-7

¹ Nitrate levels in raw FPW and WEW were < 1 mg/L and near the detection limit

² Sulfate level in raw FPW was < 6 mg/L

Table C.4, Estimated $D_{p,e}$ values for various treatment conditions and water sources

$D_{p,e}$					
Resin Dose (mL/L)	FPW	MAN	RLW	WEW	
2.5	2.60E-07	4.54E-07	3.77E-07	2.73E-07	
5	4.89E-07	9.12E-07	8.87E-07	5.30E-07	
10	9.59E-07	1.69E-06	1.92E-06	9.18E-07	
15	1.14E-06	2.67E-06	2.96E-06	1.36E-06	

Table C.5, Biot number for NO_3^- and SO_4^{2-} removal under various resin dose and source waters

	$K_D (R^2)$				
	NO_3^-		SO_4^{2-}		
	MAN	RLW	MAN	RLW	WEW
	0.807	0.869	18.22	27.32	123.01
	(0.950)	(0.972)	(0.988)	(0.974)	(0.977)
Resin Dose (mL/L)	Bi				
2.5	1024	1011	120	82	19
5	499	491	56	38	9
10	236	244	26	18	4
15	146	157	16	11	3

Appendix D

D.1 Glassware, Tools, Resins, and Sample Preparation

For more consistency in preparation, 20 mg of a standard organic isolate (purchased from International Humic Substances Society, IHSS) was dissolved in 1L of phosphate buffer (made from Milli-Q water and ACS reagent grade chemicals and filtered through 0.45 μm) on the day of experiment (Table 7.1). Waters prepared were stored in specially prepared glass amber bottles at 4°C in dark. Pipette tips were autoclaved and kept away from potential contamination. All tools (glassware, flasks, funnels, glass filters 1.6 μm) were heated at 550°C for 5 hrs according to the method described elsewhere (Mitch et al., 2003; Mitch and Sedlak, 2002).

D.2 Resins Preparation

The strongly basic resins used in this study was Purolite A860 which was selected through previous screenings conducted by the authors (Bazri and Mohseni, 2014; Monosov et al., 2012) in which this resins showed to have superior performance in removing NOM. The characteristics for A860 were water content (65-70%), resin size (300-1200 μm) and exchange capacity of 0.8 eq/L of resin according to the manufacturer¹⁰. To eliminate possible background/manufacturer contamination affecting the analysis, A860 Purolite macroporous acrylic strongly basic resins were initially regenerated using NaCl 10% (wt%) and triple-rinsed with Milli-Q water.

D.3 Analytical Methods

Total and Dissolved Organic Carbon (TOC, DOC) was measured using a Shimadzu-VCPH TOC analyzer. UV scans were carried out using a UV-Vis spectrophotometer. Nitrate was measured using ion chromatography according to standard method SM 4110 using a Dionex

¹⁰ www.purolite.com

instrument. Molecular weight distribution of NOM was assessed through liquid chromatography (LC) equipped with size exclusion chromatography column (250 mm x 20 mm, TSK HW 50S, 3000 theoretical plates, Toso, Japan), organic carbon detector (OCD), and organic nitrogen detector (OND) using a DOC-LABOR system (Germany). This is based on the size exclusion chromatography – organic carbon detection (SEC-OCD) method originally developed by Huber and Frimmel, (1991) which was later modified by them (Huber and Frimmel, (1994); Her et al., (2002)) and has been used to characterize the organic matter in various water and wastewater sources (Allpike et al., 2007, 2005; Amy and Her, 2004; Cornelissen et al., 2008; Dittmar and Kattner, 2003; Grefte et al., 2013; Grünheid et al., 2005). The detailed description of the LC-OCD method and the equipment employed in this study is provided in Huber et al., (2011).

Samples for DBPs FP test were spiked with sodium hypochlorite (NaOCl, 2M stock) and incubated in dark at 25°C for 24 hrs according to the method of Krasner et al., (2004):

$$\text{Cl}_2 \text{ (mg/L)} = 3 \times \text{DOC (mg/L)} + 7.6 \times \text{NH}_3 \text{ (mg-N/L)} + 10 \text{ mg/L}$$

After incubation samples were quenched of (and confirmed) chlorine using stoichiometric amount of ascorbic acid (Chu et al., 2010a; Weinberg, 2009) and analyzed for nitrosamines and nitrogenous by-products¹¹. Chlorine (and residual chlorine) was measured using the colorimetric DPD method according to the Standard Method 4500-Cl (Rice et al., 2012).

Identical aliquots of a given quenched sample underwent further analysis for volatile, semi-volatile, and non-volatile DBPs. The volatile compounds (Table D.1) were detected by adding the chlorine-quenched samples to vials containing ~ 2 mL H₂SO₄ (2M) and were

¹¹ To save time, number of samples and cost, samples were collected at 100 BV (1st cycle), 300 BV (3rd cycle) and 600 BV (6th cycle) only.

immediately analyzed using purge and trap injection (Tekmar Stratum PTC) combined with GCMS (Thermo ISQ) equipped with Restek RTX-VMS 60 mm x 0,32 mm df 1.8 μ m column. A volatile deuterated compound (d8-naphthalene) was added as the internal standard and boiled water served as the blank. The analysis were done according to the USEPA Method 524.3 as also described by others (Chu et al., 2014; Prakash et al., 2009; Siegal et al., 2015; Weinberg, 2009).

