THE REMOVAL MECHANISM OF NATURAL ORGANIC MATTER BY ION EXCHANGE RESINS FROM THERMODYNAMIC PERSPECTIVES

by

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Abstract

Natural organic matter (NOM), a constituent in surface drinking water sources, requires removal to minimize its negative impacts on water quality and water treatment processes. Ion exchange (IEX) has been considered as an effective technology for the removal of NOM. However, despite many studies on the IEX removal of NOM, the removal mechanism and the molecular interactions involved in the IEX process are quite unknown due to the complexity of the NOM molecular structure.

This research aimed to investigate the NOM removal with a focus on fundamentals underpinning the IEX process and the molecular interactions/forces that drive the retention of NOM onto the IEX resins. Different isolates of NOM along with some pure organic acids were studied. Hydrophobicity was found to play a key role in the removal process. The changes that the hydrophobic moieties impose to the structure of water molecules (i.e., entropy reduction) were found very influential in determining the selectivity of the IEX process. Moreover, the removal of UV-absorbing compounds (more hydrophobic fraction of NOM) was enhanced in the presence of sodium sulphate, as the electrostatic interactions are screened by added salt and consequently the entropic contribution to the removal is promoted. Nonetheless, the entropic contribution from the resin phase (i.e., hydrophobic resin backbone) was shown to negatively impact the removal of UV-absorbing compounds. Overall, combining the findings, it is concluded that the difference in the hydrophobicity (entropy) of the water and the resin phase is the main driving force in transferring NOM molecules from water to the resin. The contribution of the electrostatic and hydrophobic effects to the removal of NOM by IEX resins was further evaluated by quantitative characterization of the thermodynamic properties using isothermal titration calorimetry technique. The results confirmed the significance of entropic contribution to the removal of components with higher hydrophobic characteristics.

Findings of this research provide a quantitative framework for the interpretation of the experimental results and facilitate the proper design of the IEX process for different water sources and under various conditions.

Lay Summary

Ion exchange is a promising technology for removing natural organic matter (NOM) from drinking water sources. Despite many earlier studies on the performance of different ion exchange resins at removing NOM, there is a lack of fundamental knowledge around the phenomena driving the process. NOM is a complex mixture of organic compounds, with majority being negatively charged and of hydrophobic nature. Understanding the extent of the contribution of charged groups (electrostatic forces) and hydrophobic effects to the removal of organic matter is of great importance. In addition, the potential impacts of other solutes in water on water molecules structure are also crucial. This research aimed to understand and evaluate various forces or molecular interactions that could involve in driving the ion exchange process. The results of this work will lead to better practices of ion exchange for an efficient NOM removal from different water matrices.

Preface

I, Sonia Rahmani, was in charge of performing the literature review, defining the knowledge gaps and the subsequent research questions, designing the experiments and conducting the laboratory work (unless otherwise mentioned below), preparing the manuscripts and the conference presentations and posters under supervision of Professor Madjid Mohseni at the chemical and biological engineering department of the university of British Columbia, Vancouver.

Some chapters of this dissertation were prepared in the manuscript format for publication as listed below. Moreover, the specific contribution of the author to each chapter is elaborated in detail accordingly.

- A version of chapter 4 was published in the Canadian Journal of chemical engineering (CJChE) with the following title:

Sonia Rahmani and Madjid Mohseni; (2017) "The role of hydrophobic effect in ion exchange removal of organic compounds from water", The Canadian Journal of Chemical Engineering, 9999, 1-7.

- A version of chapters 5, 6, and 7 were prepared in manuscript formats for submission and currently are in review by the co-authors. These manuscripts are listed below respectively.

Sonia Rahmani and Madjid Mohseni; (2017) "Removal of natural organic matter (NOM) isolates by ion exchange resin in presence of inorganic anions", Internal Review.

All experiments were designed by myself and conducted with the assistance of Mr. Farbod Rahimi-Nejad a Co-op student in the advanced oxidation laboratory at the chemical and biological engineering department under my supervision. I have performed the all data analysis and the manuscript preparation for this part of the research.

Sonia Rahmani, A. Louise Creagh, Charles A. Haynes, and Madjid Mohseni; (2017) “Thermodynamics of ion exchange process for removing natural organic matter (NOM)”, Internal Review.

All experiments regarding this chapter were designed and carried out by myself in the Michael Smith laboratories (MSL) at the university of British Columbia under co-supervision of Dr. Louise Creagh, Professor Charles Haynes, and Professor Madjid Mohseni.

Sonia Rahmani and Madjid Mohseni; (2017) “The impact of the resin properties in removing natural organic matter (NOM)”, Internal Review.

The laboratory work presented in this chapter was assisted by a summer student Ms. Friederike Roots in the advanced oxidation laboratory at the chemical and biological engineering department under my supervision. The data analysis and the manuscript preparation were performed by myself.

The following is the list of the conference presentations:

- **Sonia Rahmani** and Madjid Mohseni, “The removal mechanism of natural organic matter by ion exchange resins in the presence of inorganic anions”, IWA specialist conference on natural organic matter in water (NOM 6) conference, Malmö, Sweden, September 2015.
- **Sonia Rahmani** and Madjid Mohseni, “The effect of natural organic matter (NOM) properties on the mechanism of its removal from drinking water by ion exchange resins”, 64th Canadian chemical engineering (CSCHE 2014) conference, Niagara Falls, ON, Canada, October 2014**.**

- Mehdi Bazri, **Sonia Rahmani**, Gustavo Imoberdorf and Madjid Mohseni, “Ion exchange resins for natural organic matter removal”, BC water and waste association (BCWWA) Conference, Penticton, BC, Canada, April 2012.

I also presented the following posters at RES’EAU-WaterNET annual meetings during the course of this research:

- **Sonia Rahmani**, Gustavo E. Imoberdorf, and Madjid Mohseni, “A study on adsorption of hydrophobic, hydrophilic, and neutral compounds on ion exchange resins”, presented at RES’EAU-WaterNET annual meeting, Toronto, ON, Canada, November 2012.
- **Sonia Rahmani**, A. Louise Creagh, Charles A. Haynes, and Madjid Mohseni, “Study of interactions involving in NOM removal through ion exchange process”, presented at RES’EAU-WaterNET annual meeting, Vancouver, BC, Canada, October 2013.
- **Sonia Rahmani** and Madjid Mohseni, “ Mechanism of removing natural organic matter (NOM) by ion exchange resins from drinking water”, presented at RES’EAU-WaterNET annual meeting, Whistler, BC, Canada, May 2014.
- **Sonia Rahmani** and Madjid Mohseni, “ The effect of sulphate and nitrate on the removal of NOM fractions by ion exchange resins”, presented at RES’EAU-WaterNET annual meeting, Kelowna, BC, Canada, May 2015.
- **Sonia Rahmani** and Madjid Mohseni, “The role of hydrophobic effect in ion exchange removal of organic compounds from water”, presented at RES’EAU-WaterNET annual meeting, Whistler, BC, Canada, May 2016.

All the aforementioned manuscripts were primarily written by myself and reviewed by the co-authors. This research was funded by RES'EAU-WaterNET and the Natural Sciences and Engineering Research Council of Canada (NSERC).

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List of Abbreviations

Symbol	Definition
DBP	Disinfection by-Product
DOC	Dissolved Organic Carbon
DOM	Dissolved organic matter
Eq	Equivalent
FA	Fulvic Acid
HA	Humic Acid
hr	hour
hrs	hours
IC	Ion Chromatograph
IEX	Ion Exchange
IHSS	International Humic Substances Society
ITC	Isothermal Titration Calorimetry
min	minute
MIEX	Magnetic Ion Exchange
MW	Molecular Weight
NOM	Natural Organic Matter
NSERC	Natural Science and Engineering Research Council of Canada
SBR	Strong Basic Resin
SRFA	Suwannee River Fulvic Acid
SRHA	Suwannee River Humic Acid
SUVA	Specific UV Absorbance

Symbol	Definition
T	Time
TOC	Total Organic Carbon
UV	Ultra Violet
UV_{254}	UV Absorptivity at 254 nm
WBR	Weak Basic Resin

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To

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My first teachers with strong and gentle soul who taught me to trust in myself, stay on my feet, walk and work hard to build much with little.

Without your affections, love and pray I wouldn’t become who I am now.

I will always be thankful and will do my best to make you proud.

&

My lovely and caring sister

Afsaneh

For her unconditional kindness and for believing in me

Chapter 1 : Introduction

1.1. Natural Organic Matter (NOM) in Drinking Water Sources

NOM is a macromolecular complex mixture of organic molecules, coming from the decomposition or decay of organisms such as plants and animals. Animal and human wastes, and soil are other sources for natural organic matter in water (Leenheer et al. 2003; Stevenson 1982; Peña-méndez et al. 2005). Residential or industrial failed wastewater disposal systems may also contribute to the presence of organic matter in water sources (Peña-méndez et al. 2005). Therefore, the composition, character, and properties of NOM depend on its origin and vary according to its surrounding environment. Overall, the amount of NOM in water ranges from <1 mg/L for groundwater to several tens of mg/L in surface water sources (Leenheer & Croué 2003).

NOM is a key factor in water treatment and thus the structural identification and characterization of NOM is of a great importance. However, its heterogeneous and complex structure makes NOM characterization very challenging. Methods such as size exclusion chromatography, liquid chromatography-organic carbon detection (LC-OCD), pyrolysis gas-chromatography mass spectrometry (Py-GC-MS), fractionation through resin adsorption and nuclear magnetic resonance (NMR) spectroscopy are used to characterize NOM (Frimmel 1998; van Leeuwen et al. 2002; Matilainen et al. 2011; Swietlik & Sikorska 2004). And, different scientists (Leenheer 2007; Schulten & Schnitzer 1993) propose different molecular structures for NOM and its fractions. Moreover, the NOM in water is mainly quantified through the measurement of total organic carbon (TOC) and UV absorptivity. Specific UV absorbance

(SUVA), the UV absorptivity of water sample at 254 normalized by TOC, is also introduced as a surrogate for aromatic content of NOM (Weishaar et al. 2003).

Although the precise characteristics of NOM depend on its origin and the source that it is extracted from, the average properties of NOM from different sources are similar. NOM contains hydrophobic, hydrophilic and neutral constituents with a diverse range of molecular weight (Leenheer & Croué 2003). NOM mainly consists of humic substances (i.e., fulvic acid and humic acid) with phenolic and carboxylic functional groups (Chen et al. 2002; Ritchie & Purdue 2003; Leenheer et al. 2003) and is predominantly hydrophobic (≈60%) (Nkambule et al. 2009; Yee et al. 2009). Also, NOM in water can be dissolved or particulate, and this research focuses on the dissolved organic matter (DOM), which can pass through a 0.45 μm filter.

1.2. Challenges arising from NOM and the Removal Technologies

NOM is present in nearly all surface water sources and imposes significant issues to the quality of drinking water in terms of colour, odour, and taste. NOM also affects the efficiency of many water treatment processes, e.g., it contributes to membrane fouling (Amy & Cho 1999) and absorbs ultraviolet (UV) irradiation during UV-based treatment and disinfection processes. Further, the reactivity of NOM with conventional chemical disinfectants, e.g., chlorine, leads to the formation of potentially harmful and regulated disinfection by-products (DBPs) (Minear & Amy 1996; Kitis et al. 2002; Liang & Singer 2003). Biological instability of drinking water is also attributed to NOM, regarded as being a potential source for bacterial regrowth and biofilm formation in water distribution systems (van der Kooij 1992).

Several physical and chemical technologies have been extensively studied and implemented in the industry for degrading/eliminating NOM (Ødegaard et al. 2010). These technologies include:

- *Coagulation and flocculation followed by sedimentation and filtration* – Coagulation-flocculation uses metal coagulant species (Al or Fe) that produces NOM-metal complex, which are then removed by floc separation. This process works better for the high molecular weight fraction of NOM, as it is easier to coagulate large molecules. Optimization of operational factors (pH and coagulant dose) is a challenging factor for this technology. High coagulant dose can lead to a shorter subsequent filter runs and thereby an increase in sludge production and operational costs. Nonetheless, this technology is the most common method applied for NOM removal.
- *Membrane filtration (including ultra and nano filtration)* that separates NOM molecules from water by molecular sieving. The typical problem with this technology is membrane fouling that results in reduced flux and capacity loss of the filters.
- *Oxidation* – the color of water that is caused by conjugated bonds and aromatic content of NOM can be removed through oxidation process in which these bonds break down. If color removal and disinfection is the main purpose of treatment, ozonation is usually applied; however, it may be also combined with H_2O_2 or UV to achieve an efficient NOM removal from water. A disadvantage of this method is the instability and short lifetime of the hydroxyl radicals. Oxidation methods are more efficient in UV absorptivity removal than total DOC removal. Thus, oxidation processes may be applied in combination with other treatments such as coagulation for a better removal of NOM.
- *Sorption* processes in which NOM is adsorbed onto a surface such as activated carbon. The main disadvantage of activated carbon adsorption is the pore blockage that can be caused by large NOM molecules. Thereby, this process is more suitable as post treatment for other technologies than be applied alone.

One alternative adsorption technology which has received increased attention in recent years is ion exchange (Semmens & Gregory 1974; Boyer et al. 2008; Hongve 1989; Fu & Symons 1990; Graf et al. 2014; Anderson & Walter 2013). However, in water treatment utilities, a combination of the above-mentioned processes is mainly used for an efficient removal of NOM.

1.3. Ion Exchange Process

Ion exchange process is the exchange of ions between solid ion exchangers (i.e., ion exchange resins) and an ion-containing solution. Ion exchange is mainly used in purification and decontamination of aqueous solutions as well as separation processes. Ion exchange has wide range of applications (Inamuddin & Luqman 2012; Helfferich 1962; Harland 1994) including food industry (e.g., sugar manufacturing, juice purification), pharmaceuticals, protein separation and purification processes (e.g., ion exchange chromatography), and water industry (e.g., water softening and desalination). Another application of ion exchange is the removal of inorganic anions (Inamuddin & Luqman 2012; Chabani et al. 2006; Chubar et al. 2005) such as nitrate and sulphate from water.

Ion exchange can be categorized as a sorption process and is reversible, substantiating the feasibility of regenerating the ion exchanger (i.e., resin) and its multiple use. The regeneration can be done through washing the ion exchange media with a solution containing an excess amount of the resin counter ion (Hongve et al. 1999; Rokicki & Boyer 2011). It is worth to note that brine (i.e., sodium chloride solution) is the most common resin regeneration solution in water industry.

1.3.1. Ion exchange resins

Ion exchange resins are high molecular weight insoluble polyelectrolytes that can release their counter ions to trap equally charged ions from their surrounding liquid (Dorfner 1972). Ion exchange resins are well established and widely synthesized to facilitate separation and purification processes (e.g., water softening and contaminant removal). They are normally fabricated in the form of small beads possessing a variety of properties such as porosity (Macroporous/gel), cross-linking (water content), and polymeric structure (styrene/acrylic).

Table 1.1, Categories of ion exchange resins and their functional groups.

	Ion exchange resin type	**Functional group**
Cation Exchangers	Strongly Acidic Cation Exchange Resins (SAC)	Sulphonic acid (—SO3– H+)
	Weakly Acidic Cation Exchange Resins (WAC)	Carboxylic acid (—COOH)
Anion Exchangers	Strongly Basic Anion Exchange Resins (SBA)	Quaternary ammonium (—N(CH3)3+ OH–)
	Weakly Basic Anion Exchange Resins (WBA)	Amines (—N(CH3)2)

Ion exchange resins can be classified into two general groups of cation exchangers and anion exchangers and each group has two main types differing by their functional groups (Table 1.1). Anion exchange resins are used for the removal of NOM due to the NOM’s negative charge. Besides strong basic anion exchange resins (SBA) are shown to be more effective than the weak basic anion exchangers (WBA) in NOM uptake (Fu & Symons 1990; Bolto et al. 2002); even though, WBA are more effective in terms of regeneration cost and waste disposal (Höll & Kirch 1978; Höll & Kiehling 1981; Evans & Maalman 1979).

1.3.2. Ion exchange for NOM removal

Ion exchange is proven to be an efficient technology for removing NOM from water (Bolto et al. 2004b; Drikas et al. 2002; Fettig 1999; Fu & Symons 1990; Hongve 1989), particularly as a pre-treatment step in the water treatment train. Employing ion exchange as pre-treatment can result in lower subsequent coagulant demand, less chlorine demand (Boyer & Singer 2006), and thereby lower formation of chlorinated DBPs. It also helps with the increased efficacy of UV disinfection process. The effectiveness of ion exchange for removing bromide to lessen brominated DBPs formation has also been reported in the literature (Hsu & Singer 2010).

The most important advantages of ion exchange are its simple operation and its economic feasibility compared to other conventional water purification techniques (Heijman et al. 1999). Another advantage of the ion exchange for NOM removal is its ability in removing lower molecular weight hydrophilic acid fraction as well, while conventional processes such as coagulation mainly remove the higher molecular weight hydrophobic fraction. This is important because not only hydrophobic NOM but also hydrophilic fractions of NOM are responsible for the production of DBPs (Ates et al. 2007; Bond et al. 2012; Chu et al. 2010).

However, ion exchange process also has some disadvantages with the most important one being the resin regeneration, which may cause difficulties in managing and disposal of the regenerant waste (Höll & Kiehling 1981; Edzwald 1999; Clifford 1999; Rokicki & Boyer 2011). Another disadvantage might be the inability of ion exchange process in removing the neutral (i.e., non charged) fraction of NOM, which can be a potent contributor to the formation of DBPs (Bolto et al. 2004).

1.4. Statement of Research Rationale

Despite the promising performance of ion exchange process in removing NOM from water, there are some conflicts in the literature with respect to the selectivity of various NOM fractions under different conditions (e.g., resin types, the source of NOM). Moreover, the composition of the background water (i.e., presence of inorganic anions such as sulphate and nitrate) and the NOM properties (e.g., hydrophobic, hydrophilic, aromatic content) can immensely influence the IEX selectivity and the removal efficiency as well. A fundamental approach for evaluating the effect of these factors in removing NOM is missing in the literature. One fundamental approach could be characterizing the molecular behaviour of the water solution (e.g., freedom of water molecules/entropy of the system) and evaluating the molecular interactions/forces (e.g., hydrophobic interactions, electrostatic forces) that may drive the IEX process for NOM removal. Therefore, it is of great importance to quantify the contribution of the aforementioned factors to the removal of NOM and their impact in determining the selectivity of the ion exchange process. It is also of great interest to employ a thermodynamic approach (i.e., identifying the extent of entropy/enthalpy contribution) to provide some quantitative information on the involvement of different molecular interactions to the NOM removal. Accordingly, this research was defined to close some gaps and clarify some scientific uncertainties governing the NOM removal by ion exchange resins.

1.5. Ultimate Goal of This Research

Changes in NOM quantity and quality due to its high seasonal variations pose challenges to the design and selection of a proper treatment process. The focus of this research is on ion exchange, which has a promising performance in NOM removal. The ultimate goal of this research is to achieve a detailed understanding and knowledge of the fundamentals that lead to best practices of ion exchange as a solution for efficient NOM removal. One essential step in improving NOM removal in water utilities is to quantify and characterize NOM fractions at various stages of the treatment plant. Understanding and predicting of the ion exchange performance in removing or targeting specific NOM fractions from various water sources is very vital due to high variability in NOM characteristics and other water matrix constituents. Once the composition of the source water with respect to NOM and other components is determined, the knowledge of ion exchange performance in removing NOM from different water matrixes can be used to determine the extent of NOM removal via ion exchange and its potentials compared to other technologies.

1.6. Research Scope and Objectives

The overall goal of this research is to develop a detailed understanding on the mechanism of NOM removal during the ion exchange process. More specifically, this research aims primarily to study the molecular interactions that may contribute to the ion exchange of NOM molecules. The secondary goal of this thesis is to examine how changes in solution structure influence relationships between NOM molecules and ion exchange resins through structural modifications of NOM solution in presence of inorganic anions.

The aforementioned objectives will be achieved by focusing on a number of specific sub-objectives as listed below:

Investigate the importance of NOM hydrophobic characteristic in its removal by ion exchange resins.

The results obtained from this sub-objective will yield in quantifying the contributions of ion exchange and molecular interactions to the removal of organic anions with differing hydrophobicity, NOM and its isolates.

Assess the driving force for removing NOM through ion exchange process under different conditions (e.g., solvent properties).

Given that enthalpy and entropy are good representatives of interactions strength and system dynamics, one approach to assess the forces driving the removal of NOM by ion exchange resins is to estimate how thermodynamic signatures contribute to the binding mechanism. Results of this study will provide further information in understanding of factors that are crucial in removing different fractions of NOM at various resin doses and NOM concentration. This yields in defining relationships between NOM and ion exchange resins, whether the removal process is an enthalpy- or entropy- driven and how hydrophobicity of organic anions and NOM isolates influences the driving force and thereby removal mechanism.

Study the impact of inorganic anions on the removal efficiency and selectivity of ion exchange for different NOM fractions.

This sub-objective is defined to evaluate the competition effect from different inorganic anions and will consider studying:

- ✓ Different NOM isolates,
- ✓ Various concentrations of inorganic anions,
- ✓ Different resin doses.

Establish the effect of solution structural properties on the contribution of different interactions to the NOM removal.

This sub-objective is defined to understand the influence of salt-induced modification in water structure on NOM removal and interactions happening in the solution. In order to achieve this sub-objective, the effect of salt molecules (at different concentrations) on removal mechanism and molecular interactions will be studied. The discussion will also be made in thermodynamic perspectives by performing isothermal titration calorimetric studies as well as conducting equilibrium binding isotherms.

Examine the effect of resin backbone material on NOM removal mechanism.

This study will assist in selecting an appropriate resin for various NOM isolates under different operating conditions (e.g., resin dosage) to achieve greater removal efficiency and selective removal of specific NOM fraction.