Another aliquot of the same samples was simultaneously analyzed for semi-volatile, and non-volatile DBPs (Table D.1) using solid phase extraction (XAD) combined with GCMS (Thermo ISQ, Large volume injector) equipped with Restek RXI 5-SilMS, 60 m x 0,25 mm df 0,25 μ m column. An internal standard (d8-naphthalene 0.2 μ g/L) was added and boiled water served as the blank. Kovats Index was used for better quantification when possible. The analysis were done according to the method of Weinberg et al., (2002) and Richardson et al., (1999) that has been also reported by others (Plewa et al., 2004; Richardson et al., 2007; Weinberg, 2009).

All these PTI-GCMS and XAD-GCMS analyses were conducted at Het Waterlaboratorium, Haarlem, Netherlands using GC-Analyzer program (MS-Metrix, Maarsen, Holland). Compounds with concentrations of less than 0.01 (μ g/L) were not considered in the analysis (limit of quantification). Except for the nitrosamines all concentrations of the byproducts have been measured by a screening method (i.e., semi-quantitative).

For nitrosamines measurements, samples were sent to DVGW-Water Technology Centre (TZW, Karlsruhe, Germany) overnight at 4°C and were analyzed for 8 nitrosamines (NDBA, NDEA, NDMA, NDPA, NEMA, NMOR, NPIP, NPYR). In brief, A 500 mL water samples (amber bottles containing 0.8 g/L sodium sulfite) were adjusted to pH 3 with hydrochloric acid and spiked to 40 ng/L of an internal standard solution containing NDMA-d6, NDEA-d10, NDPA-d14, and NPYR-d8 in acetone. Samples prepared were run through a mixed bed solid-

phase extraction column (C18 + activated carbon conditioned with dichloromethane-methanol, and water containing sodium di-sulfate) followed by drying the cartridge under nitrogen for 4 hours. Analytes were washed off manually with dichloromethane and the eluate was dried over sodium sulfate. Finally, the eluate was gently concentrated to a final volume of approximately 150 μ L using a rotary evaporator (HB-140 Rotavapor M, Büchi, Switzerland). Nitrosamines were measured using a GC (Agilent 6890N, Waldbronn, Germany) coupled with an inert mass selective detector (MSD, Agilent 5973) operated in positive chemical ionization (PCI) mode. The capillary column was a DB-WAX (Agilent, 30 m x 0.25 mm ID x 0.5 μ m film thickness, J&W). The GC oven temperature was held at 35 °C for 3 min, then heated at 10 °C/min to 220 °C which was held for 8.5 min (run time: 30 min). Column parameters were operated in constant flow mode with a flow of 1.2 mL/min. The transfer line temperature was kept at 250 °C. Nitrosamines were each quantified by selected ion monitoring (SIM mode) of the corresponding protonated molecule ion $[M+H]^+$. Limits of quantification for various nitrosamines are provided in Table S.2. Further details of nitrosamine measurements are described by Lee et al., (2007).

Table D.1, Analytical method used to detect compounds

Analytical Method	Compound
PTI - GCMS	acetonitrile.
	chloroform.
	tetrachloromethane
	butanal, 3-methyl-.
	butanal, 2-methyl-.
	acetonitrile, trichloro-.
	acetonitrile, dichloro-.
	butanenitrile, 2-methyl-.
	butanenitrile, 3-methyl-.
	dichloropropionitrile
	dimethyl propanoylchloride
	tetrachloroethylene
	isobutyronitrile
	dichloro nitropropane
	ethane, 1,1-dichloro-1-nitro-.
	dichloroacetone
	tetrachlorocyclopropene
	2-ethyl hexanal
	benzaldehyde.
XAD - GCMS	benzonitrile.
	4-chlorobenzeneacetonitrile
	furfural (Furan-2-carbaldehyde)
	acetone, 1,1,1-trichloro-.
	acetamide, 2,2-dichloro-.
	acetonitrile, phenyl-.
	acetamide, 2,2,2-trichloro-.
	imidazole, 2-methyl-5-nitro-.

Table D.2, Limit of quantification for various nitrosamines

Compound	NDBA	NDEA	NDMA	NDPA	NEMA	NMOR	NPIP	NPYR
Limit of Quantification (ng/L)	1	2	1	1	2	1	1	1

Table D.3, Categories of DBPs in this study

Category	Compound
Nitrosamines	NDBA, NDEA, NDMA, NDPA, NEMA, NMOR, NPIP, NPYR
THMs	chloroform
HANs	dichloro acetonitrile, trichloro acetonitrile, 4-chlorobenze acetonitrile
Nitriles	2-methyl butanenitrile, 3-methyl butanenitrile, isobutyro nitrile, benzo nitrile, fenyl-acetonitrile
Aldehydes	2-methyl butanal, 3-methyl butanal, 2-ethyl hexanal, benzaldehyde, Furfural (Furan-2-carbaldehyde)
HAcAms	2,2-dichloroacetamide, 2,2,2-tri chloroacetamide
Haloketones	dichloroacetone, 1,1,1-trichloro acetone
HNMs	dichloro nitropropane, 1,1-dichloro-1-nitro-ethane
Other DBPs	tetrachloro methane, dimethylpropanoylchloride, tetrachloroethylene, tetrachlorocyclopropene

D.4 Nitrate Profile during Multiple Loadings Test

The initial spiked nitrate level was ~ 10 mg/L- NO_3^- in PLN raw water that was reduced to 6.6 mg/L- NO_3^- (i.e., 34% reduction) after the 1st cycle and then rapidly ramped up to 9.5 mg/L- NO_3^- and ~ 10 mg/L- NO_3^- after 3rd and 6th cycles, respectively. This demonstrates the greater affinity of resins for PL molecules (i.e., organic molecules) compared to NO_3^- and this preference becomes even more significant when exchange sites become occupied/limited over multiple cycles (Clifford, 1999).

Table D.4, Profile for NOM fractions* and other quality parameters changes over multiple loadings tests

		DOC	biopolymers	building blocks	humic substances	neutrals	DON	NO₃⁻	UV₂₅₄
C1	SR	65%	52%	47%	79%	20%	-	-	74%
	PL	45%	40%	56%	72%	3%	77%	-	62%
	PLN	44%	51%	56%	69%	6%	74%	34%	60%
C3	SR	22%	24%%	9%	28%	10%	-	-	26%
	PL	39%	36%	18%	65%	16%	77%	-	55%
	PLN	39%	34%	21%	66%	15%	79%	5%	56%
C6	SR	10%	45%	5%	14%	8%	-	-	13%
	PL	40%	28%	17%	64%	18%	75%	-	53%
	PLN	40%	27%	23%	63%	18%	77%	0%	53%
Avg.	SR	33%	40%	20%	40%	12%	-	-	38%
	PL	41%	35%	30%	67%	13%	76%	-	56%
	PLN	41%	37%	33%	66%	13%	77%	13%	56%

* Low molecular weight acids were set to zero using the software available through DOC-LABOR equipment.

SUVA/SUVA₀ was also monitored to gain further insight into the affinity of resins toward UV absorbing fractions of NOM. All waters showed a drop in SUVA after the 1st cycle due to the removal of humic substances (UV absorbing compounds). In subsequent cycles, however, SUVA/SUVA₀ increased (i.e., less humic substances were removed) as exchange sites/pores became more occupied. The increase was more significant for SR as it consisted of larger molecules (i.e., more humic substances) with higher possibility of blocking pores of the resins, thereby preventing other (especially larger) molecules from adsorption/exchange. The

results obtained from the LC-OCD analysis confirmed the SUVA data showing a decrease in removal of different NOM fractions with treatment cycle (data not shown).

Table D.5, Average changes in N-DBPs and C-DBPs as result of IEX multiple loadings

Water	N-DBPs (nmol/L)	Δ (N-DBPs) %	C-DBPs (nmol/L)	Δ (C-DBPs) %
PLN Avg. Removal	75.57	49.6	465.03	14.42
PL Avg. Removal	77.52	44.8	459.43	19.15
SR Avg. Removal	33.27	3.2	609.44	13.5

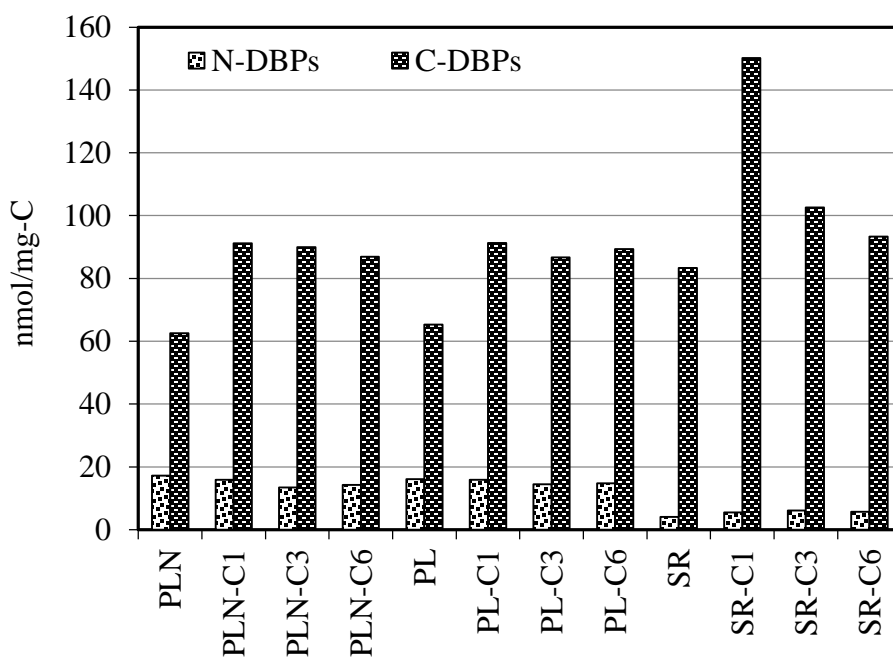


Figure D.1, Normalized DBPs FP (nmol of DBPs/mg of DOC)

Table D.6, ANOVA analysis for N-DBPs /C-DBPs vs. DOC/DON

	Coefficients	Standard Error	t Stat	p-value*
Intercept	0.3435	0.01	23.37321	4.65E-10
X= DOC/DON	-0.0024	0.0002	-12.4299	2.1E-07