1.7. Thesis Layout

This thesis represents a comprehensive experimental work conducted at UBC to address specific objectives in the study of NOM removal by ion exchange resins. This dissertation provides a detailed analysis of the available literature in the field of ion exchange for NOM removal, as well as the results obtained from detailed experimental work carried out to achieve the research objectives.

Chapter 1: Provides some background information on the NOM and problems associated with the presence of NOM in water sources as well as available technologies for removing NOM from water.

Chapter 2: Presents a comprehensive review of the available literature studying NOM removal by ion exchange resins and some other literature providing fundamental information to better define the objectives and justify the results. This chapter also contains the knowledge gap as well as research questions and objectives that are developed according to the knowledge gap followed by significance of this work.

Chapter 3: Describes the method and experimental plan conducted to address research questions. Moreover, it contains an explanation of analytical techniques and instruments applied in this research.

Chapter 4: Discusses the importance of the hydrophobicity of organic compounds in their removal from water by ion exchange resins. The influence of hydrophobicity on removal mechanism and ion exchange selectivity is also elaborated.

Chapter 5: This chapter studies:

- The removal of different NOM isolates with ion exchange resins to demonstrate the influence of NOM characteristics on its removal performance with an emphasize on the hydrophobicity.
- The governing driving force for the removal of NOM isolates under various conditions (e.g., resin dosage) and interactions contribute to the sorption of NOM onto the ion exchange resin.

- The competition effect from inorganic anions (sulphate and nitrate) and their impact on water structure and its subsequent effect on interactions involve in ion exchange treatment of NOM.

Chapter 6: Demonstrates thermodynamic analysis of ion exchange process for removing NOM, and provides a detailed information on the contribution of entropy and enthalpy to the free energy of NOM removal.

Chapter 7: Studies the effect of the resin polymeric backbone on the removal performance of NOM isolates by examining one styrene and one acrylic resin and elaborates the impact of resin hydrophobic character on the selectivity of ion exchange and the interactions contribute to the removal process.

Chapter 8: Provides a summary of the key findings along with conclusions reached by this research. Also some potential future research that may lead to an efficient application of ion exchange in water treatment plants for removing NOM is recommended.

Chapter 2 : Literature Review

2.1. NOM Removal from Water via Ion Exchange Process

Majority of NOM is negatively charged and thereby it can be removed from water by anion exchange resins. Although ion exchange is reported as a viable process for controlling NOM in drinking water supplies, the efficacy of ion exchange depends primarily on source water quality, NOM properties and ion exchange resin characteristics. Published studies to date have investigated the effect of these parameters on removal efficiency, which will be discussed and reviewed later in this chapter. Nevertheless, more fundamental research is still required to optimize the ion exchange process for removing NOM from drinking water sources due to the structural complexity of NOM and its variability with the changes in the surrounding environment.

2.1.1. Removal mechanism

In principle, two mechanisms can take place during anionic organic matter removal via ion exchange process (Li & SenGupta 2004b; Croué et al. 1999; Fu & Symons 1990). These are attributed to: 1) Ion exchange (electrostatic interaction), the release of a counter ion from resin surface accompanied by an electrostatic interaction between ionic functional groups of the resin phase and the organic matter; and 2) Physical adsorption, involving van der Waals interactions between the polymeric backbone of the resin and non-ionic moieties of the organic matter. The latter mechanism may also be expressed as hydrophobic interaction or hydrogen bonding.

Several stoichiometric studies of ion exchange for NOM removal have been employed to confirm the removal mechanisms and it has been observed that ion exchange is the predominant mechanism (Tan et al. 2005; Fu & Symons 1990; Boyer et al. 2008; Boyer & Singer 2008). Even though physical adsorption can also take place to a lesser extent (Bolto et al. 2004; Croué et al. 1999; Fu & Symons 1990), it has never been considered as controlling/predominant mechanism in the literature focusing on NOM removal by ion exchange resins. In general, in these studies, the release of chloride (the resin counter ion) was used as an indicator of ion exchange and thereby the lack of chloride release associated with NOM removal was interpreted as physical sorption.

Experiments conducted by Croué et al. (1999) at different pH values confirmed the possibility of physical adsorption of organic molecules onto the resin at acidic pH where significant amounts of both hydrophobic and hydrophilic acids were removed in the absence of chloride release. The considerable DOC removal with a weak anion exchange resin at neutral pH with no exchange capacity was further evidence for physical adsorption (Croué et al. 1999). However, it is important to note that all the resins used by Croué et al. (1999) had a polystyrene matrix which is not considered in interpreting their observations and the main focus was on the NOM characteristics.

Moreover, Pürschel et al. (2014) studied two resins with equal functional groups but different polymeric structures and concluded that polystyrene resin provided a better overall NOM removal. The authors attributed this observation to the possibility of the removal of hydrophobic neutral fraction through pi-pi stacking or hydrophobic interaction with polystyrene (i.e., hydrophobic) resin. Kanazawa et al. (2001, 2004) also developed an equilibrium equation for carboxylic organic acids removal by ion exchange resins, in which both physical adsorption and ion exchange were considered as responsible mechanisms for the retention of organic acids onto the resin. Nonetheless, none of these studies provided substantial data to verify the type and the extent of physical adsorption or the mechanisms other than ion exchange that may happen during the course of removal. Besides, there is a significant knowledge gap in understanding the molecular interactions occurring within the system under various conditions.

Studies conducted by Newcombe (Newcombe & Drikas 1997; Newcombe 1999) on the adsorption of NOM by activated carbon showed that the solution conditions (e.g., solution ionic strength) can significantly impact the contribution of different interactions/mechanisms to the overall removal efficiency. According to these studies, when electrostatic interactions govern the adsorption, presence of additional ions in water decreases the adsorption. Whereas, at high surface concentrations (i.e., when majority of the adsorbing media is covered by NOM) the non-electrostatic interactions govern the removal and the presence of ions in water may increase the adsorption by reducing the lateral repulsive electrostatic interactions. Furthermore, the repulsive force between the NOM charges may also diminish in the presence of ions that could result in a change in the shape and size of the NOM molecules. For example, linear NOM macromolecules may behave like a tightly coiled model and thereby the smaller size of the molecule allows them to better diffuse into the pores (Summers & Roberts 1988).

All in all, the removal mechanism can be influenced by various factors including NOM properties, resin characteristics and the solution properties such as ionic strength. In studying NOM removal by ion exchange resins, considering all these variables is of great importance. For example, the better removal of NOM by polystyrene resin compared to the polyacrylic resin, as observed by Pürschel et al. (2014), could be mainly because of the high amount of sulphate in the tested water that promotes the non-electrostatic/hydrophobic interaction between the hydrophobic (i.e., polystyrene) resin and the hydrophobic NOM. This is important to be considered as some other researchers have found a greater removal of NOM by polyacrylic resins (Fu & Symons 1990; Boyer & Singer 2008; Hsu & Singer 2010). Therefore, this inconsistency in the literature may be explained by considering other variables that can impact the removal such as the tested water quality in terms of NOM properties and the presence of other anions in water.

2.2. Factors Affecting the Removal Process

2.2.1. NOM characteristics

The effect of NOM properties including aromaticity, acidity, and molecular weight on kinetics and mechanism of removal has been widely investigated (Bazri & Mohseni 2016; Boyer et al. 2008; Fu & Symons 1990; Tan & Kilduff 2007). It has been demonstrated that there is a strong and positive correlation between the percentage of aromaticity and absorptivity of humic substances (Chin et al. 1994; Boyer et al. 2008), which are the main components of NOM in surface waters.

In employing a patented polyacrylic magnetic ion exchange (MIEX) resin (Singer et al. 2007; Drikas et al. 2011; Karpinska et al. 2013) for NOM removal, Fearing et al. (2004) reported removals of 60% and 70% for DOC and UV absorbing fraction, implying the preferential removal of UV absorbing molecules. Furthermore, in removing two fulvic acid extracts varying in aliphatic and aromatic carbon content by MIEX resin, Boyer & Singer (2008) have found the greater removal of the one with higher aromaticity. In another study carried out by Boyer et al. (2008) low affinity of MIEX was observed for DOM fractions with low charge density and low aromaticity. However, the authors demonstrated the charge density of DOM as an important factor in studying ion exchange removal of organic matter.

In addition to aromaticity and absorptivity of NOM, its molecular weight distribution was also demonstrated as an influential factor in the ion exchange of NOM molecules. In a column study conducted by Hongve (1989), a rapid removal of lower molecular weight and high charge density fraction of humic substances was achieved. While the removal of higher molecular weight and less charged molecules, which are mainly contribute to the color of the water (i.e., aromatic components) required more contact time. Croué et al. (1999) also observed a significant reduction in DOC removal with increasing the molecular weight from 1000 to 3000 Daltons and this was consistent for both gel/macroporous strong and weak base resins.

Moreover, Bazri & Mohseni (2016) demonstrated the molecular weight and consequently size exclusion phenomenon as an important factor that negatively influences the efficiency of ion exchange process for NOM removal. From size exclusion chromatography data obtained by Fearing et al. (2004) for removing NOM with MIEX resin , it was concluded that ion exchange was a suitable process for removing low and moderate molecular weight components, while ferric coagulation showed a better removal of moderate and high molecular weight species.

In contrast, a favourable removal of higher molecular weight NOM by styrene resin was achieved in a study conducted by Tan et al. (2005). It is also worth to note that they found a positive correlation between SUVA and molecular weight, meaning that aromatic and UV absorbing compounds are more amenable to be adsorbed on ion exchange resins. Afcharian et al. (1997) also confirmed the efficient removal of UV absorbing compounds with two styrene resins, which was comparable to the performance of granulated activated carbon adsorption in NOM removal. However, the effect of resin's styrene (hydrophobic) backbone could be also taken into account in these studies, because it might strengthen the hydrophobic interactions between the aromatic NOM and the resin, and thereby impact the affinity of the ion exchange process.

In view of the available literature on the effect of NOM characteristics on its removal by ion exchange resins, the charged fraction of UV absorbing compounds have greater affinity for the resin. And, the higher molecular weight/low charge density compounds are less amenable to adsorb onto the resin. However, it is of great importance to note that the NOM properties are interconnected. For example, the higher aromaticity corresponds to higher UV absorptivity and molecular weight, and thus the lower charge density of the NOM molecules. Therefore, in discussing NOM removal with ion exchange resins, one should consider the relative effectiveness of the NOM characteristics. Moreover, other factors such as resin properties and water matrix might also affect the selectivity of the ion exchange process, which is elaborated in the following sections.

2.2.2. Resin properties

A wide range of anion exchange resins with different properties have been investigated for removing negatively charged NOM molecules (Humbert et al. 2005; Bolto et al. 2002; Croué et al. 1999). It has been demonstrated that strong basic resins (SBRs) with quaternary ammonium functional groups are superior to weak basic resins (WBRs) for removing NOM (Croué et al. 1999; Anderson & Maier 1979). However, results reported by Croué et al. (1999) showed that NOM can be removed to a significant extent with weak anion exchange resins, and as already mentioned this was attributed to the probability of physical adsorption of NOM on resin polymeric matrix.

In addition, macroporous resins with higher water content are likely more suitable for NOM removal than the gel type resins (Bolto et al. 2002). This might be due to more open structure of macroporous resins and thereby greater potentials for molecules to diffuse through the resin pores. The polymeric skeleton of resins appears to be more important than their porosity in removing organic molecules. Regardless of whether resin was gel or macroporous, greater uptake of NOM has been reported by polyacrylic resins than resins with polystyrene backbone

(Fu & Symons 1990). The substantial removal of aromatic part of DOM by styrene resins shown in the literature (Cornelissen et al. 2008) may indicate hydrophobic interaction (attractive hydrophobic forces) between resin backbone and the aromatic moieties of DOM molecule. However, more knowledge of resins performance is still required for more efficient removal of NOM and its isolates.

2.2.3. Solution properties and presence of inorganic anions in water

Water solution properties such as pH and existence of inorganic ions, have also been regarded as important parameters in ion exchange treatment of NOM (Boyer et al. 2008). Inorganic ions such as nitrate and bicarbonate influence NOM removal in different ways. While nitrate competes with NOM for ion exchange sites (Boyer & Singer 2006), bicarbonate improves the removal of the hydrophobic NOM fraction (Croué et al. 1999). In addition, the effectiveness of NOM removal has been shown to be negatively influenced by the presence of iron due to the fouling on anion exchange resin (Hongve et al. 1999). Apart from inorganic ions, any change in the solution pH causes considerable variations in NOM removal due to the changes in acid-base equilibrium of the functional groups.

The impact of inorganic ions/salt molecules in water solution has been studied to a limited extent through the course of ion exchange process, demonstrating positive effect of bicarbonates and chloride on NOM removal (Croué et al. 1999; Cornelissen et al. 2008). Croué et al., (1999) reported an increase in hydrophobic NOM uptake by both strong basic macroporous and weak basic macroporous resins in the presence of bicarbonate ions. They also found no significant change in NOM uptake for the hydrophilic fraction of NOM with a strong basic gel type resin, suggesting a negligible competition between bicarbonate and NOM, besides the fact that the presence of bicarbonate was shown to promote the removal of some NOM fractions. They attributed this observation to the “salting out” effect that happens by increasing the solution ionic strength.

In general, the competition from sulphate was found to yield lower removal of DOC and UV absorbing compounds, however no negative competition effect from nitrate and bromide on DOC removal was observed (Tan & Kilduff 2007; Boyer & Singer 2006; Boyer et al. 2008). This could be due to the higher charge density of the sulphate and thereby its greater competition effect compared to nitrate and bromide. Although sulphate has an adverse impact on DOM removal, it may influence the selectivity of ion exchange process and shift the selectivity towards a specific fraction of DOM. Tan & Kilduff (2007) studied the DOM removal by ion exchange resin from two different water sources and found two significantly different behaviours for the change in SUVA values. One central difference in the structure of the two studied water sources was their sulphate concentration. To elaborate this observation, the authors spiked sulphate into the water with low sulphate concentration and observed a decrease in molecular weight and SUVA of DOM in treated water with increasing the sulphate concentration, indicating a preferential removal of higher molecular weight and high SUVA components in the presence of sulphate. Therefore, UV absorbing compounds exhibit a better and stronger competition with sulphate for ion exchange sites. Fu & Symons (1990) also found 3% reduction in the removal of 5-10 KD (Kilo Daltons) fraction of organic matter in the presence of sulphate while this number was 12% for <1KD fraction. The authors explained the results by the low charge number of smaller molecules and thereby their weak competition with sulphate.

As already mentioned, the number of studies on the impact of inorganics on NOM removal is very limited and the discussions were mainly made around the competition effect from inorganic anions. Some researchers have investigated the impact of ionic strength and salt induced effects on the contribution of different interactions to the activated carbon adsorption of NOM. One such study was conducted by Newcombe & Drikas (1997) on the impact of solution ionic strength on the contribution of electrostatic and non-electrostatic effects to the adsorption of NOM onto activated carbon. They found that at high surface concentrations (i.e., when surface is covered by adsorbed NOM) the increase in ionic strength promoted adsorption which was attributed to the salt induced screening of repulsive electrostatic interaction between adsorbed and non-adsorbed NOM. However, the presence of salts in solution (i.e., increased ionic strength) showed an adverse impact on NOM adsorption at low surface concentrations where the electrostatic attraction between NOM and surface was the dominant mechanism. Moreover, the unexpected increase in the adsorption of fractionated humic acid onto a positively charged activated carbon with increasing the ionic strength was observed by Summers & Roberts (1988). Accordingly, the authors measured the effective diffusion size of the humic acid and concluded a reduction in the size of humic acid by increasing the ionic strength of the solution.

From all these available literature, one may conclude that the behaviour of inorganic anions in water and their impact on molecular interactions within the system are of great importance that is missing in the body of literature on ion exchange removal of NOM. It is noteworthy that many attempts have been made to increase the retention of proteins on hydrophobic ligands by enhancing salt concentrations in the solution (Tsai et al. 2002). Hence, this approach may be potentially relevant to NOM binding on ion exchange resins. Accordingly, in the next section below, a review on the classification of inorganic anions based on their behaviour in aqueous solutions and thereby their impact on molecular interactions is provided.

2.3. Classification of Inorganic Anions Based on Hofmeister Effects

Inorganic anions are ordered in terms of their behaviour in aqueous solutions and their influence on biological processes, which is called Hofmeister series. Hofmeister series are mainly pronounced for anions and their usual order is shown in Figure 2.1.

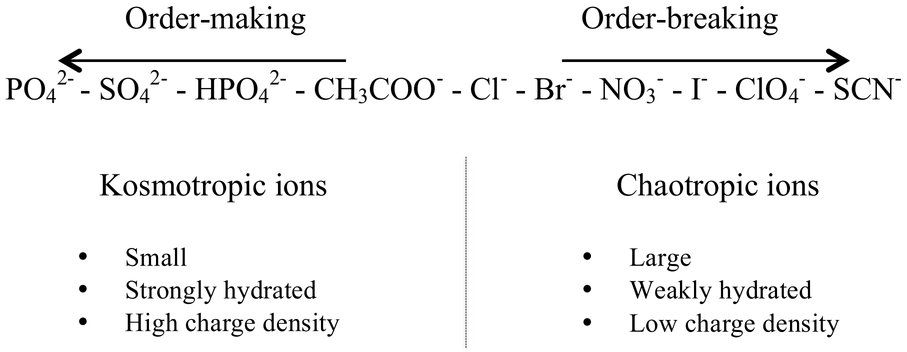

Figure 2.1, Classification of ions based on Hofmeister effects (Yang 2009; Nucci & Vanderkooi 2008; Zhang & Cremer 2006)**.**

The Hofmeister ions are characterized as Kosmotrope (order-making) and chaotrope (order-breaking) (Russo 2008) based on their ability to nature or denature biological macromolecules by altering the hydrogen bonding of water network. Kosmotrope salts stabilize solute structure in water by increasing the order of water molecules surrounding the solute, whereas, chaotrope salts destabilize solute and allow more structural freedom of the solute through the breakage of the hydrogen-bounded network of water molecules and increasing its surface tension (Moelbert et al. 2004). However, the mechanism of Hofmeister series is not clear enough. Zhang & Cremer (2006) demonstrated that hofmeister phenomena can not only be explained by their impact on bulk water structure, but also the interactions between ions and macromolecules are of importance and need to be taken into account in studying the influence of solution conditions on biological systems. In contrast, the study conducted by Nucci & Vanderkooi (2008) suggested that the salt induced modification of the solvation properties plays a major role in Hofmeister effects even if specific interactions occur between the ion and the protein. Moreover, Melander and Horváth (1977) provided a theory describing the dual nature of salt effects accounting for the effect of salts on both electrostatic and hydrophobic interactions in chromatographic behaviour of proteins. They also proposed a three-parameter equation in which the electrostatic interaction parameter is directly proportional to the charge of the protein and inversely dependent on the charge valence of salts counter ion; and the magnitude of the hydrophobic interaction parameter is dependant on the hydrophobic contact area of the protein and the salt's surface tension increment.

Consequently, changes in water structure caused by kosmotropic and chaotropic agents can affect the water-solute interactions, and subsequent thermodynamic profile of the binding systems. For example, the increase in the removal of hydrophobic fraction of NOM in the presence of bicarbonate that was obtained by Croué et al. (1999) may be explained by the capability of salt molecules in increasing the entropy of the system by interfering with hydrophobic effects. This leads to disordering of water molecules adjacent to the NOM, thereby denaturing and solubilizing of hydrophobic NOM molecules. However, utilizing the potential benefits of salts at increasing NOM removal efficiency requires more in-depth knowledge and experimental data on a range of salt types and concentrations.

2.4. Thermodynamics of NOM Removal by Ion Exchange Resins

One strategy to study interactions between ion exchange resins and NOM molecules could involve measuring changes of the thermodynamic parameters associated with the NOM removal. Despite investigations made to understand the mechanism of NOM removal and interactions happening in the NOM-resin binding system, no directly measured thermodynamic data has been reported to illustrate the removal mechanism or the impact of NOM characteristics, e.g., hydrophobicity, aromaticity, and NOM structure on the extent of removal. However, this approach has been extensively used to study protein binding mechanism on different types of ligands for protein purification systems (Bronowska 2011; Melander & Horváth 1977; Lin et al. 2001; Chen et al. 2007; Stites 1997), substantiating that thermodynamic parameters play an important role in the assessment of binding mechanism and the relationship between molecular structure and interaction activity.

Binding between two compounds is associated with Gibbs free energy (ΔG) which has both entropic ($-T\Delta S$) and enthalpic (ΔH) components (Bronowska 2011). The entropic term of free binding energy reflects changes in dynamics of the overall system, and the enthalpic term indicates the strength of interactions occurring in a binding system (Bronowska 2011). This means that the binding process comprises both dynamic and structural changes of each compound and any changes in a binding system may possess different thermodynamic characteristics.

While there is no study on NOM removal thermodynamics, Li & SenGupta (2001, 2004) investigated the removal of some pure hydrophobic anionic molecules by ion exchange resins and reported the process to be endothermic and entropy driven (positive entropy change). Nonetheless, a negative Gibbs free energy (negative $\Delta G^{\circ}_{overall}$) indicated a favourable removal process. When a hydrophobic compound is added to water, the water molecules rearrange themselves in clusters through hydrogen bonding, resulting in an overall entropy decrease in the system. Therefore, during the removal of hydrophobic anions, an increase in entropy was observed due to the collapse of the water clusters. It was concluded that, although the organic anions removal by resins follows a 1:1 ion exchange stoichiometry, the removal of organic molecules, specifically hydrophobic anions, could be significantly influenced by the hydrophobicity.

Tan & Kilduff (2007) also investigated the effect of entropy change in ion exchange removal of NOM through manipulating the solution by adding methanol as a co-solvent to the water. Their findings indicated a reduction in NOM removal from methanol-water mixture compared to that of water only, substantiating the importance of entropic driving force in the ion exchange of NOM. This reduction in dissolved organic matter (DOM) removal was more significant at low resin doses, where competition is at its highest level and only compounds with higher selectivity adsorb onto the resin, indicating the impact of entropic driving force in promoting the selectivity of some DOM components. Tan & Kilduff (2007) also provided evidences that the contribution of entropy to the removal process is greater in waters containing sulphate. The findings of Tan & Kilduff (2007) are consistent with the high ionic strength of sulphate resulting in screening the electrostatic interactions, either attractive or repulsive (Stuart et al. 1991). At low resin doses where the repulsive forces between adsorbed compounds may reduce NOM uptake, the sulphate's screening effect positively impacts NOM removal.