*at 95% confidence level

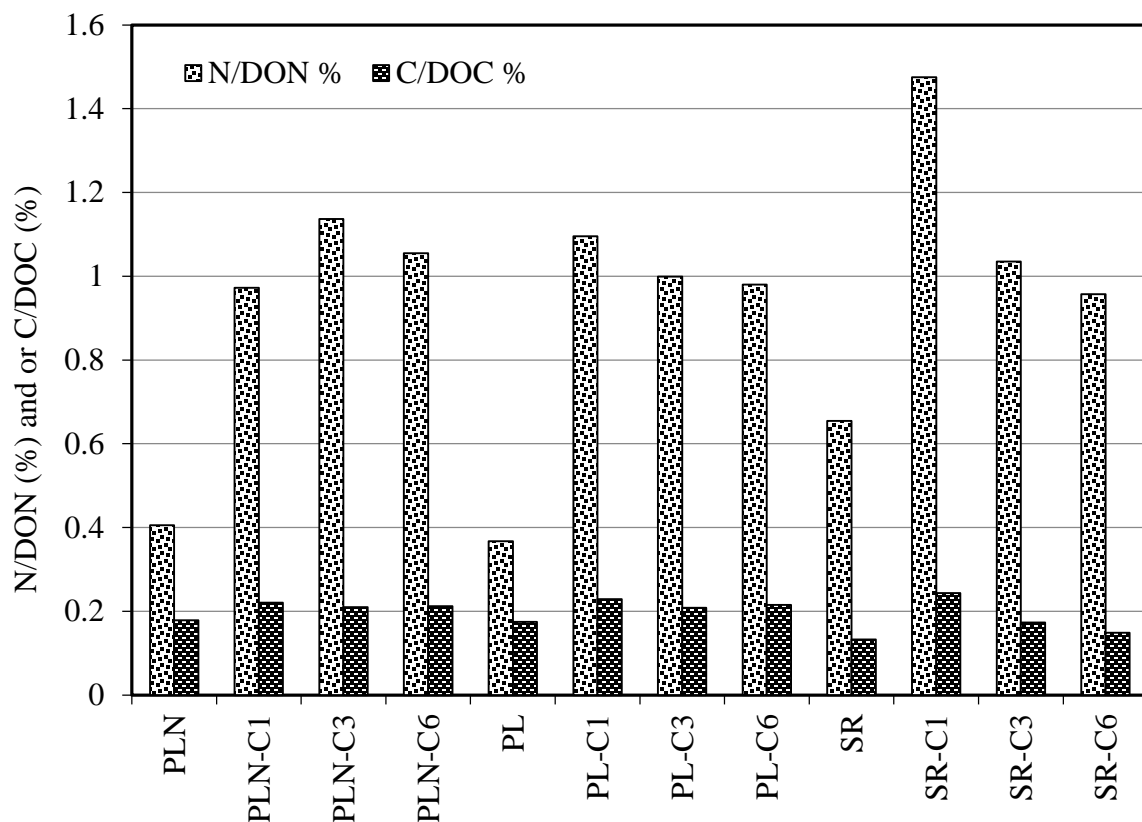


Figure D.2, Fractional contribution of dissolved organic nitrogen and carbon into DBPs

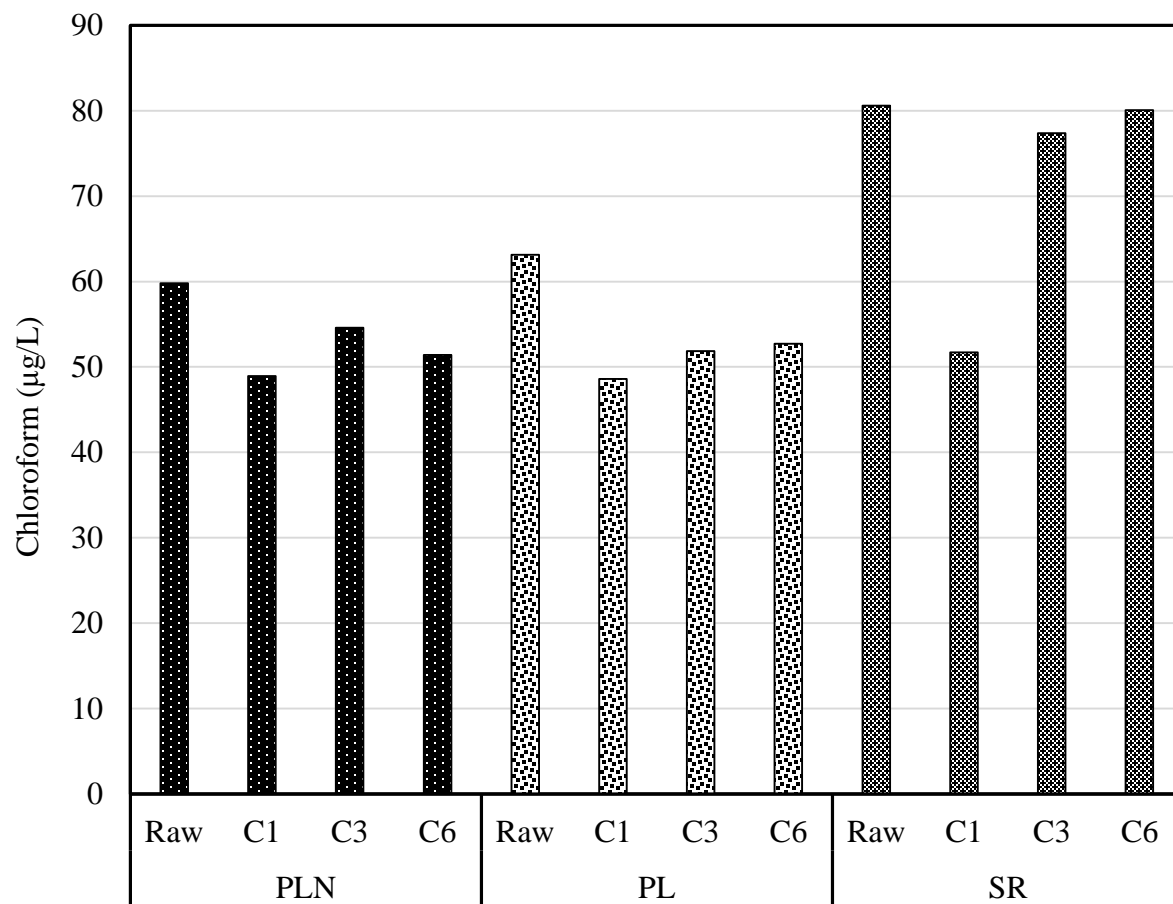


Figure D.3, Chloroform formation potential for waters under IEX treatment

Table D.7, Percentage removal of DBPs over 600 BV of treated waters

	THM	HANs	Nitriles	Aldehyde	HAcAm	HaloKetone	HNMs
PLN-C1	18%	44%	49%	25%	52%	9%	60%
PLN-C3	9%	52%	45%	23%	60%	34%	44%
PLN-C6	14%	54%	43%	20%	51%	18%	52%
PL-C1	23%	47%	44%	17%	44%	10%	63%
PL-C3	18%	51%	42%	14%	37%	17%	59%
PL-C6	17%	53%	39%	24%	42%	19%	38%
SR-C1	36%	57%	38%	38%	56%	35%	-
SR-C3	4%	-32%	-50%	-11%	32%	8%	-
SR-C6	1%	-71%	7%	14%	17%	0%	-
PLN Avg.	14%	50%	46%	23%	55%	21%	52%
PL Avg.	19%	50%	42%	18%	41%	16%	53%
SR. Avg	13%	-15%	-2%	13%	35%	14%	-

Table D.8, Pearson's coefficient for DBPs removal% and removal% in water quality parameters

	UV₂₅₄	DOC	DON	SUVA	DOC/DON
THM	0.91	0.94	0.80	0.83	-0.43
HAN	0.77	0.73	0.83	0.83	-0.74
Aldehyde	0.73	0.68	0.83	0.83	-0.78
Nitriles	0.82	0.82	0.80	0.79	-0.54
HAcAm	0.95	0.93	0.92	0.91	-0.72
Haloketones	0.82	0.83	0.77	0.75	-0.56
HNMs	0.97	0.96	0.94	0.97	-0.87

Appendix E

E.1 Glassware, Tools, and Resins Preparation

For more consistency in preparation, 20 mg of a standard organic isolate (purchased from International Humic Substances Society, IHSS) was dissolved in 1L of phosphate buffer (made from Milli-Q water and ACS reagent grade chemicals and filtered through 0.45 μm) on the day of experiment (Table 8.1). Waters prepared were stored in specially prepared glass amber bottles at 4°C in dark. Pipette tips were autoclaved and kept away from potential contamination. All tools (glassware, flasks, funnels, glass filters 1.6 μm) were heated at 550°C for 5 hrs according to the method described elsewhere (Mitch et al., 2003; Mitch and Sedlak, 2002).

E.2 Resins Preparation

The strongly basic resins used in this study was Purolite A860 which was selected through previous screenings conducted by the authors (Bazri and Mohseni, 2014; Monosov et al., 2012) in which this resins showed to have superior performance in removing NOM. The characteristics for A860 were water content (65-70%), resin size (300-1200 μm) and exchange capacity of 0.8 eq/L of resin according to the manufacturer¹². To eliminate possible background/manufacturer contamination affecting the analysis, A860 Purolite macroporous acrylic strongly basic resins were initially regenerated using NaCl 10% (wt%) and triple-rinsed with Milli-Q water.

E.3 Analytical Methods

Total and Dissolved Organic Carbon (TOC, DOC) was measured using a Shimadzu-VCPH TOC analyzer. UV scans were carried out using a UV-Vis spectrophotometer (Varian). Nitrate was measured using ion chromatography according to SM 4110 method using a Dionex

¹² www.purolite.com

system. Molecular weight distribution of NOM was assessed through liquid chromatography equipped with size exclusion and organic carbon and nitrogen detectors using a DOC-LABOR system and according to the method of Huber et al., (2011). Building blocks were the second highest fraction in the treated water. Accounting for BBs was contrary to the observation of Huber et al., (2011) who reported almost no BBs for IHSS-HA isolates in their study. This discrepancy is to the integration method used to quantify LC-OCD chromatograms and also user discretion while integrating the peaks. Nonetheless, findings here are of significant importance as they could be used to envisage the quality of IEX-treated water with respect to biological stability.

E.4 Impact of Filtration on Ijssel Lake Water Quality

AOC determined for IL raw water in here ($19.25 \pm 4.31 \mu\text{g/L}$) greatly differs from the historical values obtained by PWN and HWL ($< 200 \mu\text{g/L}$). The reason being is that the IEX resins had to be separated from water after IEX treatment and prior to further analysis. Therefore, to eliminate the interference of filtration, the original IL water was initially filtered (prior to mixing with resins) through $1.6 \mu\text{m}$ glass filter (baked at 550°C). This resulted in creation of a thick green algae-like layer on the filter and $\sim 2.2 \text{ mg/L}$ reduction in TOC. The AOC of the unfiltered water was $383.75 \pm 51.27 \mu\text{g/L}$. Hence, the removed TOC (2.2 mg/L as a result of $1.6 \mu\text{m}$ filtration) was responsible for $\sim 95\%$ of the total AOC and remaining TOC (5.9 mg/L) only contributed to $20 \mu\text{g/L}$ ($\sim 5\%$ of total) of the total AOC. The AOC and TOC values obtained for the 30 min IEX treated IL water were in the same range ($\sim 12\text{-}13 \mu\text{g/L}$, $\sim 1.7\text{-}2 \text{ mg/L}$, respectively) as that of the historical AOC data available for IX-MF combination at PWN-T. The biopolymer and HS fractions of IL water showed to have DON of approximately 180 and 60 ($\mu\text{g/L-N}$), respectively, making the total DON estimate to be $\sim 240 (\mu\text{g/L-N})$. This number

differs significantly from the historical values for IL water which showed DON to be 800 -1100 $\mu\text{g/L-N}$. A very likely source for this difference could be the impact of the abovementioned filtration (i.e., the caked formed on the filter is believed to be enriched in DON). This data suggests the 1.6 μm filtration step functioned similar to the MF step in the actual treatment train.