Therefore, one approach to facilitate the study of binding mechanism and the forces driving the interaction is to elucidate the binding thermodynamics and its correlation with the structures of compounds. Furthermore, this approach may facilitate the understanding of the impact of inorganic anions on removal mechanism and can support a quantitative explanation of the ion-induced changes in removal efficiency of different NOM fractions.

2.4.1. Isothermal titration calorimetry technique (ITC)

One method to measure the enthalpy and entropy contributions of free binding energy is to apply the isothermal titration calorimetry (ITC) technique, which is commonly and primarily used for evaluating binding mechanisms during biomolecular interactions (Perozzo et al. 2004). Isothermal titration calorimetry is a biophysical technique for analyzing molecular interactions in solution through the measurement of thermodynamic parameters. ITC is unique in its sensitivity and accuracy in providing quantitative binding thermodynamics including Gibbs free energy, enthalpy and entropy in a few experiments. The use of ITC has been initiated in the second half of the 1960s (Grolier & del Río 2012), and its sensitivity has been improved from mJ to µJ range (Grolier & del Río 2012; Freyer & Lewis 2008) over the years. The number of published papers related to the use of ITC from the 1980s to 2010 (Ghai et al. 2012; Falconer & Collins 2011; Falconer et al. 2010; Grolier & del Río 2012) indicates the evolution of ITC as a widely used technique and its rapid diffusion in the scientific community.

The significance of calorimetry rests in its ability in direct measurement of thermodynamic quantities (Freire et al. 1990). Binding thermodynamics serves as a useful analytical tool for the characterization of structural and functional chemistry of a binding system. Binding thermodynamics reflects the molecular mechanism of binding (Doyle 1997) and contributes to a better understanding of the structural-functional relationships (Ladbury & Chowdhry 1996) underpinning the molecular interactions. Since any reaction as well as NOM removal by resins is accompanied by a heat exchange between the system and its surroundings, calorimetry has been adopted as a technique for providing information that can be helpful in understanding the correlation between structural and thermodynamic contributions towards interactions in a system. Among the commercially available calorimeters, isothermal titration calorimeter (ITC), which uses the power compensation measurement method, has much improved capabilities in detecting even smaller heat effects.

As already indicated, the main application of ITC has been on the understanding of the mechanisms of bio molecular interactions. Protein interactions and their macromolecular assemblies (Ghai et al. 2012; Bello et al. 2008; Neuwirth et al. 2007; Norwood et al. 2011; Cho et al. 2010) is an example in which ITC has been employed to understand the binding mechanism and conformational changes during assembly. Another application of ITC is in bioinorganic chemistry (Grossoehme et al. 2010), studying the metal ions binding to biomolecules. Published reviews of ITC and its applications prove the increasing importance of ITC in drug design and development projects (Renaud & Delsuc 2009; Freire 2009; Freyer & Lewis 2008). ITC has also been used for analyzing the aggregation process of surfactants into micelles, and determining thermodynamics of micelle formation (Bouchemal et al. 2010; De Lisi et al. 2009). Moreover, in the past few years, ITC has been shown to be a powerful tool for monitoring enzyme reactions and characterizing the process kinetics (Murphy, Baumann, et al. 2010; Murphy, Borch, et al. 2010; Noske et al. 2010). ITC has also been used by the food science community to study the binding properties of tannins to proteins (Poncet-Legrand et al. 2007; McRae et al. 2010; Frazier et al. 2010) and all these gave an indication of the suitability of ITC in studying a broad range of applications.

2.5. Knowledge Gaps in NOM Removal Research

Although ion exchange, as a pre-treatment process, has been studied extensively for NOM removal by investigators, the more efficient removal of NOM requires more knowledge of the fundamental principles pertaining to NOM binding onto ion exchange resins. Several factors go into determination of NOM removal mechanism with the most important factor being NOM characteristics and challenges they impose on removal mechanism due to the complexity of its structure. Accordingly, this research has focused on responding to a number of questions that help address the fundamental knowledge gaps related to the removal of NOM during ion exchange process. The specific research questions and the corresponding knowledge gaps are as follows:

Question 1: How may hydrophobic characteristics of NOM impact its removal by ion exchange resins?

Different NOM characteristics including its ionic charge, molecular weight distribution, aromatic carbon content and UV absorptivity were widely investigated in the literature. It is hypothesized that these properties are not absolutely unrelated. That is, as also reported by Croué et al. (1999), the higher molecular weight, the lower charge density and the stronger hydrophobicity of NOM. It is believed that the hydrophobic characteristic of NOM might be a good parameter to be taken into account in studying ion exchange of different NOM fractions and may help to better understand the removal mechanism. To evaluate this factor, the removal of mono carboxylic acid organic compounds varying in their hydrophobicity has been tested with ion exchange resin. Moreover, different NOM isolates have been examined under various conditions (i.e., manipulating water structure by adding salts such as sodium nitrate or sodium sulphate).

Earlier studies relying on isotherms and analytical tests (e.g., TOC, UV absorbance, size exclusion chromatography) conducted for NOM removal showed greater affinity of lower molecular weight hydrophilic fractions of NOM towards strong basic resins (SBRs) compared to higher molecular weight hydrophobic fractions. In addition, isotherm tests carried out with single organic molecules revealed that hydrophobic characteristic of non-polar moieties of organic compounds has a significant impact on their removal performance (Li & SenGupta 2001; Li & SenGupta 2004b). While it is well understood how different types of resins perform for NOM removal, present knowledge and experience lacks data regarding the concept of critical hydrophobicity of NOM and its influence on removal mechanism; that is hypothesized to affect removal efficiency as well. Restated, it is still unclear how well the ion exchange treatment deals with a variety of organic molecules and NOM fractions at different solution hydrophobicity.

Question 2: What is the primary driving force for the ion exchange removal of NOM, and what are the possible molecular interactions involved in the process?

Prior fundamental studies on ion exchange process have indicated that removal of organic anions is not only governed by ion exchange, but also influenced by non-electrostatic interactions that are believed to play a significant role in removal procedure. Nevertheless, it is not well understood how these interactions may interplay and affect the removal performance.

Research in NOM removal by ion exchange resins has shown the possibility of a non-ion exchange interaction between resin and NOM, which is mainly called as physical adsorption or Van der Waals interactions between NOM and the resin polymeric backbone. Given that NOM possesses hydrophobic characteristics and considering its aromatic carbon content, it is hypothesized that the aforementioned physical adsorption may also include hydrophobic interactions that occur concurrently with electrostatic interactions (ion exchange). Still, it is proven in the literature that ion exchange is the predominant mechanism and governs the removal of NOM from water. However, Li and SenGupta (2001) demonstrated that despite ion exchange being the dominant mechanism for removing hydrophobic organic compounds, hydrophobic effect plays a significant role. That is, the authors believed that hydrophobic characteristic of organic compound leads to an entropic driving force for their removal and thus they reported an entropy-assisted sorption for the ion exchange of hydrophobic organic molecules. Tan & Kilduff (2007) also reported on the importance of the entropic driving force and its influence on DOM removal efficiency as well as the selectivity of ion exchange process. It is interesting to note that the authors approached these findings through manipulating the hydrophobicity of the solvent (i.e., water) by adding a hydrophobic co-solvent. Based on this information, it is believed that not only the hydrophobic characteristic of NOM results in the contribution of entropy to the removal, but also the solvent properties and its hydrophobicity are of importance.

Therefore, it is hypothesized that any change in the hydration of hydrophobic moieties may impact the ion exchange removal of hydrophobic NOM. It is also believed that solvent properties, NOM-solvent interaction, presence of other compounds in water and their molecular behaviour within solution need to be considered in elaborating the removal mechanism of NOM by ion exchange resins. To answer this question, this research has focused on studying the removal of different NOM isolates varying in terms of charge density, molecular size and aromatic carbon content under different solution conditions.

Available literature on activated carbon adsorption of NOM provides some information on the contribution of electrostatic and non-electrostatic interactions to the process (Newcombe & Drikas 1997; Newcombe 1999): however, to the author’s knowledge, there is no study on the involvement of different interactions in ion exchange removal of NOM. Therefore, it is unclear how different interactions may interplay during the course of ion exchange process for NOM removal and how the contribution of these interactions may differ with NOM characteristics. Thereby, the following research questions are developed based on this knowledge gap to attain the contribution of hydrophobic effect and other interactions to the removal efficacy of ion exchange process.

Question 3: How does the presence of salts such as sodium nitrate and sodium sulphate affect the removal efficiency of NOM, and does this have any impact on the contribution of hydrophobic effect to the removal performance?

Certain investigators have concluded that existence of salts/inorganic molecules in water solution can affect the removal efficiency of NOM. Nonetheless, due to the lack of data with respect to the effect of salts on the interactions between NOM and ion exchange resins or between NOM and water molecules, there is no definite answer whether the potential of salts in structural modification of water solution can improve treatment outcomes.

Overall, the relative significance of entropy-assisted sorption of NOM, and how the presence of salt molecules in the water solution affects the removal mechanism, is unknown. Consequently, hydrophobicity of the solution has to be taken into consideration due to its important role in entropy changes of the system and thereby in removal efficiency.

Considering the behaviour of different anions in water (i.e., Hofmeister effect), it is hypothesized that anions with stronger kosmotropic effect may promote the contribution of hydrophobic effect to the removal of NOM and thereby a better removal of hydrophobic fraction of NOM may be obtained. To evaluate this hypothesis, the author has studied the removal of NOM and its isolates in presence of two different inorganic anions: sulphate and nitrate, which are categorized as kosmotrope and chaotrope agents, respectively.

Question 4: How thermodynamic parameters associated with NOM removal change with NOM characteristics and solution properties?

One direct approach to evaluate the interactions involving in a system is to measure the thermodynamic parameters associated with that process. There is limited number of studies that qualitatively discussed the contribution of thermodynamic properties to the NOM removal by ion exchange resins but there is no quantitative measurement of thermodynamic parameters associated with NOM removal. It is definitely difficult and very challenging to measure the thermodynamic parameters i.e., enthalpy and entropic contributions to the free energy of NOM removal. However, as already discussed, isothermal titration calorimetry (ITC) technique, which is proven as an effective and accurate method to measure the thermodynamic parameters of biological systems, is believed to be applicable in NOM removal from water by ion exchange resins.

Question 5: Does the polymeric backbone of ion exchange resin have any impact on the removal mechanism of NOM from water?

It is hypothesized that styrene resins with hydrophobic characteristics decrease the entropy of the system when suspended in water, leading to a hydrophobic interaction including pi-pi stacking between aromatic NOM and the resin matrix. To answer this question, this research compared the removal of NOM isolates with both styrene and acrylic ion exchange resins under the same operating conditions to better evaluate the resin backbone factor. Besides, the selected resins are similar in other properties such as porosity and water content.

2.6. Significance of this study

This research will elucidate thermodynamic phenomena underlying the removal process of NOM through ion exchange. Thermodynamic characterization of the interactions involved in NOM binding on ion exchange resins will provide a new approach to determine the predominant interactions and governed driving force in removing NOM. Additionally, studying a broad spectrum of organic molecules differing in hydrophobicity will yield further insight into the role of hydrophobicity in removal behaviour at different operating conditions.

Furthermore, this research will be the first to take advantage of isothermal titration calorimetry (ITC) as an alternative technique for studying the thermodynamic properties of NOM removal during the ion exchange process, thereby helping with better and more detailed understanding of the NOM removal mechanism.

More importantly, the results obtained from the second goal of this study (i.e., salt-induced modifications in water structure) will provide knowledge on the possibility of altering the intricate structure of NOM or its interaction with water molecules to favour the binding of NOM onto the ion exchange resin, which is a vital step in maximizing NOM removal efficiency, and also in improvement of resin performance. It can also help in a better designing of water treatment plants.

Chapter 3 : Experimental Methodology

This chapter describes the general experimental procedure followed during the course of this research. Specific methodologies and information regarding materials used in each part of this research will be presented within the related chapters.

3.1. Water Samples Preparation

3.1.1. Batch binding experiments

Synthetic water samples containing standard Suwannee River organic matter isolates (i.e., Suwannee River NOM, Suwannee River Fulvic Acid, and Suwannee River Humic Acid) were prepared as a stock solution of 100 mg/L. The pH of the stock solutions was adjusted to neutral range (6.5-7) by adding the appropriate amount of NaOH (0.1 N) and then filtering using 0.45 μm membrane filters. The stocks were stored at 4°C in 1 L bottles. Prior to experiments, the water samples were prepared by diluting a certain amount of the stock solutions and the final dissolved organic carbon (DOC) and pH of the water as the feed sample properties were measured.

3.1.2. Isothermal Titration Calorimetric (ITC) tests

Water samples used for ITC tests were prepared at high concentrations of ≈ 750 mg/L of DOC. To be consistent in all experiments, in every sample preparation about 30 mg of either of the NOM isolates was added to 15 mL Milli-Q pure water and stirred for few hours to ensure that majority of the NOM is dissolved. The solution was then adjusted to 6.5 using NaOH and HCl solutions and filtered using 0.45 μm syringe filters (the syringe and filter were pre rinsed with Milli-Q pure water) and transferred in a 20 mL glass vials.

3.2. Resins Preparation

At every batch of the resin preparation, an approximate amount of 100 mL resin (equals to 100 g resin) was rinsed with 2 L of Milli-Q water to eliminate any potential manufacturing contaminants. Afterwards, the water was decanted and a 2L of 10 % Wt. brine solution was added and mixed with the resin for one hour in order to regenerate the resin. Then, the regenerant was decanted and the resin was rinsed with Milli-Q water for 30 minutes. The rinsing water was freshened and this rinsing process continued until the amount of released chloride ion to the water by 100 mL resin was below the detection limit (~ 0.2 mg/L) of the ion chromatograph.

The prepared resin was stored in fresh Milli-Q water and prior to use, a certain amount of the resin was taken and then the excess water was decanted. Afterwards, in order to accurately weigh the resin and to be consistent during the course of the project, the resin was air-dried and stored in desiccator for at least 24 hrs prior to weighing.

The resins used for ITC tests were crushed using a mortar and pestle in order to be able to inject the resin into the instrument using the specific needle designed for ITC. This was one of the main limitations in employing ITC; however, the batch control experiments that were conducted with the crushed resin confirmed that the resin has nearly the same performance as before. Thereafter, a 1.25 g of the crushed resin was weighed and added to the 250 mL of Milli-Q pure water. A 15 mL of the suspended solution was transferred into a 20 mL glass vial and then the pH was monitored, which was usually 6.5.

3.3. Batch Binding Experiments

Batch experiments were conducted using a Lab Companion SI-600 Benchtop Shaker at room temperature. Every batch experiment was carried out using 100 mL of the synthetic water mixed with a certain dose of the prepared resin in a 250 mL flask. The shaker rate was set to 200 rpm in all experiments during the course of this work. Accordingly, the required time for equilibrium over kinetic tests was determined and will be discussed in the next chapters. Control experiments were also conducted during which 100 mL of Milli-Q water with the resin was stirred using the same conditions as the batch tests and the sample was analyzed for chloride ion and DOC.

After ion exchange treatment, 40 mL of the treated water was taken from the flask for the following analytical measurements:

- Dissolved organic carbon (DOC) measurements

To quantify the amount of organic matter (NOM/FA/HA), a Shimadzu VCPH total organic carbon (TOC) analyzer was used. This instrument uses combustion catalytic oxidation/NDIR method[*] for measuring total carbon. Given that the studied model waters contained no inorganic carbon, all the measured carbon represents the amount of DOC in the samples.

All TOC vials used in this study were carefully washed and rinsed with both tap water and then Milli-Q pure water. Thereafter, vials were baked at 550°C for at least 2 hrs. Nonetheless, a control test was always conducted to ensure that TOC vials are clean in which the amount of DOC in a blank sample (i.e., Milli-Q water in a TOC vial) was measured.

- Ion Chromatography (IC)

The amount of anions (i.e., chloride, nitrate, and sulphate) in water samples was measured using a Dionex 1100 Ion Chromatograph equipped with Dionex AS22 Fast column and an electrical suppressor. The chloride ion in the feed (untreated) water sample was also measured and if the value was above the detection limit, it was considered in the calculations.

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[*] http://www.ssi.shimadzu.com/products/literature/toc/toc-v-series.pdf (accessed on December 28, 2016)

- Ultraviolet (UV) Absorption (UV_{254})

The absorptivity of samples at 254 nm was measured using a UV-Vis spectrophotometer (Agilent Cary 100) with cell path length of 1 cm. The reference sample used in all the measurement was Milli-Q pure water. The quartz cuvette (cell) was also triple rinsed between the measurements to avoid any potential contamination from previous sample.

3.4. Isothermal Titration Calorimetric (ITC) Tests

The most important feature of the ITC is its sensitivity in running experiments and accuracy in providing the data. Prior to experiments, the prepared solutions (i.e., NOM isolates and the suspended resin solution) were degased twice each for 5 minutes to ensure the dislodgment of any air bubbles that may be trapped within the solution. Afterward, the cell of 1.4 mL volume was filled with the suspended resin solution and the injecting syringe with a volume of 250 µL was loaded with organic matter solution.

Figure 3.1 shows a schematic of an ITC in which the reference cell contains water or buffer, and the sample cell is usually filled with adsorbent (the resin solution in this research). The titrant, which is usually a macromolecule like protein or NOM, is injected into the sample cell by the injecting syringe. Sensitive thermocouples are used for detecting temperature differences between two cells and between cells and jacket. To maintain an isothermal environment, heaters are located on the jacket and cells, will be activated when necessary. Prior to injection a continuous power is applied to the reference cell. A signal is sent to sample cell to activate the heater, and this signal is the baseline signal. Depending on the nature of interaction between titrant and adsorbent (whether the reaction is endothermic or exothermic), heat can be either absorbed or released. Therefore, to maintain equal temperatures between the two cells, the feedback circuit increases or decreases power to the sample cell. Observable signal is the power per unit time that has been applied to the sample cell (Freire et al. 1990; Grolier & del Río 2012; Pierce et al. 1999).

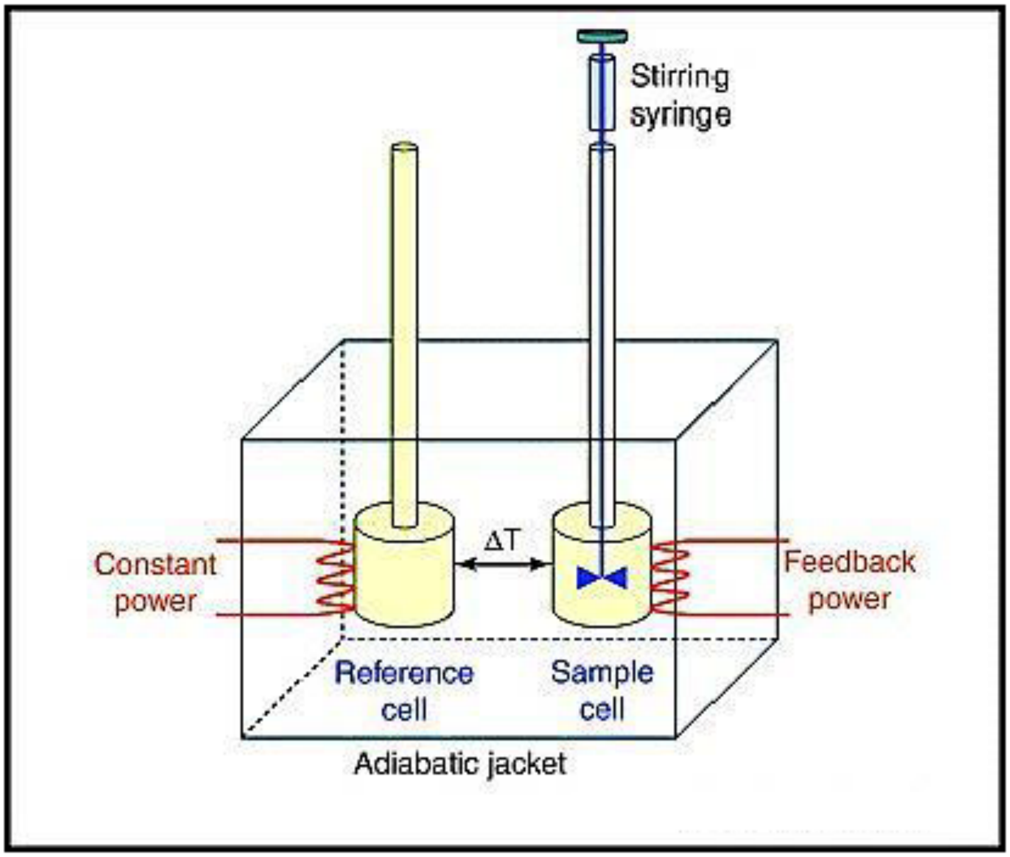

Figure 3.1, Schematic of an ITC[*]

The ITC that was used in this study is controlled by MicroCal software and the parameters of an ITC run are an input in this software including the time of injections, the number and volume of injections and the molar ratio of the organic molecule to the anion exchange resin. The time between injections was in a range that allows the organic matter

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[*] http://pharmaxchange.info/press/2012/08/isothermal-titration-calorimetry-application-in-drug-discovery/ (Accessed on December 28, 2016).

solution and the resin solution to be well mixed and reach equilibrium. Based on preliminary results, the following conditions were considered for this study:

- Number of injections in one experiment: 24
- Injection volume: 10 µL/each injection
- Time between injections: 300 sec

3.4.1. Control experiments to determine the dilution heat

To determine the net heat of binding, a control test is required to measure the other heat effects involved in the observed heat, including the contributions from the dilution heat and mechanical aspects as well as the one arising from temperature mismatch between the resin solution in the cell and the organic matter solution in the injecting syringe. Control tests were conducting in this research involving the injection of the organic matter solution into the Milli-Q pure water.

3.5. Reproducibility of the Results

In order to ensure the reproducibility of the results, all the batch tests were repeated three times and the ITC tests were done in duplicate, because ITC experiments are time-consuming process and necessities system cleaning after each test. In addition, sample analysis including IC, UV_{254}, and TOC measurements were duplicated. The errors of TOC analyzer and ion chromatograph were 2% and 2 – 3%, respectively. According to the range of the DOC of the water samples analyzed in this work (0 – 6 ppm), all the data points presented here have an error range of ± 0.02 – 0.1 ppm. The values obtained by IC are within the range of ± 0.05 ppm, which for example for chloride measurement in terms of equivalent is equal to ± 0.0015 meq/L. To improve the reproducibility of the experimental procedure, prepared resins were kept in desiccator 24 hours prior to weighing and organic content (model water) solutions that were stored in the fridge were returned to the room temperature prior to use. All the other details regarding the experimental method can be found in the corresponding chapters.

Chapter 4 : The Role of Hydrophobic Properties in Ion Exchange Removal of Organic Compounds from Water

This chapter presents the research carried out to assess the effect of hydrophobic characteristics of dissolved organic matter during the course of the ion exchange process. The approach involved investigating the sorption of three ionisable organic compounds, which are identical in terms of ionic charges and different in their non-polar moieties, in order to better evaluate the contribution of the hydrophobic properties to the affinity of these compounds for ion exchange. The higher uptake of hydrophobic compounds and lower competition effect from inorganic anions on the removal of these compounds provided evidence for the importance of the hydrophobic effect. The hydrophobic characteristics of organic compounds and the favourable entropy change that they impose during de-solvation had a great contribution to the ion exchange selectivity of these compounds.

Furthermore, this chapter presents the experimental results for the removal of the studied organic compounds in the presence of inorganic anions to evaluate the impact of the solvent properties. Increasing the ionic strength of the solution by adding high charge density anions, such as sulphate, to the water diminished the contribution of the electrostatic interactions; hence, the potential physical adsorption between the resin and the organic molecule predominated the removal mechanism. No change in removal mechanism was observed in the presence of inorganic anions with low charge density such as nitrate.

4.1. Introduction

Many organic compounds, either synthetic or natural, contain acid groups. As a result they are soluble in water and can be found in natural water sources. Ion exchange has been introduced as an effective technology for the removal of organic molecules from aqueous solutions (Bolto et al. 2002; Croué et al. 1999; Fu & Symons 1990; Hongve 1989; Mergen et al. 2008; Fearing et al. 2004), as organic molecules with strong acidic groups and high charge density are less amenable to removal by hydrophobic sorbents such as activated carbon.

The ion exchange of organic anions is always accompanied by desorption of counter ions from the resin phase. Most studies have shown a 1:1 stoichiometry between the uptake of organic molecule and the release of resin counter ion in terms of meq/L (Li & SenGupta 2001; Boyer & Singer 2008). However, some researchers have shown that physical adsorption (van der Waals interactions) can possibly take place between non-ionic moieties of organic molecule and the resin polymeric backbone (Bolto et al. 2002; Cornelissen et al. 2008; Li & SenGupta 2004b). Significant uptake of organic matter was observed by Croué et al. (1999) through physical adsorption under acidic conditions. Kanazawa et al. (2001; 2004) have also developed an equilibrium model for the adsorption of aliphatic and aromatic carboxylic acids, in which both physical adsorption and ion exchange are considered as two independent mechanisms occurring during the course of adsorption.

Even if the removal mechanism is governed by ion exchange, Li and Sengupta (2004) demonstrated that the hydrophobicity of organic compound is an important variable that plays a significant role in the overall sorption equilibrium. The removal of hydrophobic compounds from water is a favourable process (negative ΔG) (Li & SenGupta 2001; Li & SenGupta 2004b) because it follows the increase in the entropy of the system. Therefore, the removal of hydrophobic compounds from water is called as an entropy-assisted sorption in the literature (Li & SenGupta 2001; Li & SenGupta 2004b; Li & Sengupta 1998; Tan & Kilduff 2007).

Moreover, some literature provide evidence of increased removal of hydrophobic organic acid in presence of some inorganic anions (Croué et al. 1999; Tan & Kilduff 2007). Increasing the ionic strength of solution may reduce electrostatic interactions. This is often called the effect of screening (Newcombe & Drikas 1997; Stuart et al. 1991), and thereby other variables such as hydrophobic effect may dominate the adsorption process in presence of inorganic anions. The effect of increased ionic strength on the contribution of electrostatic (ion exchange) and non-electrostatic (physical adsorption) interactions is widely studied for the adsorption of polyelectrolytes and proteins on different types of adsorbents (van de Steeg et al. 1992; Newcombe 1999; Melander & Horváth 1977; Chen et al. 2007). However, information on the influence of ionic strength on the removal of organic compounds by ion exchange resins is not sufficient.

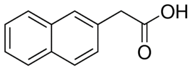
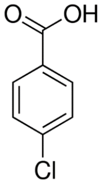
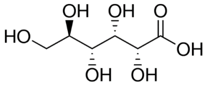
Understanding the fundamentals underlying ion exchange process especially in removing natural organic matter from water is of great importance. Natural organic matter is composed of different organic compounds and its complex structure makes it challenging to study the hydrophobic effect, driving forces and molecular interactions involved in the removal process. To better evaluate the role of hydrophobic effect and distinguish its influence on the removal mechanism and interactions happening during the ion exchange process, the removal of three pure organic compounds was studied. The selected compounds have similar characteristics in terms of molecular weight and ionic charge and a major difference in their non-polar head group. The removal of these compounds in the presence of nitrate and sulphate was also examined to better address the impact of inorganic anions with different charge densities. The specific objectives of this work were threefold; to quantify the contribution of hydrophobicity to the removal efficiency, to investigate its importance in ion exchange selectivity especially in the presence of competing inorganic anions, and finally to establish how the presence of different inorganic anions in water may impact the removal mechanism and the relative contribution of electrostatic and non-electrostatic interactions during the course of organic compounds removal by ion exchange.

4.2. Materials And Methods

4.2.1. Water samples

Table 4.1 provides some information on chemistry of the compounds studied in this research. Three monocarboxylic organic compounds were used in this study including naphthalene acetic acid (NAA), chlorobenzoic acid (BA), and gluconic acid (GA). The compounds were purchased from the Aldrich chemical company in Canada. Three model waters were prepared by adding the mentioned organic compounds to Milli-Q pure water. Water samples were filtered through 0.45 μm membrane filters prior to experiments and the initial dissolved organic carbon (DOC) concentration of all three water samples was set to 5.7-6 mg C/L; the pH of the water solutions was also adjusted to 6.5 (the range of pH in natural water sources is 6 to 8.5) using a 0.1 M reagent grade sodium hydroxide solution.

Table 4.1, The chemical characteristics of organic compounds used in this study.

Compound	Molecular formula	Molecular weight (g/mol)	pK_a	LogP [1]	LogD [2]
2-Naphthalene acetic acid		186.21	4.2 [3]	2.736	0.43
4-Chlorobenzoic acid		156.57	4.0 [4]	2.65	0.15
D-Gluconic acid		196.16	3.7 [5]	-1.87	- 4.67

[1] Experimental Partition-Coefficient values are taken from https://pubchem.ncbi.nlm.nih.gov and http://www.chemspider.com accessed on 14 November 2016.

[2] Distribution-Coefficients are calculated using the following equation: $LogD = logP - \log(1 + 10^{(pH - pK_a)})$ for pH=6.5.

[3] (Norris & Bukovac 1972; Dippy et al. 1954)

[4] (Pearce & Simkins 1968)

[5] (Ramachandran et al. 2006)

4.2.2. Ion exchange resin

An anion exchange resin (Ionac MacroT from Sybron Chemicals Inc., reported exchange capacity by manufacturer: 1.1 eq/L) was used in this study. This resin has a polyacrylic macroporous structure with strong-base functional groups and was received from the manufacturer in a moist state in an airtight polyethylene container. The resin was cleaned and pre-conditioned prior to use. In each cycle of resin treatment, approximately 100 mL of moist resin was rinsed twice with 2L Milli-Q water each for 30 minutes by means of a magnetic stirrer plate to remove any impurities. In order to make sure that the resin is completely in chloride form, it was regenerated with NaCl (10 % by weight) solution by stirring in a 2L Erlenmeyer flask for 2 hours. To remove the residual NaCl, resin was rinsed with deionized water several times. To ensure that the NaCl was fully removed, the amount of chloride ion in water was measured using an ion chromatograph. Once the amount of chloride ion was less than 0.05 ppm, the resin was stored in de-ionized water in sealed glass bottles.

Prior to experiments, in order to accurately dose the resin, a desired amount of pre-treated resin was decanted in a vacuum-driven filter using Whatman No.1 filter paper to remove the excess water, and was kept in desiccator for 24 hours to dry the excess moisture and then was weighed.

4.2.3. Ion exchange isotherm experiments

Batch isotherm experiments were conducted in which 100 mL of model waters was mixed with varying amounts of resin (200-1500 mg/L) for 15 hours using a shaker-incubator. Rate studies indicated that 15 hours was sufficient for Macro-T resin to reach equilibrium. After equilibrium, about 40 mL of treated solution was withdrawn for chemical analysis. A Shimadzu TOC-V_{CPH} total organic carbon analyzer was used to measure DOC. This instrument uses combustion catalytic oxidation/NDIR method for measuring total carbon. Given that the studied model waters contained no inorganic carbon, all the measured carbon represents the amount of DOC in the samples. The amount of chloride in the samples was also monitored using a Dionex 1100 ion Chromatograph equipped with Dionex AS22 Fast column.

As control experiments, the same amount of resin was equilibrated with 100 mL de-ionized water for 15 hours and samples were taken and analysed for DOC and chloride. All experiments were carried out at laboratory ambient temperature (22-23 °C) and they were all duplicated.

4.3. Results and Discussion

4.3.1. The role of non-polar head group of organic compounds

Naphthalene acetic acid (NAA), chloro-benzoic acid (BA) and gluconic acid (GA) are identical electrostatically; all have one carboxylic group that dissociates in water and forms an ionic form of these acids with one negative charge. However, NAA has two aromatic rings in its non-polar group, BA has only one aromatic ring and GA consists of a six-carbon chain with five hydroxyl groups. These three compounds with a main difference in their non-polar head group were selected to study the role of hydrophobic effect in removing organic compounds from water by ion exchange resins.

As shown by Li and SenGupta (1998), the hydrophobic characteristics can significantly impact the ion-exchange sorption of organic compounds. Hydrophobic domains on organic compounds decrease the entropy of the solution, which results in a thermodynamically favorable removal of the compound from the solution. In literature, this is called an entropy-assisted sorption. The dehydration of hydrophobic molecules is endothermic because the cluster like structured water molecules require heat to be broken. Once the de-solvation of hydrophobic moieties of molecules happens, they interact with ion exchange resin through electrostatic interaction, which is an exothermic process. Additionally, the sorption of organic molecule follows the release of hydration water from the resin too, which results in an increase in the entropy of the system. Li and SenGupta (Ping Li and SenGupta 2001; Ping Li and SenGupta 2004; P Li and SenGupta 1998) have shown that the overall process is endothermic and this signifies the importance of entropic contribution during the course of ion exchange process for removing hydrophobic organic compounds.

Our approach to evaluate the hydrophobic effect on ion exchange of organic molecules was to compare the removal efficiency of two organic compounds with one and two aromatic rings (BA and NAA respectively) and one hydrophilic molecule (GA). As these three compounds have one ionic charge and very similar molecular weights, so the impact of charge and size of the molecule can be neglected and discussion is made based on the difference in their non-polar group.

The uptake of three selected organic compounds by anion-exchange resin having an acrylic matrix is shown in Figure 4.1. The greatest uptake was observed for NAA over a wide range of resin dose. The difference in adsorption amount of NAA, BA and GA was more significant at lower resin concentration where less ion exchange sites are available for the sorption of organic anions. The significantly higher uptake of NAA and BA compared to GA correlated with the higher hydrophobicity of NAA and BA, confirming the importance of the entropy-assisted sorption during the course of ion exchange process. In particular, at low resin dose where lower amount of ion exchange sites is available, the impact of hydrophobicity on removal efficiency is more evident. Even at higher resin doses, 90 % of NAA and BA were removed while only 70 % of GA was adsorbed on the resin, and this observation is interpreted as an evidence of the entropy-assisted sorption. In other words, the rejection of non-polar moieties by water molecules (i.e., polar solvent) promoted the uptake of organic compounds (Li & Sengupta 1998; Tan & Kilduff 2007). However, it has to be noted that this illustration might be different when the studied compounds are not equal in terms of charge and molecular size, then the impact of these factors has to be also taken into account.

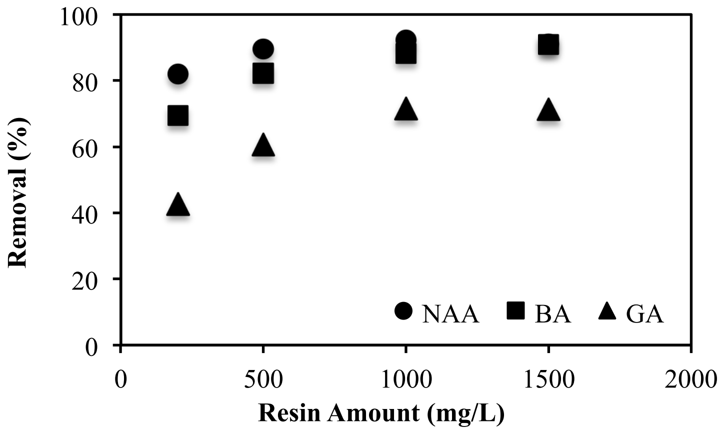


Figure 4.1, Uptake of NAA, BA and GA by MacroT resin at different doses (pH=6.5).

According to Table 4.1, GA has the lowest pK_a value and dissociates in water more than NAA and BA (if the pH of the water is close to the pK_a values), thereby a better removal is expected for GA than the other two compounds if the electrostatic interactions are the only responsible forces for the ion exchange of the organic molecules. Accordingly, experiments were conducted to compare the removal of studied three organic acids without adjusting the pH of the solution and the results are shown in Table 4.2. The higher uptake of NAA and BA compared to GA was achieved, demonstrating the importance of hydrophobicity and its role as a driving force in the ion exchange removal of organic compounds.

Table 4.2, The removal of organic compounds without adjusting the pH of the water solutions (resin dose: 200 mg/L).

Compound	pH of the solution	DOC removal (%)
NAA	4.38	74.0
BA	4.17	67.3
GA	4.07	34.7

4.3.2. Effect of inorganic anions

To better evaluate the role of hydrophobic effect in the ion exchange of organic compounds, two competing anions; nitrate and sulphate; were added to the model water samples.

Sorption of the organic compounds in the presence of 0.1 mM sodium nitrate or sodium sulphate (equivalent to 6 mg/L of nitrate and 9 mg/L of sulphate concentrations in the solution) was measured in batch tests. Figure 4.2 shows the removal percentage of NAA, BA, and GA in the presence of nitrate and sulphate at different resin doses. For a better comparison, the results of control experiments in the absence of salts are also presented. As illustrated in Figure 4.2, with the addition of inorganic anions, the removal of organic molecules decreased at low resin doses, indicating a competition effect from inorganic anions for ion exchange sites. The competition effect from sulphate was more significant as it has two charges while nitrate has only one charge. At higher resin doses, the removal of organic compounds increased with resin dose, as it did in the absence of the competing inorganic anions too.

The effect of competition from inorganic anions on GA is clearly more significant even at higher resin doses. This correlates with the hydrophobic effect of non-polar groups of NAA and BA, which provides an entropic driving force (according to Li and SenGupta (2001)) for the adsorption of organic molecules. Therefore, the behaviour of organic compound in water and its interaction with water molecules can significantly influence the ion exchange selectivity. The favourable interaction between GA and water molecules diminishes its affinity for ion exchange sites especially in the presence of competing inorganic anions. Therefore, in the ion exchange of organic compounds, not only does the ionic charge of the molecule drive the process, but also the type of interaction between solvent molecules and organic solute is of great importance. This is consistent with the findings of Li and SenGupta (Li & SenGupta 2001; Li & SenGupta 2004b) and Tan et al. (Tan & Kilduff 2007). The experiments were also conducted at different salt concentrations with results presented and elaborated in Appendix A.

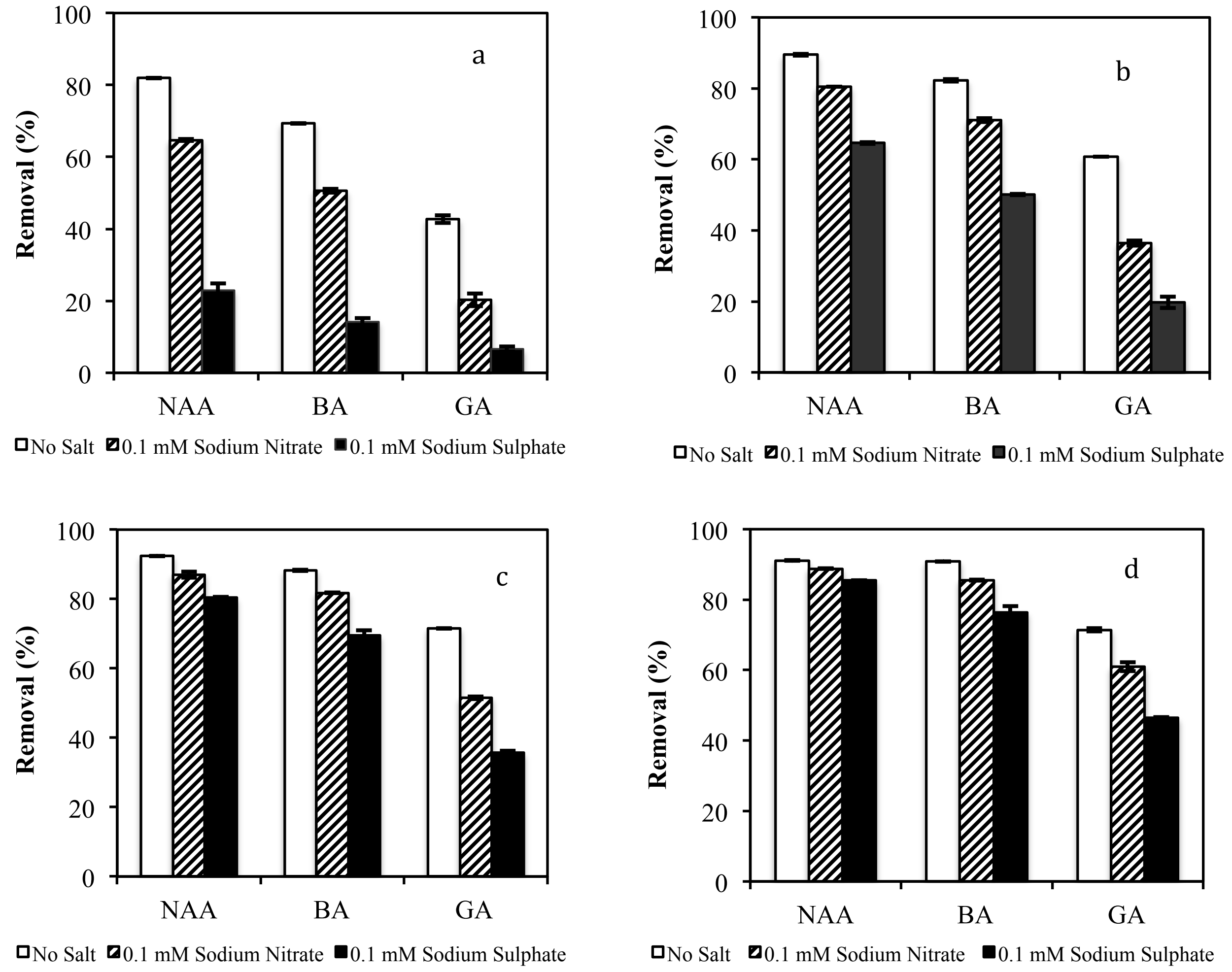


Figure 4.2, Effect of nitrate and sulphate on removal efficiency of NAA, BA, and GA at different resin doses: (a) 200 mg/L; (b) 500 mg/L; (c) 1000 mg/L; (d) 1500 mg/L resin. Error bars represent standard error.

4.3.3. Sorption stoichiometry

The chloride and sulphate concentrations in water after anion exchange treatment were also measured using an ion chromatograph. The results are plotted against the change in organic compound concentration after treatment (Figure 4.3). The initial concentration of organic compounds in the studied model water solutions was 5.7-6 mg C/L. With an increase in resin dose, the concentration of both nitrate and sulphate decreased for all three different organic molecules. This indicates that regardless of the type and structure of organic compound, inorganic anions were preferentially removed by ion exchange resin. However, sulphate was removed better than nitrate and as shown in Figure 4.3(b), the sulphate concentration was reduced to below detection limit even at very low resin doses, and this is attributed to the higher ionic strength of sulphate compared to nitrate.