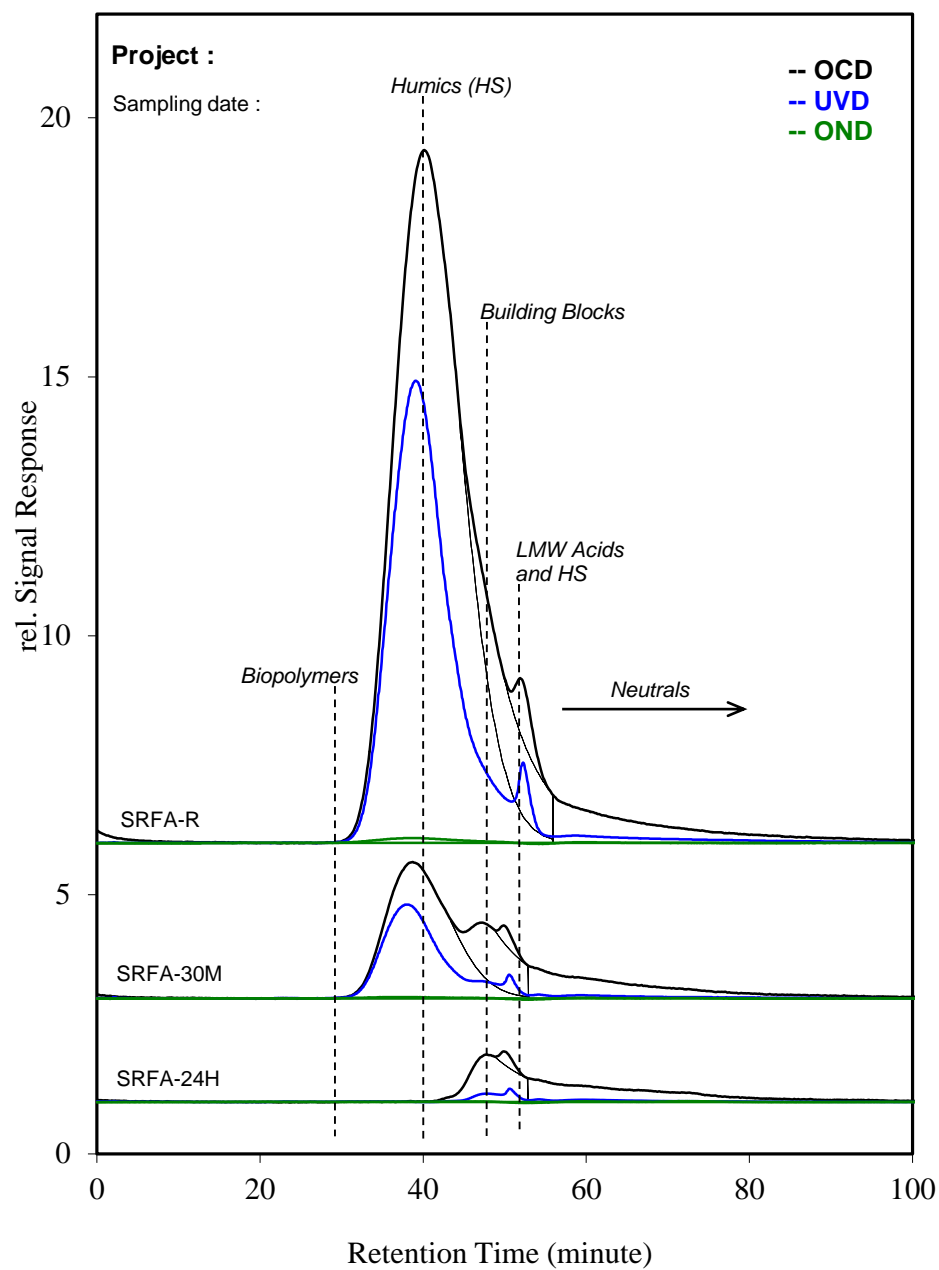


Figure E.1, LC-OCD chromatogram for raw and IEX treated SRFA

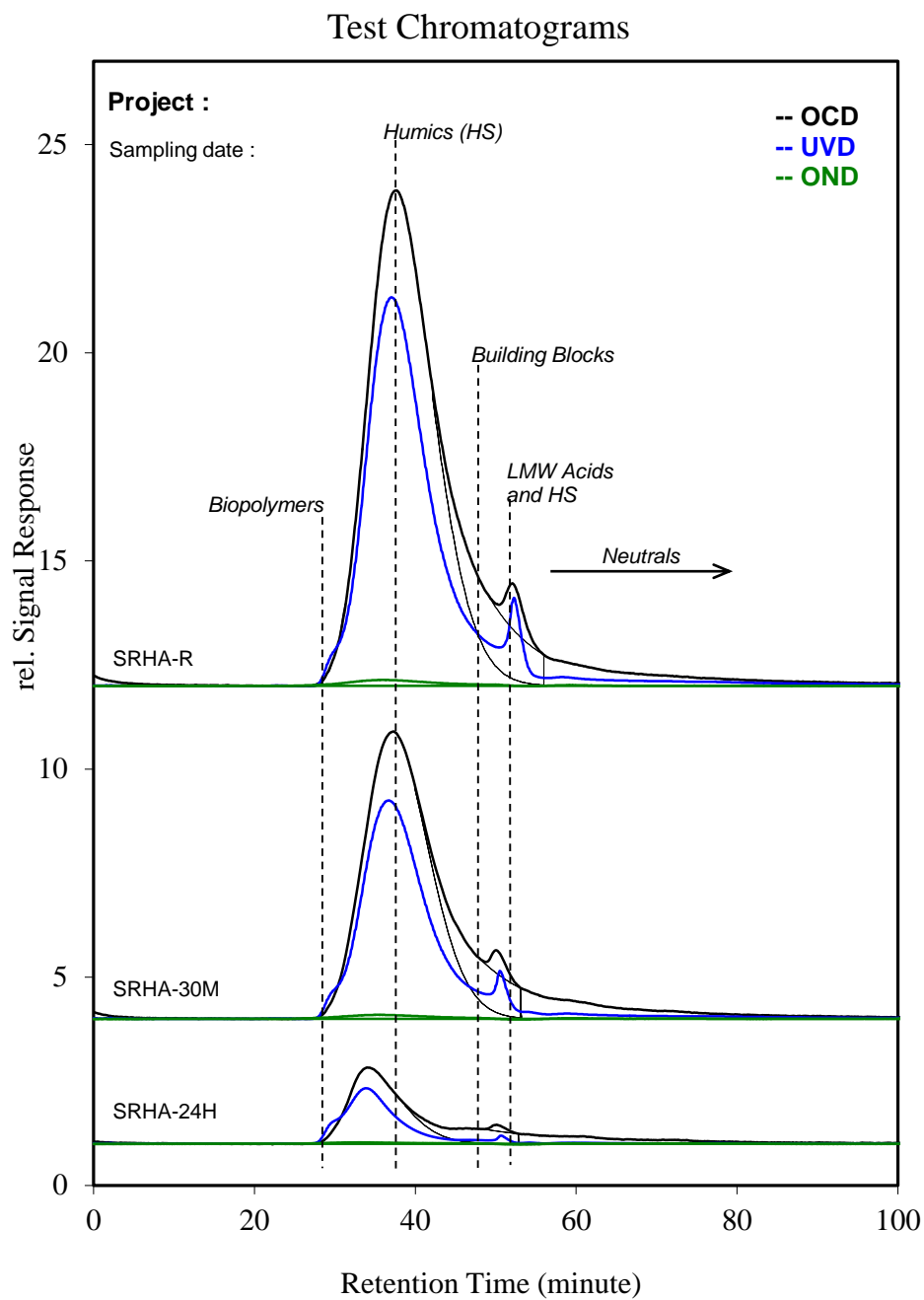


Figure E.2, LC-OCD chromatogram for raw and IEX treated SRHA

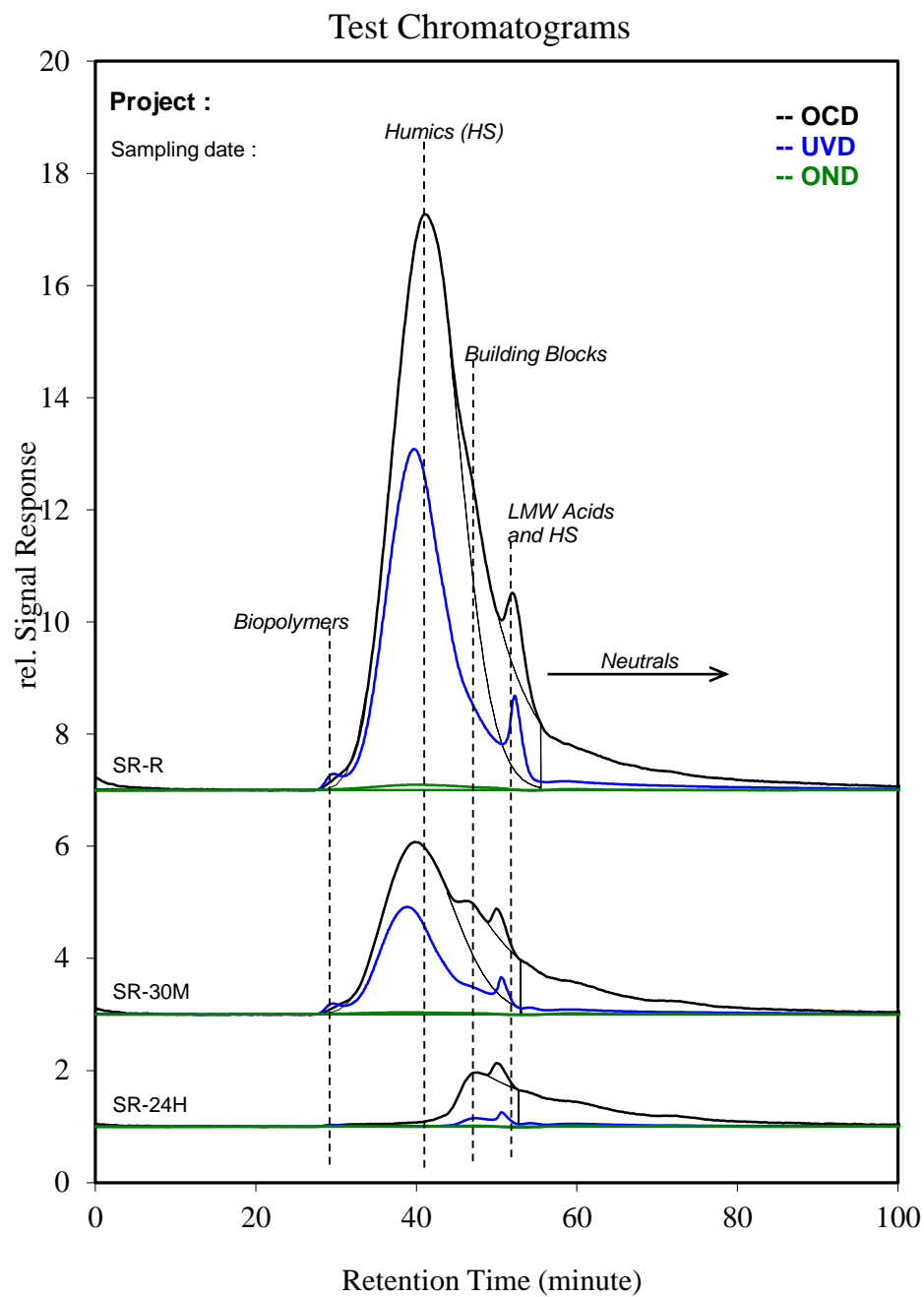