Furthermore, as illustrated in Figure 4.3, organic compounds can favourably compete with nitrate, specifically those with hydrophobic characteristics (i.e., NAA and BA). At low resin doses, where significant amount of nitrate was still present in water, more than 3 mg/L of DOC uptake was observed for NAA and BA, while this value was about 1 mg/L in presence of sulphate. DOC uptake increased with an increase in resin dose and this is consistent with the amount of available sites on the resin for ion exchange and thereby lower competition effect from inorganic anions at higher resin doses. The pattern of increase in DOC removal with an increase in resin amount is nearly the same for NAA, BA, and GA in the presence of nitrate. However, in the case of sulphate, once sulphate was depleted, DOC uptake for NAA and BA was increased significantly with resin dose, but the pattern is different for GA and the only increase in GA removal was 2 mg C/L by increasing the resin amount from 200 to 1500 mg/L. If the competition from sulphate is the only contribution to the lower removal of organic solutes, the uptake of organic molecule should significantly increase with increasing the resin dose. This can be explained by the screening effect of sulphate at resin surface (Newcombe & Drikas 1997; Stuart et al. 1991), and thereby reducing the electrostatic attraction between organic molecule and resin. This effect was significant for GA removal where the electrostatic attraction is the predominant driving force in adsorption. Also, referring to Figure 4.2, at very low resin dose (200 mg/L), the adsorbed amount of GA fell significantly in presence of sulphate, because the only responsible interaction for adsorption of GA, i.e. electrostatic attraction between resin and

GA, was progressively screened by sulphate. However, in removing NAA and BA, as the hydrophobic effect and thereby the entropic driving force governs the removal, the screening effect of sulphate was not that significant compared to GA, especially at higher resin doses.

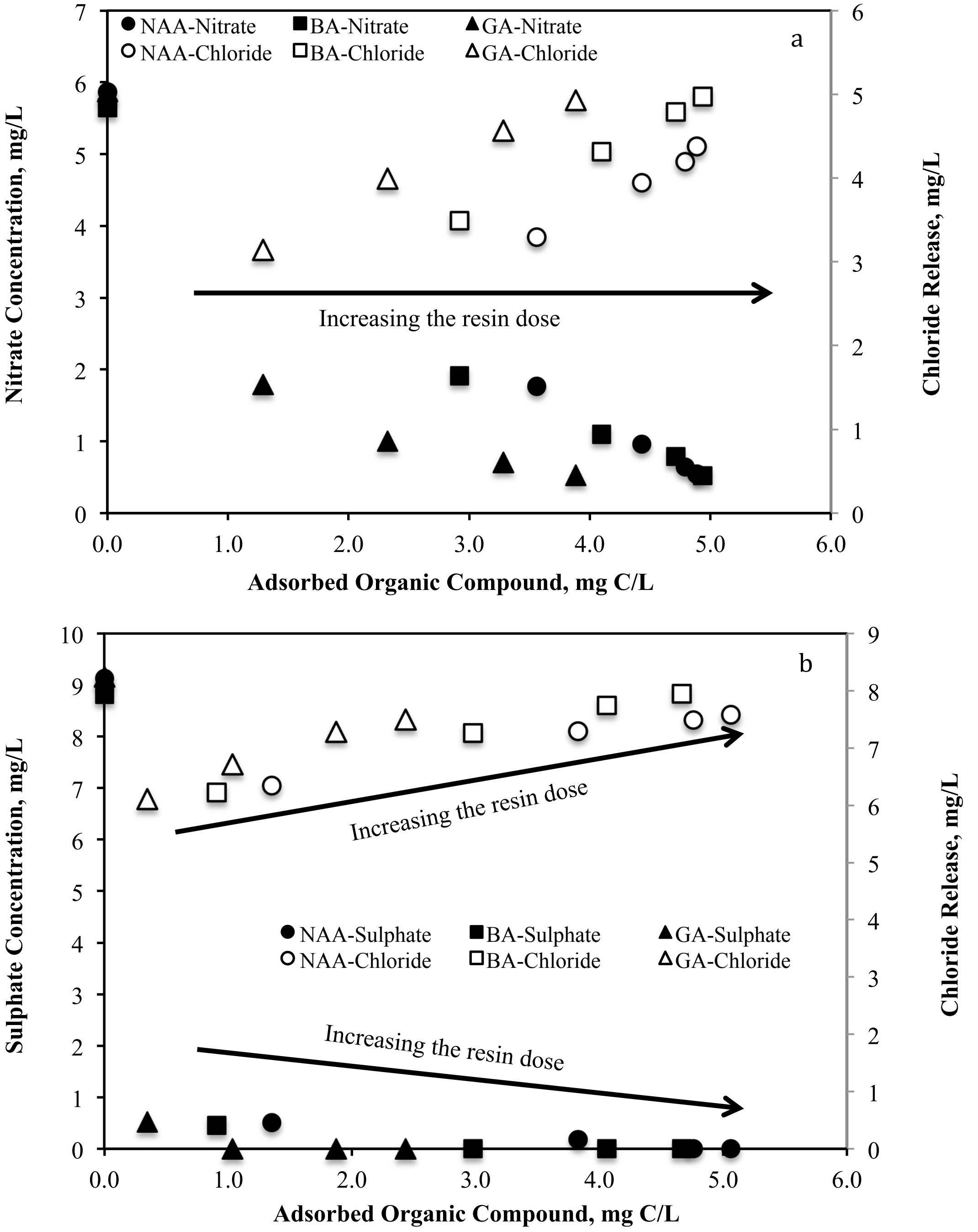


Figure 4.3, Stoichiometry of the ion exchange process for removing organic compound and inorganic anion at different resin doses. (a) nitrate ($C_0 \approx 6$ mg/L); (b) Sulphate ($C_0 \approx 9$ mg/L). See Appendix F for standard error values of the data points, which range between 0.0000 and 0.1228.

Moreover, for all three organic compounds, the relationship between chloride release and DOC uptake is linear. After most sulphate or nitrate ions were removed, chloride release increased indicating the removal of organic compounds by ion exchange. However, it is clear from the data in Figure 4.3 that chloride release per mg organic carbon adsorbed (chloride release vs. DOC uptake slope) is lower in the case of sulphate. Considering that some of the chloride release is associated with the exchange of sulphate ion, this is consistent with the uptake of some organic molecules by physical adsorption.

4.3.4. Sorption mechanism

To better evaluate the impact of sulphate on the adsorption mechanism of organic compounds, the results are plotted in terms of meq/L. If the removal of organic molecules from water is happening through the exchange of ions between the resin (solid phase) and water (liquid phase), for any equivalent of organic molecule that is adsorbed on the resin, the same equivalent of chloride is expected to release to the water. In other words, for a purely anion exchange process, the decrease in the concentrations of organic compound and inorganic anion must equal the increase in the concentration of chloride in water.

Figure 4.4 shows the results for DOC uptake versus chloride release for NAA, BA, and GA in the absence of any inorganic anion in terms of meq/L. The DOC and chloride concentrations in meq/L were calculated from the measured concentrations in mg C/L and mg/L, respectively. As shown in Figure 4.4, all of the data points are clustered about the y=x line which represents the stoichiometric exchange of chloride for organic molecule, and this verifies that all three compounds were removed via ion exchange. The observed extra chloride release is attributed to the trapped chloride in resin pores during the resin regeneration and preparation process. As illustrated in Figure 4.4, this value is very small (about 0.2 mg/L which is equal to

0.006 meq/L chloride), and for this reason it was not observed in control experiments as it is below the detection limit.

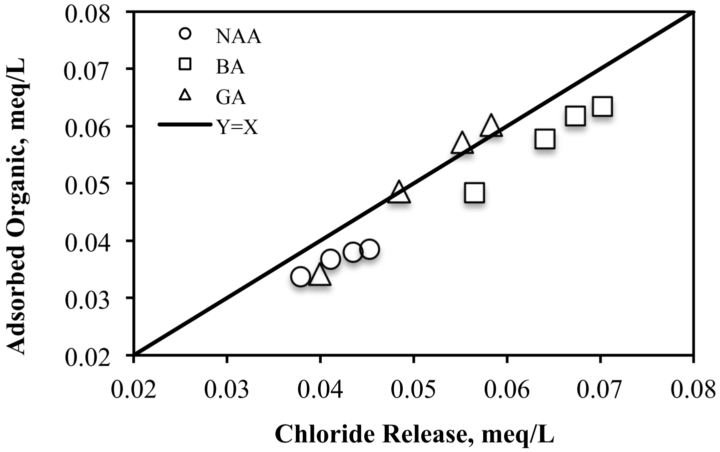


Figure 4.4, Ion exchange stoichiometry for MacroT resin and corresponding model waters containing NAA, BA, or GA. See Appendix F for standard error values of the data points, which range between 0.000000 and 0.001354.

Of particular interest are the data points for the experiments in the presence of inorganic anion (i.e., nitrate and sulphate). Figure 4.5 shows the amount of chloride release for the net decrease in the concentrations (meq/L) of organic molecule and nitrate/sulphate together. In the case of nitrate (Figure 4.5(a)), the points are tightly clustered about the y=x line, while in the presence of sulphate (figure 4.5(a)), the data points for all three compounds are slightly above the y=x line, meaning that less chloride was released for the equivalent amount of anions that was adsorbed on the resin at equilibrium. To better understand this observation, control experiments were conducted in which nitrate/sulphate was added to Milli-Q water and equilibrated with different resin doses for 15 hrs. Samples were analyzed for the amount of chloride release and sulphate/nitrate removal.

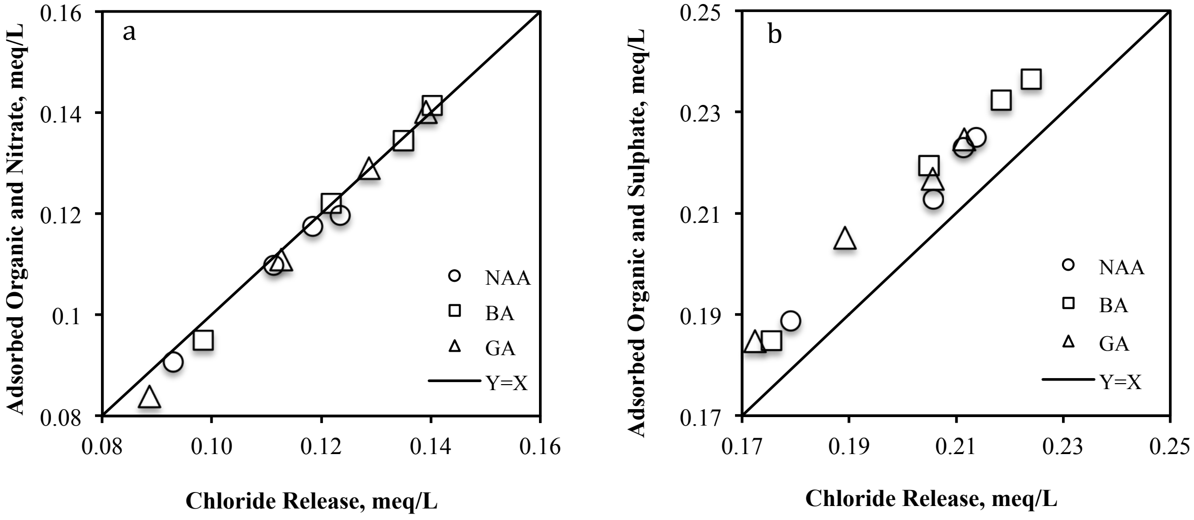


Figure 4.5, Ion exchange stoichiometry for MacroT resin and corresponding model waters containing one organic compound (NAA, BA, or GA) and (a) 0.1 mM sodium nitrate; (b) 0.1 mM sodium sulphate. See Appendix F for standard error values of the data points, which range between 0.000010 and 0.004228.

Figure 4.6 shows the results from control experiments and it confirms that both nitrate and sulphate were exclusively removed via ion exchange. Combining this observation with those in Figure 4.5, suggests the involvement of another mechanism in addition to ion exchange in removing organic compounds in the presence of sulphate. This is consistent with findings of Newcombe (Newcombe & Drikas 1997) and other researchers who studied the effect of ionic strength on the contribution of electrostatic and non-electrostatic interactions in adsorption processes. Generally, an increase in ionic strength of solution reduces the electrostatic interactions, either attractive or repulsive. Therefore, in the removal of organic compounds by resins where ion exchange is the dominant mechanism, an increase in ionic strength decreases adsorption and the potential non-electrostatic interactions between resin and organic molecule govern the removal. When the resin dose is sufficiently low, the impact of ionic strength is higher. At very low resin dose (i.e., 200 mg/L) about 0.18 meq/L of sulphate was removed and according to control experiments, 0.18 meq/L of overall chloride release corresponds to sulphate removal. Also, as shown in Figure 4.5(b), the amount of overall chloride release at low resin dose is about 0.17-0.185 meq/L; meaning that all the organic compounds were removed via physical adsorption and no chloride was exchanged for the adsorption of organic molecule on the resin. Clearly, the involvement of ion exchange in the removal process increases with the resin dose. This impact of ionic strength was not observed by nitrate, which is attributed to its lower charge density and thereby not exhibiting sufficient screening effect and only reduced the overall removal percentage to some extent by occupying some ion exchange sites on the resin.

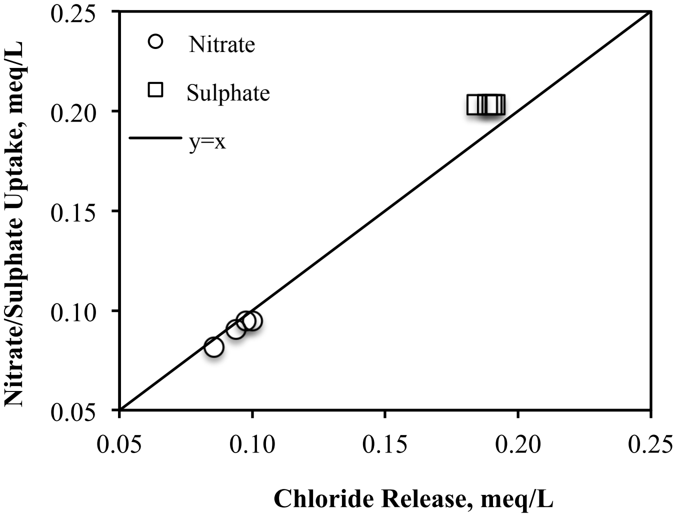


Figure 4.6, The ion exchange stoichiometry for MacroT resin and corresponding nitrate/sulphate removal (control experiment).

4.4. Conclusions

The adsorption of organic compounds on anion exchange resins involves several interactions and mechanisms. Even though, ion exchange is proven to be the predominant mechanism, higher uptake of hydrophobic organic molecules compared to hydrophilic ones, is an evidence for the significance of hydrophobicity and its role in assisting the uptake of organic molecules from water. The results from this research suggest that solute-solvent interaction is of great importance influencing the sorption affinity of organic compounds. Also, the lower competition effect from inorganic anions in removing hydrophobic organic molecules confirms the dominant role of the hydrophobic effect and the contribution of entropy-assisted sorption in the uptake of hydrophobic organic compounds. Furthermore, presence of inorganic anions with high ionic strength such as sulphate favours the physical adsorption between organic molecule and the resin by exhibiting screening effect and thereby diminishing the electrostatic interactions happening in the system. Therefore, there is a potential for physical adsorption between resin and organic compounds; and the contribution of ion exchange or physical adsorption to the removal mechanism may differ under different solution conditions.

Chapter 5 : Removal of NOM Isolates by Ion Exchange Resins in the Presence of Inorganic Anions

The results obtained from previous chapter clarified the importance of the hydrophobic effect and the contribution of entropy-assisted sorption to the removal efficacy and the ion exchange selectivity of organic compounds. Moreover, the significance of solution ionic strength in removal mechanism was demonstrated. Accordingly, this chapter aimed to interpret the ion exchange removal mechanism of NOM by elucidating the contribution of hydrophobic and electrostatic effects to the selectivity of the ion exchange under different solution conditions.

The experimental data for the ion exchange removal of three NOM isolates (i.e., Suwannee River NOM (SRNOM), Suwannee River fulvic acid (SRFA), and Suwannee River humic acid (SRHA)) in the absence/presence of inorganic anions are presented. Despite the prevalence of ion exchange mechanism, the presence of competing inorganic anions had less impact on SRHA (i.e., the most hydrophobic fraction), signifying the contribution of entropy to the ion exchange selectivity. Furthermore, in the presence of sulphate, the removal of UV-absorbing compounds was enhanced as the electrostatic interactions were screened by added salt, and consequently entropic contribution to the removal was promoted. Nitrate had almost the same influence on UV-absorbing removal for SRFA and SRHA; however, in the case of SRNOM, it did not affect the removal pattern, which is explained by its lower charge density that could not govern the strong electrostatic interactions between small hydrophilic NOM molecules and the resin.

5.1. Introduction

The ion exchange removal of NOM can be influenced by several parameters such as NOM characteristics and water matrix. Majority of NOM is hydrophobic and as already discussed in this research, entropy assisted sorption (the release of free water molecules due to the dehydration of hydrophobic moieties) is an asset for the ion exchange of hydrophobic NOM. Therefore, the interaction between the solute (i.e., organic compound) and the solvent (water) plays an important role and presence of inorganic anions in water could influence the ion exchange selectivity by manipulating these interactions. In a study conducted by Tan and Kilduff (2007), a preferential removal of high MW NOM species from waters containing high concentrations of sulphate was observed. They explained this observation by entropy-assisted sorption and the significance of hydrophobic effect (that might be promoted in presence of sulphate) in determining the ion exchange selectivity for high MW compounds. Similar results were obtained by Croué et al. (1999) suggesting an increase in the removal of hydrophobic fraction by increasing solution ionic strength (i.e., addition of sodium chloride or bicarbonate), which was attributed to the "salting out" effect. Considering that ion exchange is the predominant mechanism in removing organic matter (Boyer & Singer 2008; Boyer et al. 2008; Fu & Symons 1990), increasing hydrophobic character may improve the removal affinity due to their weak interaction with solvent (i.e., water) molecules. Gustafson & Lirio (1968) have also obtained high selectivity for the removal of organic molecules in which both electrostatic interaction and hydrophobic effect contribute to the process. Accordingly, this property may be explained by solvophobic theory, which is a theoretical framework for the interpretation of the combined electrostatic and hydrophobic effect (Vailaya & Horváth 1997; Melander et al. 1989; Melander & Horváth 1977).

With respect to the influence of NOM properties, this study compares the removal efficiency of different NOM isolates encompassing different elemental composition to better evaluate the key factors affecting the process with a major focus on hydrophobic character and the role of entropy-assisted sorption. Furthermore, although there are some studies on the impact of inorganic anions, those findings are still inconclusive and the importance of solution conditions (i.e., presence of anions with various properties and concentrations) is not well documented. This work also focuses on the influence of inorganic anions (i.e., nitrate and sulphate) on the interplay of hydrophobic effect and electrostatic interactions to better evaluate the significance of solution properties (i.e., water structure) and water-solute interactions in the ion exchange removal of NOM.

5.2. Materials and Methods

5.2.1. DOM isolates

Three different DOM isolates purchased from international humic substances society (IHSS) were used in this study. The estimates of carbon distributions of these samples determined from carbon-13 nuclear magnetic resonance spectra (NMR) are represented in Table 5.1.

Table 5.1, Chemical properties of DOM isolates in terms of carbon distribution using ^{13}C NMR estimates [a].

DOM isolate	Carbonyl 220-190 ppm	Carboxyl 190-165 ppm	Aromatic 165-110 ppm	Acetal 110-90 ppm	Heteroaliphatic 90-60 ppm	Aliphatic 60-0 ppm
Suwannee River NOM (SRNOM)	8	20	23	7	15	27
Suwannee River Fulvic Acid (SRFA)	5	17	22	6	16	35
Suwannee River Humic Acid (SRHA)	6	15	31	7	13	29

[a] Numbers represent the electronically integrated percentages of peak area and references for these data are IHSS website and the work performed by Thorn et al. (Thorn et al. 1989).

5.2.2. Water samples

Synthetic waters were made by dissolving a certain amount of NOM isolates and filtered through 0.45 μm membrane filters to ensure the removal of any undissolved matter. The final pH of water samples was adjusted to ~6.5 using a 0.1 M reagent grade sodium hydroxide. The characteristics of synthetic water samples used in this study are presented in Table 5.2.

Table 5.2, Characteristics of water samples.

Water source	[a]Charge density (meq/g C)	TOC (mg/L)	TOC (meq/L)	SUVA (L/mg.m)	[b]MW (Da)
Suwannee River NOM (SRNOM)	9.27	5.5-6	0.051-0.056	4.3	1030
Suwannee River Fulvic Acid (SRFA)	10.21	5.5-6	0.056-0.061	4.8	1070
Suwannee River Humic Acid (SRHA)	7.99	5.5-6	0.044-0.048	7.2	1520

[a]The values are estimated at pH=6.5 using the equation and fitting parameters provided by (Ritchie & Perdue 2003) and IHSS website .

[b] (Bazri & Mohseni 2016)

5.2.3. Resin Preparation

A strongly basic macroporous and polyacrylic anion exchange resin (Ionac MacroT, with an exchange capacity of 1.1 eq/L) was used in this study. Previous research showed that this resin exhibits an effective removal of DOC, and its performance is similar to that of magnetic ion exchange (MIEX) and other polyacrylic rsins (Boyer & Singer 2008). The resin was preconditioned and regenerated using sodium chloride solution (brine, 10% wt.) and rinsed with Milli-Q water to remove excess chloride. Prior to experiments, the required amount of pre-treated resin was decanted and dried in desiccator for 24 hours.

5.2.4. Ion exchange batch experiments

Using a shaker incubator, 100 mL of synthetic waters was mixed with different amounts of resin; 200, 500, and 1000 mg/L corresponding to 0.21, 0.53, and 1.06 meq/L of resin, respectively. Experiments were conducted for a wide range of contact times between 30 min to 15 hrs (9 time intervals in total).

5.2.5. Impact of inorganic anions

To evaluate the impact of inorganic anions with different charge densities on the removal of DOM isolates, batch tests were also conducted with spiking sodium nitrate /sodium sulphate into the water samples. The salts were purchased from Thermo Fisher Scientific and EMD Chemicals Inc. in Canada, respectively. To have a comprehensive assessment, the removal efficiency of ion exchange process was investigated in the presence of a broad range of nitrate/sulphate concentrations (i.e., 0.1, 1, 10, 20, 30, and 40 mM).

5.2.6. Analytical methods

DOC of samples was measured on a Shimadzu TOC-V_{CPH} total organic carbon analyzer. The amount of inorganic anions including chloride, nitrate and sulphate was measured using a Dionex 1100 Ion Chromatograph equipped with Dionex AS22 Fast column. Ultraviolet (UV) absorbance of the samples was monitored using an Agilent Cary 100 UV-Visible Spectrophotometer.

5.3. Results and discussion

5.3.1. DOC and UV removal

Figure 5.1 compares the removal of NOM isolates in terms of DOC removal as a function of time at different resin doses. Clearly, the overall removal efficacy for all three NOM isolates increased with resin dose. For SRNOM and SRFA, the required time to reach equilibrium decreased with resin dose (i.e., higher removal rate at higher resin doses). In earlier studies, pore diffusion was reported as the main rate controlling factor in removing organic compounds by macro porous resins (Bazri & Mohseni 2016; Boyer & Singer 2008; Weaver & Carta 1996). Hence, it can be concluded that increasing the resin dose led to a faster removal of organics and accordingly faster equilibrium because of the more available surface area (i.e., the lower intra-particle mass transfer limitation) at higher resin doses. However, the results were significantly different for SRHA, where the removal rate was almost constant at any resin dose. A possible explanation for this is that the adsorption of SRHA was mainly taking place on the outer surface of the resin and could be attributed to its molecular size and inability to penetrate into the resin pores.

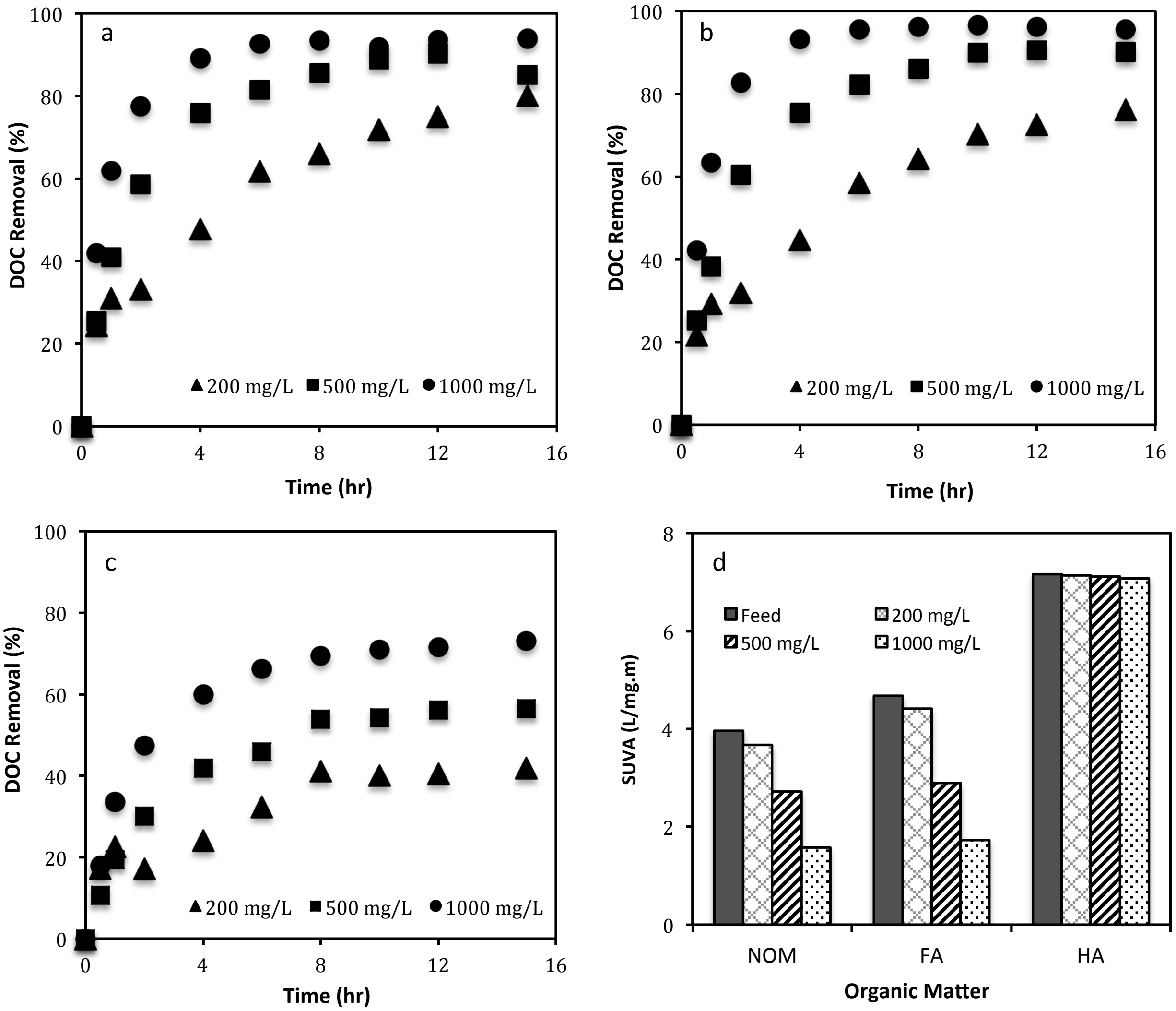


Figure 5.1, DOC uptake for SRNOM (a), SRFA (b), SRHA (c) vs. time, and SUVA values at equilibrium (d).

DOM has a heterogeneous structure and may result in a competitive removal of components with different adsorption properties. In this work, the competition between DOM components was studied by measuring the change in SUVA values after treatment of studied model waters at different time intervals. The results at equilibrium are illustrated in Figure 5.1(d) for different resin doses. The change in SUVA value was quite significant at various resin doses for SRNOM and SRFA, confirming the competition among components comprising NOM and FA. However, the effect of resin dose was not observed for SRHA and the SUVA value for SRHA remained constant. Given that DOC uptake increased for SRHA by resin dose (Figure 5.1(c)), this observation suggests that SRHA has less heterogeneous structure and species comprising SRHA are similar in terms of UV absorptivity and affinity for ion exchange sites. It is noteworthy that some other researchers have also found a proportional removal of DOC and UV absorbing substances (equivalent SUVA value of raw and treated water) in treating natural waters with high SUVA values (i.e., >3 L/mg.m) (Singer & Bilyk 2002; Johnson & Singer 2004; Boyer & Singer 2005).

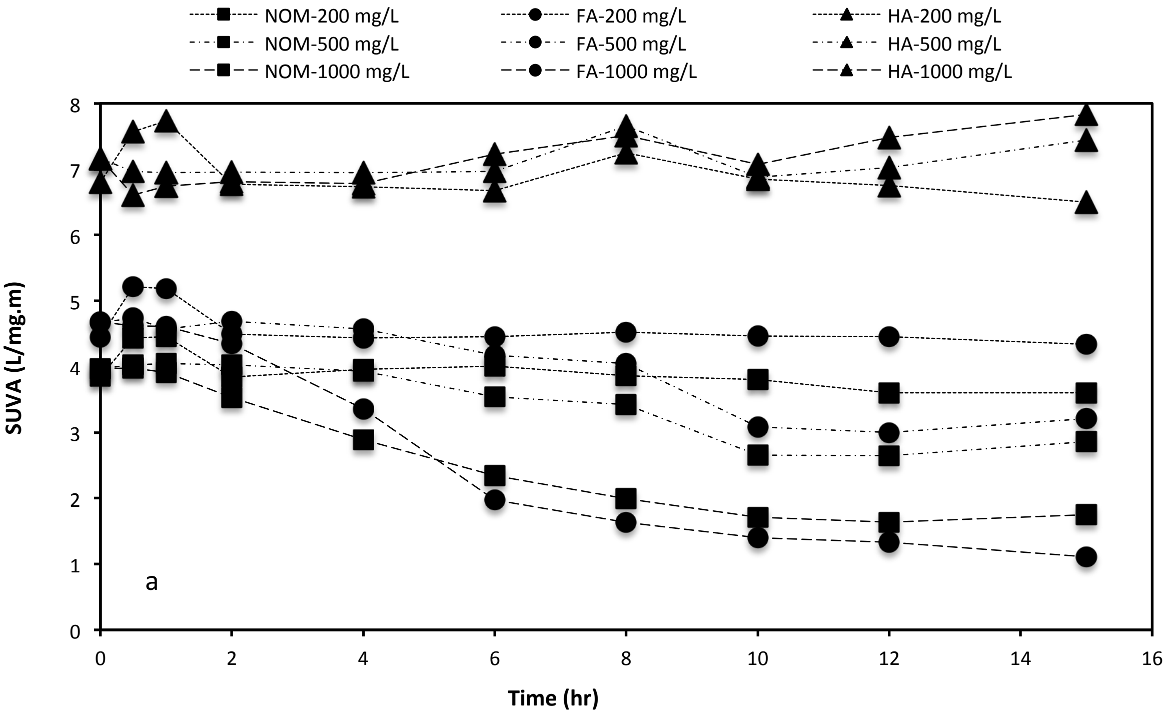


Figure 5.2, SUVA profile for the removal of NOM isolates with different resin doses.

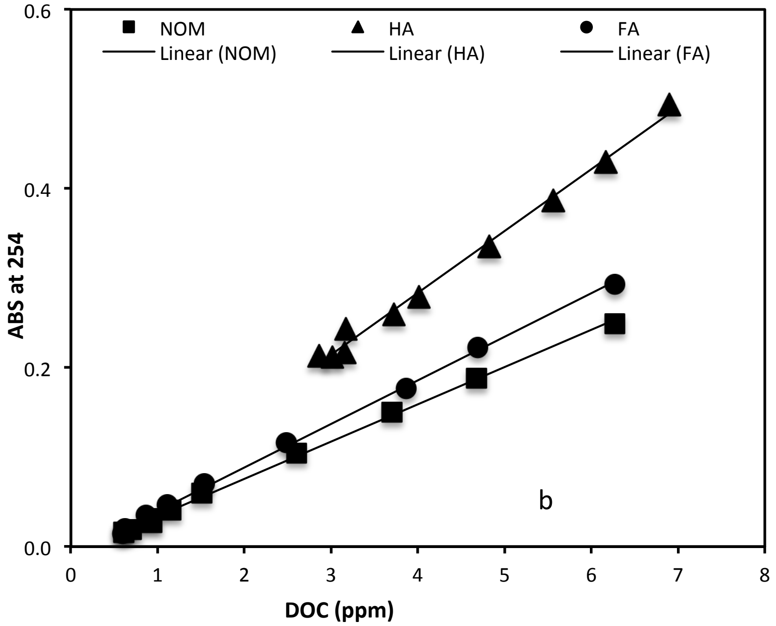


Figure 5.3, UV absorptivity vs. DOC for a resin dose of 500 mg/L, other resin doses yielded the same trend (data are presented in Appendix B, B.1).

To have a better evaluation, the change in SUVA value of treated water over time is also shown in Figure 5.2. As demonstrated in Figure 5.2, at a low resin dose (200 mg/L), the SUVA value initially increased and then decreased, indicating a faster removal of non-UV absorbing (low SUVA value) compounds. There is a positive correlation between SUVA value and molecular size (Chin et al. 1994; Tan et al. 2005), thus the slower removal of UV absorbing compounds was expected due to the mass transfer limitations. This is also in a good agreement with the finding of Hongve (1989). However, when the equilibrium was achieved (after 10 hours), the SUVA of treated water was always below the initial SUVA value, confirming the preferential removal of UV absorbing compounds by the ion exchange resin. In addition, increasing the resin dose resulted in a significant decrease of SUVA for SRFA and SRNOM waters. Therefore, compounds with higher SUVA value appear to be more amenable to ion exchange sites. The reduction in SUVA value by increasing the resin dose is more significant for SRFA than SRNOM. Increasing the resin amount from 500 mg/L to 1000 mg/L reduced SUVA for SRFA and SRNOM by 41% and 25%, respectively. According to Table 5.2, the distinct difference between SRFA and SRNOM is that SRFA has more aliphatic carbon compared to SRNOM. Also, SRNOM contains hydrophilic organic carbon, while SRFA has only hydrophobic compounds. A possible explanation for this observation could be the competition among NOM species. The competition is greater when ion exchange sites are limited (i.e., low resin dosage). Therefore, by increasing the resin dose, the removal of the compounds with lower affinity (i.e., non-UV absorbing hydrophilic components) increases.

Moreover, according to a study conducted by Singer et al. (2007), polyacrylic MIEX resin has removed hydrophobic fraction of DOC more effectively than the hydrophilic fraction. Therefore, the higher DOC and UV uptake of SRFA compared to SRNOM at high resin doses can be attributed to its higher hydrophobic carbon content and more hydrophobic characteristics. For further information and future discussions, the change in UV absorbance at 254 nm versus

DOC is also demonstrated in Figure 5.2, representing a linear relationship. The same linearity was observed at other resin doses as well (i.e, 200 mg/L and 1000 mg/L); data are shown in Appendix B, B.1.

5.3.2. Impact of inorganic anions on removal efficacy

The approach of this work to evaluate the importance of molecular interactions in the ion exchange removal of the organic matter was to first study the removal performance in the presence of competing inorganic anions. The removal efficacy of NOM isolates under different concentrations of sodium nitrate and sodium sulphate was then studied. The results in terms of DOC and UV uptake at equilibrium are presented in Figure 5.4. Moreover, the removal of NOM isolates in the presence of inorganic anions was also studied at different time intervals and the results are presented in Appendix B.

In presence of both inorganic anions (i.e., nitrate and sulphate), the overall DOC removal (Figures 5.4(a) and 5.4(b)) decreased for SRNOM and SRFA. However, in the case of SRHA, the DOC removal slightly increased in presence of nitrate. Given that SRHA is the most hydrophobic isolate, this observation is consistent with the previously reported data by Croué et al. (1999) showing that increasing the ionic strength improves the removal of hydrophobic acid fraction of NOM. It is important to note that this was not observed for sulphate, which may be attributed to the stronger competition effect by sulphate compared to nitrate. But, still the reduction of DOC removal for SRHA in the presence of sulphate was very small compared to SRFA and SRNOM, confirming the significance of hydrophobic effect in removing organic compounds from water.

Moreover, according to Figures 5.4(a) and 5.4(b), the negative impact of inorganic anions on DOC removal was in the order of SRNOM>SRFA>SRHA. The SRHA and SRFA that were used in this study contain only hydrophobic organic acid (referring to IHSS website*). Additionally, according to the characteristics of the NOM isolates shown in Table 5.2, SRHA possesses more hydrophobic characteristics (i.e., higher molecular weight, higher aromaticity and higher SUVA value). Therefore, it can be concluded that the impact of inorganic anions on DOC removal had an adverse relationship with the hydrophobicity of the organic matter. The occupation of some ion exchange sites on the resin by inorganic anions had less impact on compounds with more hydrophobic characteristics. This observation confirms the presence of another force rather than electrostatic interactions in driving the ion exchange process for removing hydrophobic organic matter. According to Li and SenGupta (2004), the rejection of a hydrophobic compound by solvent (i.e., water) due to its weak interaction with water molecules is the main driving force in the adsorption of higher MW/low charge density hydrophobic compounds. The removal of hydrophobic compounds results in the freedom of water molecules and thereby increasing the entropy of the system, which is thermodynamically favourable. Therefore, the ion exchange removal of hydrophobic organic matter is an entropy-assisted process (Li & SenGupta 2001; Tan & Kilduff 2007).

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* http://www.humicsubstances.org/isolation.html (Accessed on January 10, 2017)

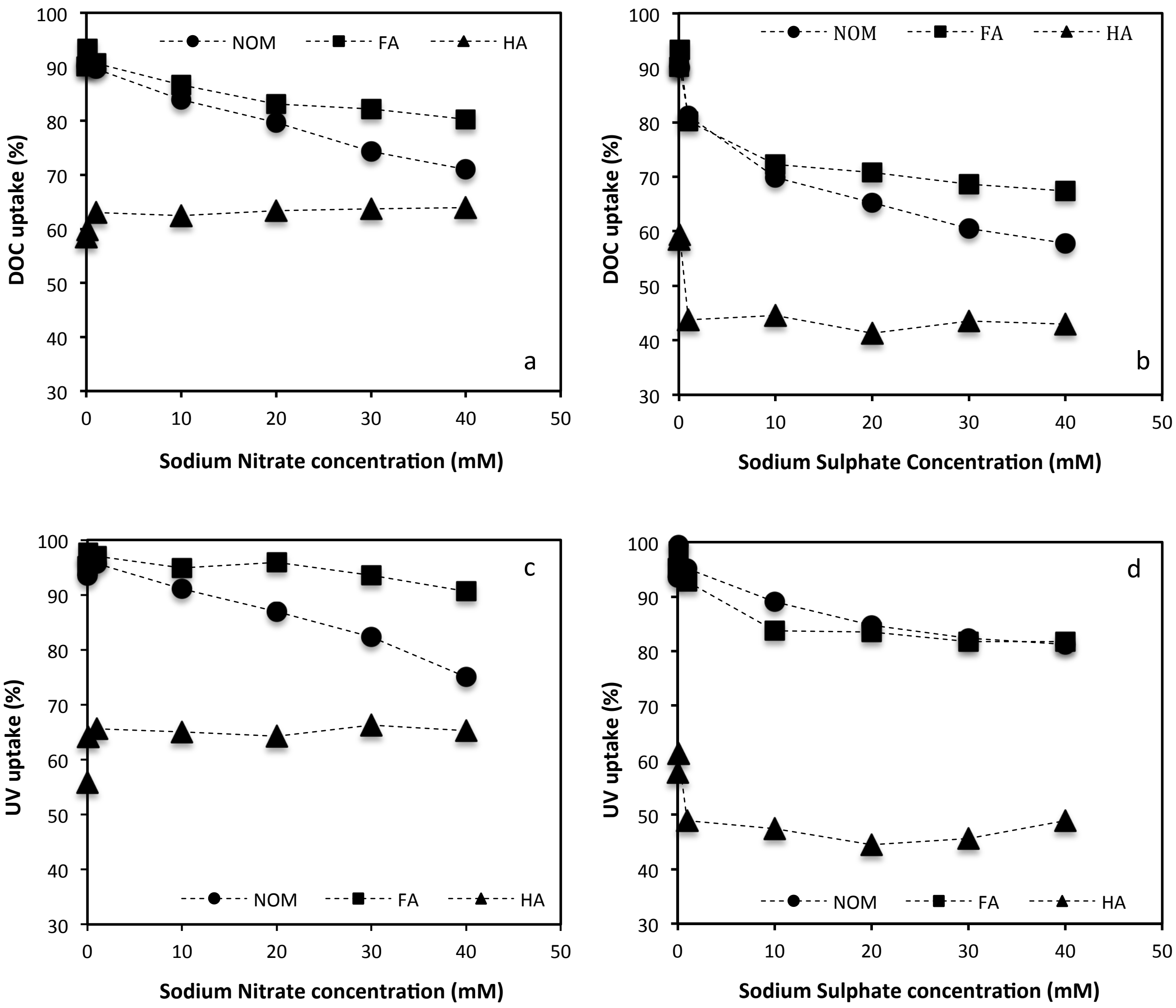


Figure 5.4, DOC and UV uptake for NOM isolates in presence of inorganic anions with various concentrations (resin amount: 500 mg/L). See Appendix F for standard error values of the data points, which range between 0.15 and 3.14.

5.3.2.1. The influence of inorganics on SUVA removal

SUVA values (SUVA=UV_{254}/DOC) were also calculated for water samples after ion exchange treatment. Figure 5.5(a) shows the SUVA values for treated waters containing different concentrations of nitrate. As represented in Figure 5.5(a), SUVA increased for SRNOM and at high concentrations of nitrate it was even greater than that in the absence of salt (i.e., the data point at zero salt concentration). This was expected due to the overall reduction in the removal efficacy at high salt concentrations. However, for SRFA, despite the competitive effect from nitrate, SUVA values decreased. This suggests the preferential removal of UV-absorbing fraction of SRFA in presence of nitrate.

The SUVA values of the treated waters containing sulphate were also shown in Figure 5.5(b). The SUVA value for both SRNOM and SRFA decreased, indicating an increase in the selectivity of the resin towards UV absorbing compounds in presence of sulphate. The preferential removal of UV absorbing compounds in the presence of sulphate is in good agreement with the findings of other studies conducted on natural water sources. Tan and Kilduff (2007) studied the DOC and SUVA removal from two different natural water sources and reported that high SUVA compounds were preferentially removed from the water with high sulphate content. This is consistent with our findings and can be explained by the impact of sulphate that facilitates the removal of UV-absorbing compounds. Summers and Roberts (1988) studied the adsorption of humic substances by activated carbon and reported a conformational change in humic substances with increasing the ionic strength of solution (they have used sodium chloride for this purpose). They reported that this structural change reduces the molecule's effective size, which allows the molecule to diffuse into the pores and increase its access to more surface area.

In the case of SRHA, no significant change in SUVA is observed in presence of inorganic anions. As discussed earlier, this observation is attributable to the homogenous structure of SRHA and thereby the proportional changes in DOC and UV absorptivity during ion exchange process. To have a detailed evaluation on the impact of inorganic anions in the selectivity of the resin towards different fractions of organic matter, the relationship between DOC and UV absorptivity of treated waters is discussed in the following section.