Figure E.3, LC-OCD chromatogram for raw and IEX treated SRNOM

Test Chromatograms

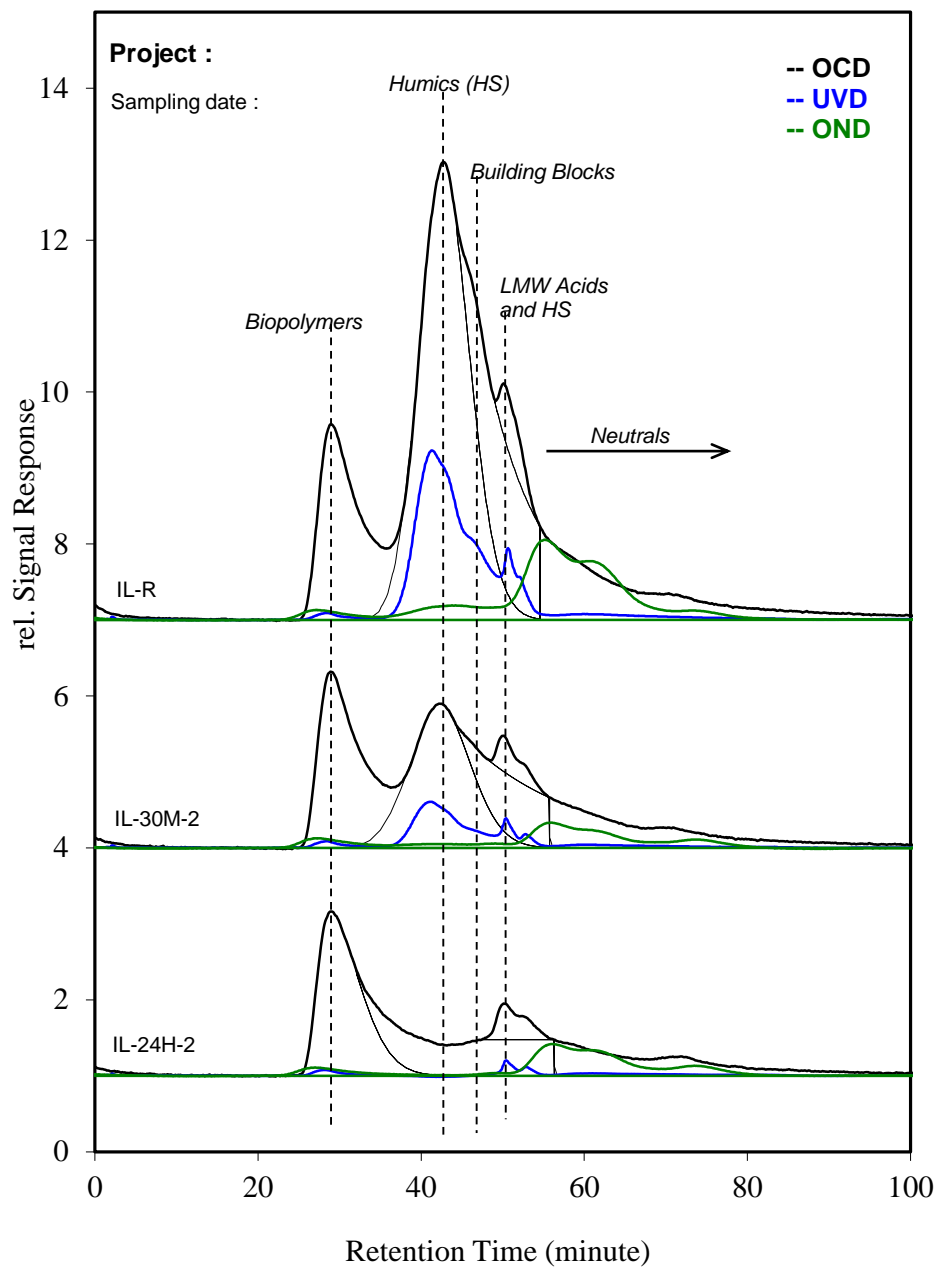


Figure E.4, LC-OCD chromatogram for raw and IEX treated IL

Table E.1, Average removal (%) of various DOC fractions during 30 min and 24 hr of IEX treatment

		Avg. Removal %				
		DOC	Biopolymers	Building Blocks	Humic Substances	Neutrals
30 min	SRFA	73%	-	52%	81%	26%
	SRHA	34%	-	37%	40%	6%
	SR	57%	-	56%	68%	18%
	IL	44%	2%	58%	60%	38%
24 hrs	SRFA	89%	-	59%	100%	39%
	SRHA	80%	-	72%	85%	58%
	SR	84%	-	58%	100%	36%
	IL	63%	11%	31%	100%	50%