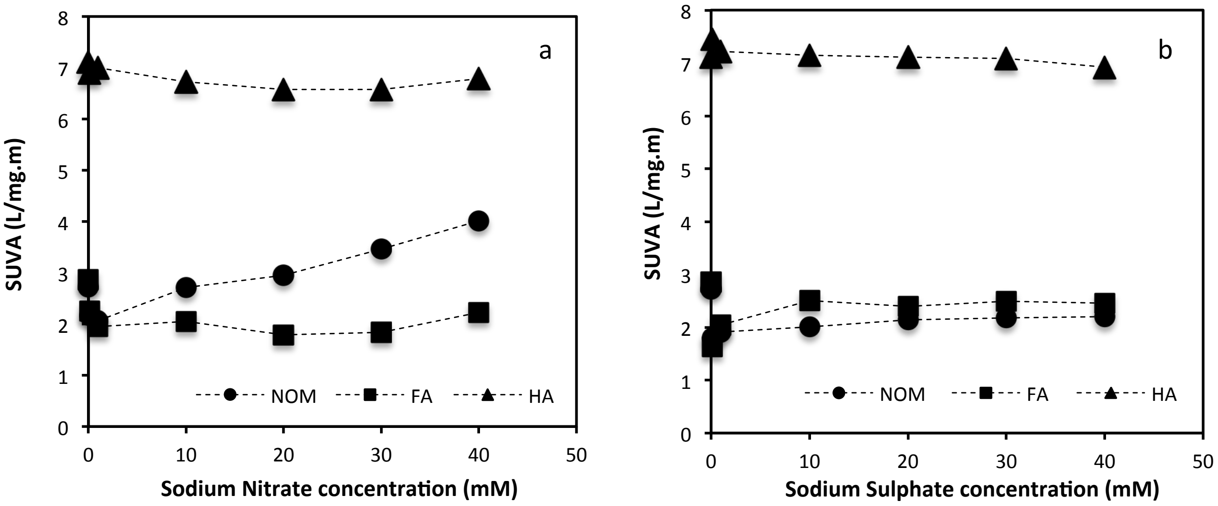


Figure 5.5, SUVA value of treated water at equilibrium for NOM isolates in presence of inorganic anions, nitrate (a), and sulphate (b) with various concentrations (resin amount: 500 mg/L). The SUVA value at zero concentration of inorganic anion represents the SUVA of treated water in the absence of salts.

5.3.2.2. Relationship between DOC and absorptivity

Figure 5.5 shows the absorptivity of water samples (i.e., treated water after equilibrium) at 254 vs. DOC in mg/L. To have a better observation, the dashed lines in the graphs represent the relationship between absorptivity and DOC in the absence of salts as presented earlier in Figure 5.2(b).

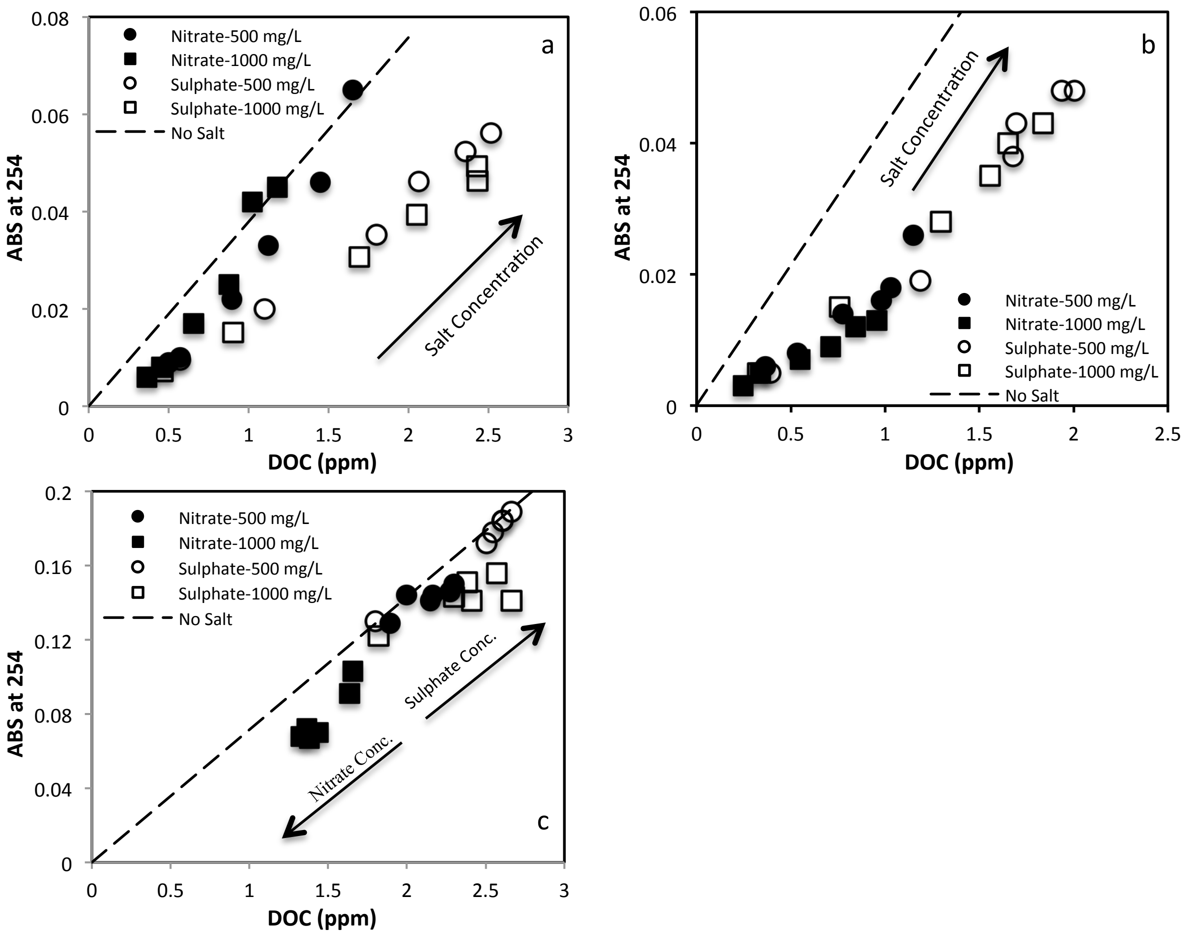


Figure 5.6, Absorptivity VS DOC at different salt concentrations for two resin doses of 500, and 1000 mg/L. (a) SRNOM; (b) SRFA; (c) SRHA.

In the case of SRFA (Figure 5.6(b)), both nitrate and sulphate promoted the removal of UV absorbing compounds to a significant extent, especially at high salt concentrations. However, the presence of nitrate, which exerts lower competition effect led to a better removal of UV absorbing compounds and the overall DOC. According to Table 5.2, SRFA is hydrophobic and contains more aliphatic carbon, and it also has a high charge density. Considering that the removal of hydrophobic organic compounds by ion exchange resins is an entropy-assisted process (Li & SenGupta 2001; Tan & Kilduff 2007), it can be said that both entropy and ionic groups (i.e., electrostatic attractions) contribute to the removal of SRFA by ion exchange resins. Furthermore, presence of salts in solution diminishes the electrostatic interactions (whether attractive or repulsive) (Melander et al. 1989; Newcombe 1999), but the type of salt and its ability to alter water structure (i.e., the hydrogen bonding network of water) is also crucial. Ions with higher charge density such as sulphate can structure water molecules and low charge density ions such as nitrate can break the water structure (Zhang & Cremer 2006). Therefore, both nitrate and sulphate promote the removal of UV absorbing compounds, nitrate by increasing the solubility of hydrophobic domains and disrupting hydrogen bonds within solution (Moelbert et al. 2004) and sulphate by creating more hydrophobic environment through stabilizing the hydrogen bonds between water molecules (i.e., increasing the entropic contribution) (Collins & Washabaugh 1985; Moelbert et al. 2004).

The impact of sulphate on SRNOM removal was similar to that of SRFA, meaning that in the presence of sulphate, the preferential removal of UV absorbing compounds was achieved. However, the results were significantly different in the presence of nitrate (Figure 5.6(a)). An explanation for this can be the hydrophilic fraction of SRNOM that is not present in SRFA and SRHA. As nitrate decreases the entropic contribution by increasing the solubility of hydrophobic domains, the electrostatic attraction becomes more considerable and thereby high charge density hydrophilic molecules will better compete for ion exchange sites. In contrast, in the presence of sulphate, the removal of hydrophilic fraction of NOM is reduced due to the suppression of electrostatic interactions, which is the main driving force for the removal of hydrophilic species.

In the case of SRHA, the impact of inorganic anions on absorptivity removal was low which may be attributed to the higher molecular size, low charge density and higher aromatic carbon content of SRHA. Moreover, as discussed earlier in this chapter, UV absorptivity changes proportional to DOC due to the homogeneous structure of SRHA. However, at higher resin doses (i.e., 1000 mg/L) the impact of nitrate and sulphate on the removal of UV absorbing components of SRHA was more significant. Therefore, in presence of inorganic anions, when sufficient amount of resin surface is available (i.e., high resin doses), the removal of these compounds can be promoted.

5.3.3. Mechanism and stoichiometry of the removal

Figure 5.7 presents the sulphate/nitrate and chloride, obtained at different time intervals, versus DOC uptake in mg/L. Irrespective of the NOM isolate present in water, both nitrate and sulphate were preferentially removed by ion exchange resin to a significant extent, indicating the higher affinity of resin for sulphate and nitrate. However, the affinity of resin for sulphate was higher than that for nitrate and this is consistent with the findings of Boyer et al. (2008), who used MIEX resin, which is also a polyacrylic one. The amount of sulphate in all treated waters was below the instruments detection limit (~ 0.2 mg/L), and only ~ 13% of nitrate remained in water after ion exchange treatment (it should be noted that these values are only valid for the initial concentration of 0.1 mM nitrate/sulphate). Once sulphate/nitrate depleted, chloride concentration kept increasing, indicating the removal of organic compounds via an ion exchange process. In an ion exchange process, for a certain equivalency of molecule that adsorbs on the resin, the same equivalency of resin counter ion (i.e., chloride) is released to the solution. Accordingly, to better understand the removal mechanism, the results have been reported in meq/L in Figure 5.7 based on the charge density values in Table 5.1.

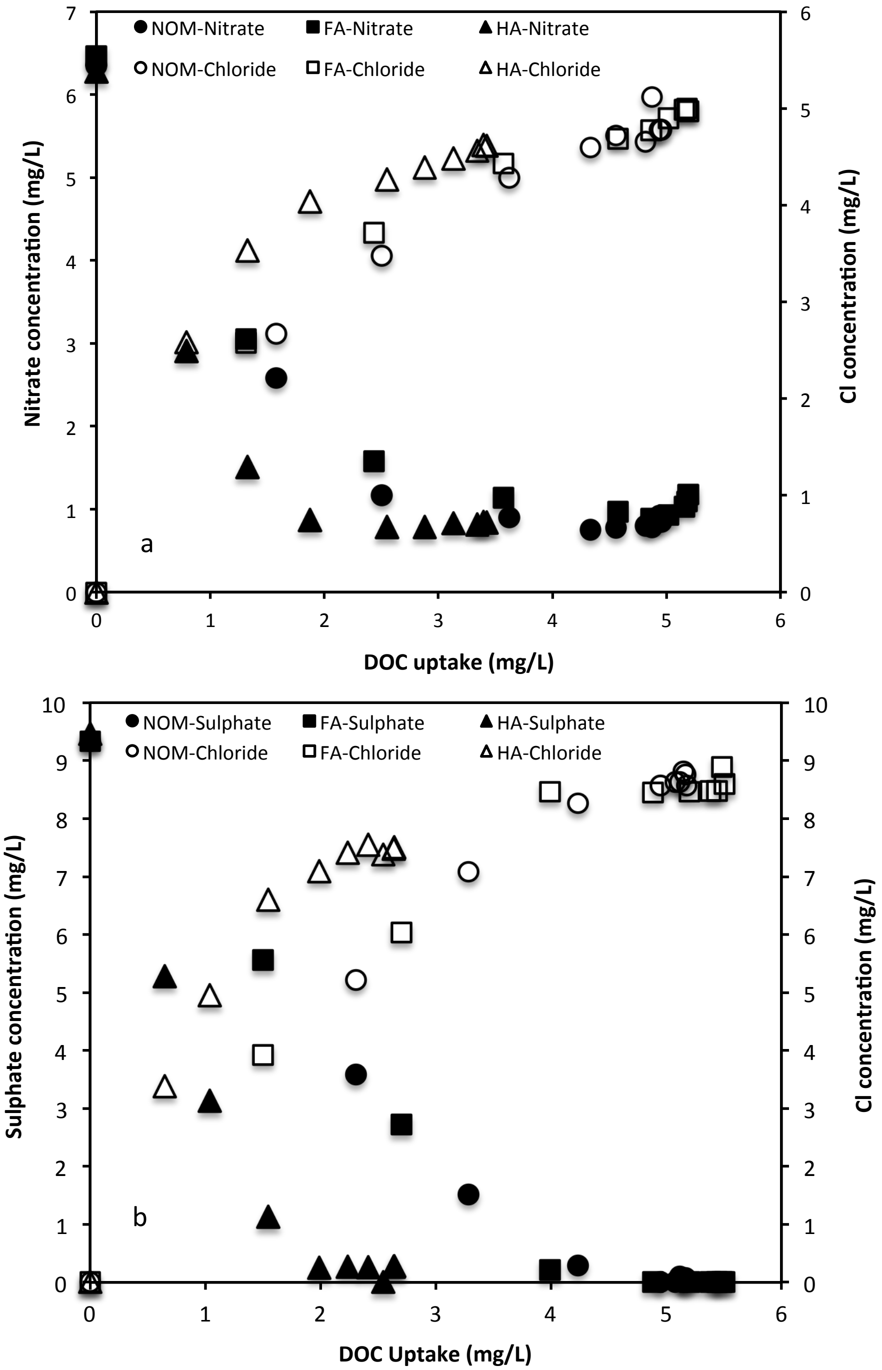


Figure 5.7, Effect of DOC removal on the chloride and nitrate/sulphate concentrations (resin amount: 500 mg/L). (a) nitrate ($C_0 \approx 6$ mg/L equals to 0.1 mM); (b) Sulphate ($C_0 \approx 9$ mg/L equals to 0.1 mM).

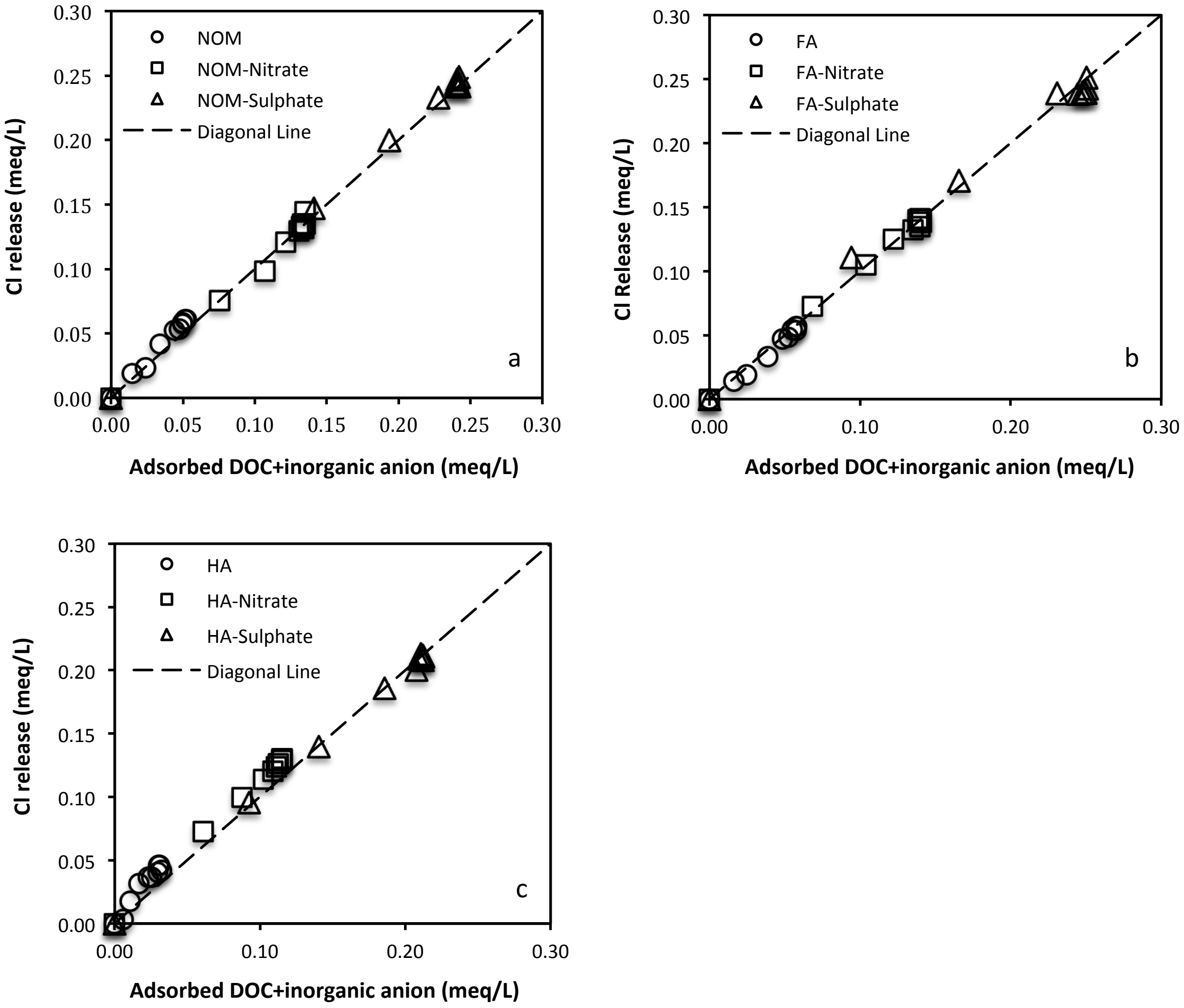


Figure 5.8, Stoichiometry of the removal by ion exchange (resin amount: 500 mg/L, and nitrate/sulphate concentration: 0.1 mM). (a) SRNOM; (b) SRFA; (c) SRHA.

As shown in Figure 5.8, irrespective of the type of NOM isolates and presence of inorganic anions, all data points are clustered around diagonal line, indicating that the removal mechanism was entirely governed by ion exchange. The results are consistent with studies conducted by other researchers (Boyer & Singer 2008; Boyer et al. 2008). However, some researchers have reported that physical adsorption may also occur in addition to ion exchange during the course of organic matter removal. Croué et al. (1999) reported the physical adsorption to appear between hydrophobic fraction of organic material and the resin. A very small amount of physical adsorption for SRFA and SRNOM in the presence of sulphate was also observed at high resin dosage (i.e., 1000 mg/L), where more surface area is available (data are presented in Appendix B, B.3). This may be attributed to the impact of sulphate in increasing the possibility of hydrogen bonds between the resin surface and organic matter.

5.4. Conclusions

The removal of three standard organic matter isolates by ion exchange resin was investigated conducting extensive experiments to evaluate the importance of NOM properties with a focus on hydrophobicity and its impact on removal efficacy. The removal rate increased with resin dosage except for SRHA, which was related to its adsorption on the resin surface due to the higher molecular size. The preferential removal of UV absorbing compounds was also achieved at high resin doses again except for SRHA, indicating a homogeneous structure and proportional changes of absorptivity and DOC.

Although stoichiometric studies revealed an ion exchange mechanism, the physico-chemical properties underlying the process was considered to play a major role in driving the adsorption of organic molecules. This property was evaluated in presence of inorganic anions. Components with higher hydrophobicity exerted a better competition with inorganic anions for ion exchange sites indicating the importance of entropy and its contribution to the removal. Moreover, an increase in ionic strength of solution facilitated the removal of UV absorbing compounds, which possess hydrophobic characteristics and are removed mainly through an entropy-assisted sorption. The only exemption was for SRNOM in presence of nitrate, and this was reasonable because of the lower capacity of nitrate to shield the strong electrostatic attraction between smaller MW hydrophilic fraction of SRNOM and the resin.

Chapter 6 : Thermodynamics of Ion Exchange Process for Removing Natural Organic Matter (NOM)

The involvement of different interactions in removing NOM from water by ion exchange resins was investigated in this research through conducting batch experiments with NOM isolates under various solution conditions. In previous chapters, the results of batch experiments were elaborated and discussed with respect to changes in DOC, UV absorptivity and SUVA values. In order to enhance the interpretation of the results and to better understand the role of different interactions in NOM removal, this chapter analyzes thermodynamic parameters associated with the ion exchange process. Thermodynamic analysis has been a great approach to study the molecular interactions and the forces driving an adsorption process. Determining the thermodynamic parameters associated with the removal of NOM from water is challenging due to the complex and unknown structure of NOM. This chapter aimed to apply the isothermal titration calorimetric (ITC) technique for thermodynamic characterization of NOM adsorption onto ion exchange resins. To evaluate the contribution of NOM characteristics to the system thermodynamics, ITC tests were conducted for NOM and its two isolates (i.e., fulvic acid (FA) and humic acid (HA)). The results revealed the interplay of electrostatic and hydrophobic effects and the fact that the contribution of entropy was more significant for components with higher hydrophobic characteristics (i.e., low charged aromatic fraction of NOM).

Furthermore, the impact of solvent properties was investigated by adding sodium nitrate/sodium sulphate to the water. The reduction in entropic contribution and the increase in enthalpy were observed in the presence of nitrate, and attributed to the diminished dehydration heat. The converse results were obtained in the presence of sulphate and the only exemption was for HA. This was attributed to the contraction of low charged higher molecular weight HA in presence of sulphate. In general, the salt-induced alterations in water molecules structure and its impact on enthalpy-entropy compensation were shown to be of great importance.

6.1. Introduction

The complex structure of NOM makes it difficult and challenging to quantify the contribution of different interactions to the removal process. Previous researches on isotherm studies of ion exchange process for removing NOM revealed ion exchange as the predominant mechanism (Boyer et al. 2008; Boyer & Singer 2008; Fu & Symons 1990); nonetheless, the results demonstrated that NOM characteristics and solution conditions must also be taken into account in evaluating the removal mechanism. Li and SenGupta (Li & SenGupta 2004a; Li & SenGupta 2001; Li & Sengupta 1998) have measured the thermodynamic parameters for the ion exchange of hydrophobic ionisable organic compounds by applying isothermal batch experiments at different temperatures. They reported an endothermic and entropy-driven process, substantiating the importance of hydrophobic characteristics in determining the ion exchange selectivity. In studying the removal of NOM by low charged ion exchange resins, Bolto et al. (2004) have proposed the existence of a non-electrostatic interaction between NOM and the resin matrix. Tan el al. (2007) have also found the entropic contributions as a significant factor in ion exchange removal of NOM specially at low resin doses and in presence of competing inorganic anions. Evidences have been provided by Croue et al. (1999) regarding the occurrence of both physical adsorption and ion exchange mechanisms during NOM removal by ion exchange resins. Additionally, they observed an increase in the removal of hydrophobic acid fraction of NOM with increasing the solution ionic strength, which is explained by structural modifications resulting in reduced molecular size of hydrophobic NOM. In spite of all these information gained by isotherm studies, there is a lack of quantitative description of molecular interactions and the forces govern the process under various conditions.

A more effective application of ion exchange for NOM removal from water requires a detail understanding of the fundamentals underlying the process and one approach could be the thermodynamic analysis. Every spontaneous adsorption process has a negative free energy associated with the changes in enthalpy and entropy of the system. The correlation of thermodynamic parameters with interactions involved in binding systems has been a great approach to understand the forces driving the process under different conditions and to assess the contributions from different interactions. To the author's knowledge, there are no thermodynamic studies on NOM removal by ion exchange resins and this work is the first in measuring thermodynamic properties associated with the removal of NOM and its isolates by ion exchange resins. This research also aims to investigate the impact of solvent properties and the contribution of solute-solvent interactions to the removal by determining the changes in thermodynamic parameters in presence of two different inorganic anions (i.e., nitrate and sulphate) in the water. One common technique to quantify thermodynamic properties of a binding system is isothermal titration calorimetry (ITC) (Freire et al. 1990; Freyer & Lewis 2008; Grolier & del Río 2012; Jelesarov & Bosshard 1999; Ladbury & Chowdhry 1996). ITC has been frequently used to directly measure the thermodynamic parameters associated with molecular binding events (Creagh et al. 1996; Wilcox 2008; Garidel et al. 2000) such as biopolymer binding interactions (Freire et al. 1990) and enzyme activity (Todd & Gomez 2001; Williams & Toone 1993). ITC has been also used to study the interactions involving in binding of amino acids or proteins on hydrophobic surfaces (Lin et al. 2001; Tsai et al. 2002) and ion exchange resins (Chen et al. 2007; Cheng et al. 2006). ITC method is also applied in this work and it is worth noting that this is the first attempt in taking the advantage of ITC for studying NOM adsorption on ion exchange resins and should result in extending the practical usefulness of ITC and more developed ITC in future.

6.2. Materials and Method

6.2.1. Natural organic matter samples

Suwannee River natural organic matter (NOM) and its two isolates fulvic acid (FA) and humic acid (HA) were purchased from international humic substances society (IHSS) as dried solid powders. To make organic matter solutions, 30 mg of the isolate dissolved in 15 mL of Milli-Q water and the pH of each solution was adjusted to 6.5 using a 0.1 N sodium Hydroxide. The solutions were filtered through 0.45 µm membrane filters and the final total organic carbon content (TOC) of the samples was measured using a Shimadzu TOC-V_{CPH} total organic carbon analyzer. To assess the contribution of the presence of inorganic anions to the overall driving force for NOM removal, two more sets of experiments were conducted in which the NOM samples were made by dissolving the isolates in 15 mL of 10 mM sodium nitrate/sodium sulphate solution. The carbon distribution of the NOM isolates is presented in Table 5.1.

6.2.2. Ion exchange resin

A strongly basic macroporous and polyacrylic anion exchange resin called Ionac MacroT was used in this work. According to manufacturer, this resin has an exchange capacity of 1.1 eq/L and the bead size of 0.3-1.25 mm. Prior to use, the resin was regenerated by 10% wt. brine and rinsed with Milli-Q water and then decanted and dried in desiccator. In order to be able to load the resin into the ITC sample cell, the pre-treated resin was crushed using a mortar and pestle and a suspension solution of the resin was made at a concentration of 5000 mg/L (see Appendix D.1 for determining the appropriate resin concentration).

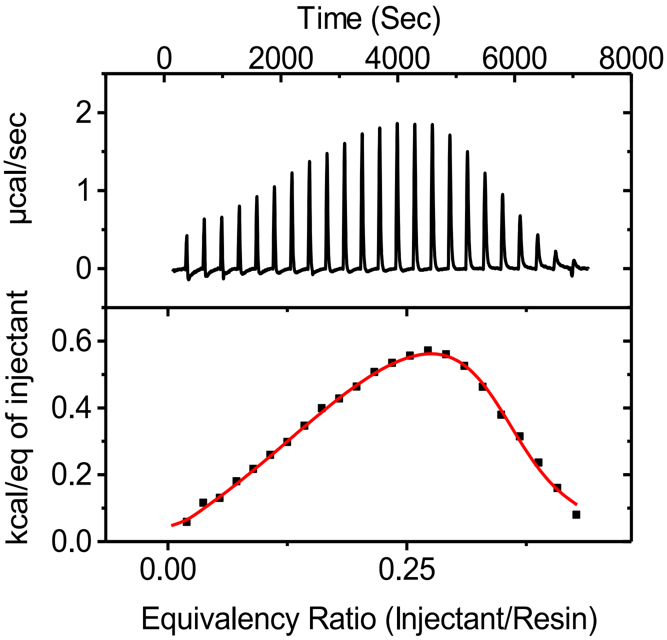
6.2.3. Titration calorimetry

All solutions were degassed under vacuum prior to loading in the ITC. The resin solution was loaded into the 1.3528 mL sample cell and was given few hours to equilibrate to the set-point temperature (i.e., 25 °C). Afterwards, the organic mater sample was injected into the cell from a 250µL Syringe at 5-min intervals of twenty-five, 10µL injections. Control experiments were also carried out to measure the dilution heat in which the titrant (i.e., organic matter solution) injected into Milli-Q water. Dilution heat was deducted from ITC data and the two-site model used to fit the integrated heat data yielding K and H. All ITC data were reported in equivalency of injectant (i.e., titrant, which is the organic matter solution) and the resin because NOM is a mixture of different components with a wide range of molecular weight distribution. The equivalency of organic isolates were estimated at pH=6.5 using the equation and information provided by Ritchie and Purdue (2003) , and the manufacturer (international humic substances society (IHSS)).

6.3. Results and Discussion

6.3.1. Thermodynamics of NOM removal by anion exchange resin

Figure 6.1 represents the calorimetric heat for the adsorption of NOM onto ion exchange resin at pH 6.5 and 25°C. The overall adsorption heat is positive, meaning that the removal of NOM by ion exchange resin is an endothermic process, reaching a saturation heat at 14.7 kJ/mole ≈ 0.68 kcal/eq_{NOM}. The titration profile for NOM indicates the complexity of this adsorption process and suggests the involvement of considerable molecular interactions to the process. According to ITC profile, it is found that at first injections where there are more resin sites available, the binding event is overall less endothermic and as the resin saturates, it gets more endothermic. This may attribute to the number of available ion exchange sites on the resin that results in a less endothermic binding event at the beginning due to the more contribution of electrostatic attraction between NOM and the resin (i.e., negative H_1). While the number of available ion exchange sites decreases, the contribution of electrostatic attraction reduces resulting in a more endothermic process. In the case of NOM adsorption on the ion exchange resin, two-sites model (see Appendix C for more details on the curve fitting models and equations used with the software) is found as the best fit for calorimetric data in which the overall adsorption heat is the sum of enthalpy changes for the adsorption of high affinity (ΔH_I) and low affinity (ΔH_{II}) binding of NOM. Figure 6.1 also shows the best fit of the integral calorimetric heat data with two sites model and the thermodynamic results are reported in Table 6.1. To calculate ΔG and ΔS, the estimated molecular weight for organic isolates available from an earlier study (Bazri et al. 2016; Bazri & Mohseni 2016) was used. Accordingly, in this work, the thermodynamic data (ΔG, ΔH, and ΔS) were viewed qualitatively rather than quantitatively and were only used to better compare and evaluate the changes in system thermodynamics at different operating/solution conditions.



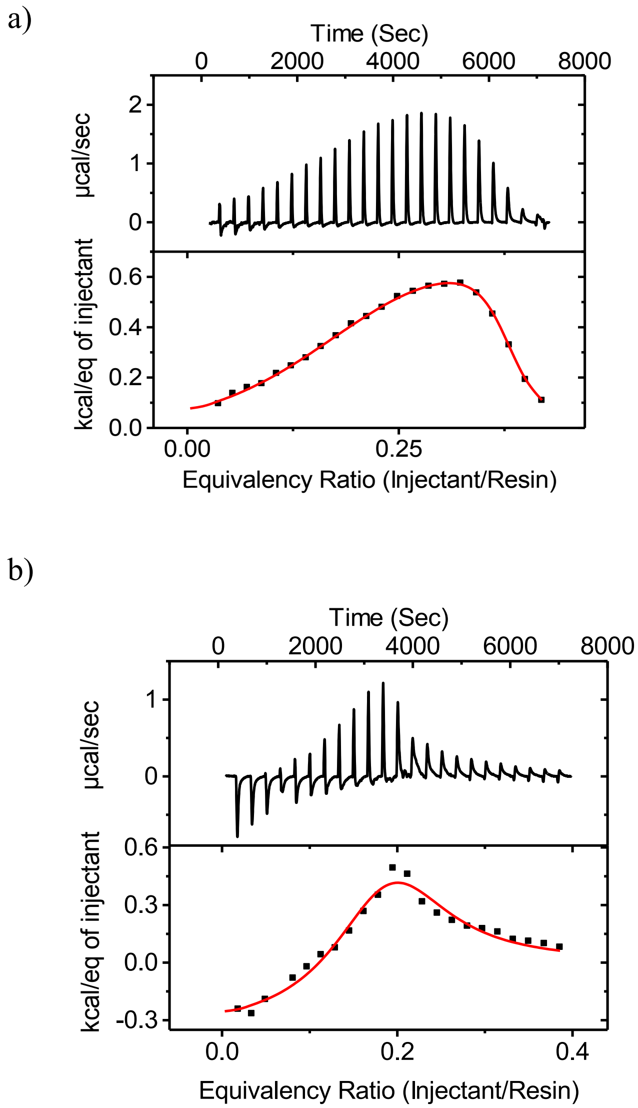
Two sites model data fitting parameters			
K_1	1.47E5	K_2	3.89E4
H_1	-288 cal/eq	H_2	1.01E3 cal/eq

Figure 6.1, ITC data for titration of NOM into ion exchange resin at 25°C and pH 6.5.

The value obtained for ΔH_I from the integral calorimetric heat data is relatively small and negative, i.e. -5.8 kJ/mol, meaning that the binding is favourable and exothermic. However, the significant contribution of the entropy to the free energy (ΔG), which is about 80% according to Table 6.1, substantiates the strong and favourable effect of entropy in driving NOM removal. The low affinity adsorption of NOM is also entropy driven with a negative contribution of ΔH_{II}= 20.5 kJ/mol to the overall removal process (ΔG). This large difference in the enthalpy changes for the low affinity and high affinity adsorption of NOM points to a complexity in NOM structure. Overall, the entropy has the dominant contribution to ΔG, confirming that majority of NOM is hydrophobic. However, the high affinity adsorption of NOM, i.e. negative ΔH_I, can be attributed to the high charge density fraction of NOM, which involves a significant contribution of electrostatic attraction to the overall driving force.

6.3.2. The impact of NOM characteristics on system thermodynamics

To better evaluate the impact of structural characteristics of NOM on thermodynamics of overall removal process, calorimetric studies were conducted on two different NOM fractions as well. These NOM fractions are fulvic acid (FA) and humic acid (HA). According to the manufacturer, they both contain only hydrophobic organic carbon. The principle difference is their charge density, molecular size, and aromaticity. However, it is worth noting that charge density and molecular size are not two distinct characteristics; the higher charge density, the lower molecular size. According to previous studies (Bazri & Mohseni 2016) and manufacturer, fulvic acid has higher charge density and lower molecular weight compared to humic acid; besides, humic acid is very rich in terms of aromatic carbon content. Therefore, it can be concluded that humic acid is the most hydrophobic fraction of NOM and is expected to convey a large contribution of entropy to the overall driving force for the adsorption onto the ion exchange resin.



Two sites model data fitting parameters			
K_1	6.15E5	K_2	1.05E5
H_1	-68.9 cal/eq	H_2	823 cal/eq

Two sites model data fitting parameters			
K_1	6.16E4	K_2	8.39E3
H_1	-369 cal/eq	H_2	2.35E3 cal/eq

Figure 6.2, ITC data for titration of FA (a) and HA (b) into ion exchange resin at 25°C and pH 6.5.

The calorimetric heat for the adsorption of FA and HA are shown in Figure 6.2 and thermodynamic values obtained after the best fit of the integrated heat data with two sites model are represented in Table 6.1. In terms of FA and for the high affinity adsorption, the contribution of entropy to the overall driving force is higher compared to NOM. The ΔG value for FA is smaller than NOM and considering that ΔH_1 makes almost no contribution to the removal (≈5%), it can be concluded that entropy strongly favours the removal of FA.

Table 6.1, Thermodynamic data of the uptake of organic matter by anion exchange resin obtained using two sites model fit to integrated calorimetric heat data.

	I			II		
Organic Matter	***ΔG_I (kJ/mol)**	****ΔH_I (kJ/mol)**	*****$T\Delta S_I$ (kJ/mol)**	***ΔG_{II} (kJ/mol)**	****ΔH_{II} (kJ/mol)**	*****$T\Delta S_{II}$ (kJ/mol)**
NOM	-29.5	-5.8	23.7	-26.2	20.5	46.7
FA	-33.0	-1.6	31.4	-28.6	19.7	48.3
HA	-27.3	-9.8	17.5	-22.4	62.8	85.2

* $\Delta G = \Delta H - RT\ln K$ where R is the gas constant (8.314 $J/mol^{-1}K^{-1}$).

** The integral calorimetric heat data.

*** $\Delta G = \Delta H - T\Delta S$.

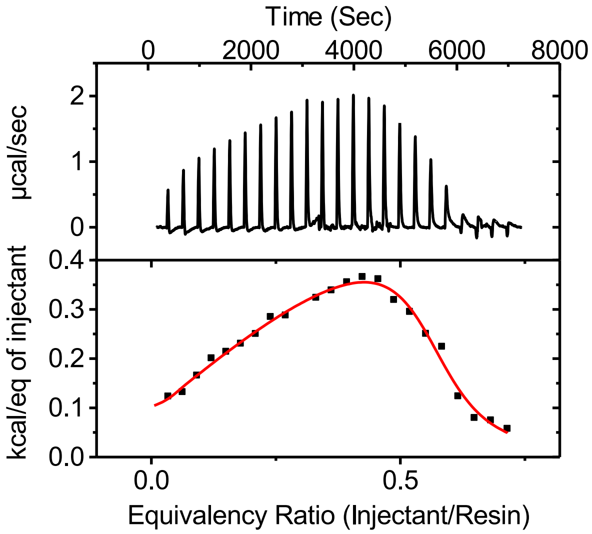
For HA, the overall enthalpy change is relatively high as expected, confirming the dominant contribution of entropy to ΔG and the driving force for the removal of HA. One interesting observation is the value of $\Delta H_{I,}$ which is even lower than that of NOM and FA. The expected driving force for HA which is the most hydrophobic and less charged fraction of NOM is entropy and given that HA has a lower charge density, this favourable enthalpy change can be an evidence for the presence of another strong interaction between HA and the resin. A central difference between HA and FA/NOM is the greater aromatic carbon content of HA which may result in physical adsorption (including pi interactions) between aromatic chain of HA and the resin backbone matrix. The existence of physical adsorption between organic matter and ion exchange resin has been also proposed by Croue et al. (1999) and Bolto et al. (2004).

The large positive entropy change that is achieved by ITC measurements indicates that the dehydration effects dominate the adsorption (Creagh et al. 1996; Lin et al. 2001) of HA. From this, it is concluded that the structure and conformational freedom of organic compound in water is of a great importance. The increased degrees of freedom of the water molecules released from the dehydration during the removal of organic matter results in a large positive entropy change. Moreover, the lower binding capacity of ion exchange resin was observed for HA which is attributed to its higher molecular weight and that the adsorption is mainly happening on the surface due to the diffusion limitation (i.e. size exclusion phenomena) (Boyer & Singer 2008; Bazri & Mohseni 2016) which increases the possibility of pore blockage leading to a faster saturation of the resin.

6.3.3. The impact of salts on thermodynamics of organic isolates removal

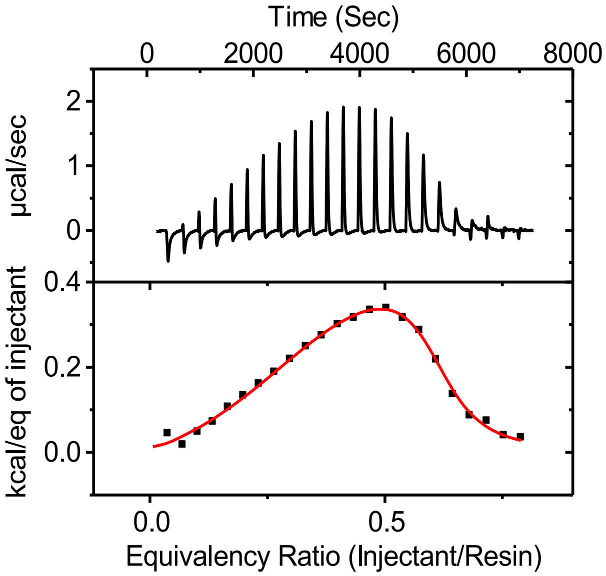
To investigate the electrostatic and non-electrostatic contributions to the binding of NOM onto the ion exchange resin, the ionic strength of the solution was manipulated using sodium nitrate or sodium sulphate.

a)



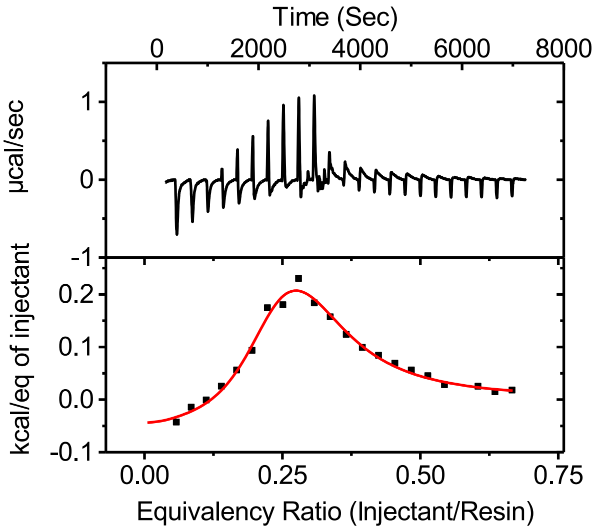
Two sites model data fitting parameters			
K_1	5.75E4	K_2	3.07E4
H_1	-624 cal/eq	H_2	788 cal/eq

b)



Two sites model data fitting parameters			
K_1	1.64E5	K_2	3.15E4
H_1	-100 cal/eq	H_2	551 cal/eq

c)



Two sites model data fitting parameters			
K_1	7.42E4	K_2	4.79E3
H_1	-66.9 cal/eq	H_2	624 cal/eq

Figure 6.3, ITC data for titration of NOM (a), FA (b), and HA (c) solution containing 10 mM sodium nitrate.

In the presence of nitrate, as demonstrated in Figure 6.3 and Table 6.2, both ΔH and ΔS values decrease, indicating that less heat is required for the dehydration of hydrophobic domain and the contribution of enthalpy to the removal increases. Sodium nitrate favours a reduction in the endothermic heat required for dehydration and consequently reduces the change in the entropy of the system and may promote the electrostatic attraction between the resin and organic matter. However, the favourable reduction in enthalpy change in presence of nitrate does not necessarily mean that electrostatic interaction between organic compound and the resin increases. As there is only a very small change in the free energy of binding, this observation can be a reflection of the water molecules behaviour. In other words, it is claimed that the compensation of enthalpy and entropy contributions of solute-solvent interactions to the adsorption process plays a major role. This is consistent with other binding processes occurring in aqueous media that signifies the importance of enthalpy-entropy compensation effect (Lumry & Rajender 1970; van Oss 1997; Dunitz 1995) . The favourable effect of nitrate in the reduction of endothermic dehydration heat is more significant for HA. Because HA has higher molecular weight and more hydrophobic characteristics resulting in more structured water molecules and thereby the disruption of hydrogen bonds in presence of nitrate (Moelbert et al. 2004) increases the entropy of the system and reduces the dehydration heat to a more significant extent.

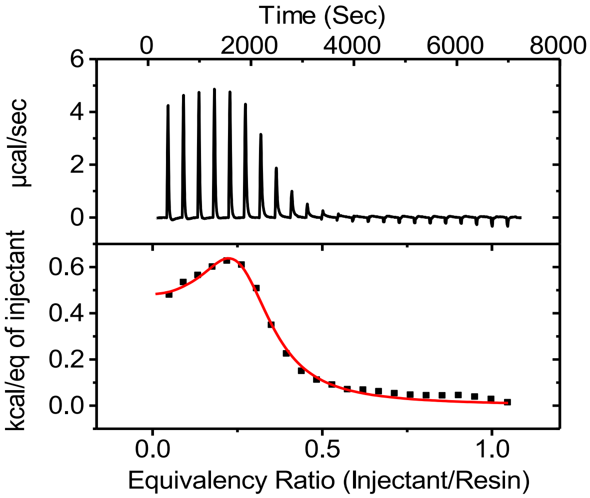
In contrast, as shown in Table 6.2, both ΔH_I and ΔS_I increased for HA in presence of sodium nitrate. A possible justification for this can be the presence of another interaction between HA and the resin, which is screened in presence of sodium nitrate. This interaction as discussed earlier might be a physical adsorption or pi interaction between resin backbone and the side chain of organic compound.

Table 6.2, Thermodynamic data of the uptake of organic matter by anion exchange resin in presence of 10 mM sodium nitrate.

Organic Matter	I			II		
	ΔG_I (kJ/mol)	ΔH_I (kJ/mol)	$T\Delta S_I$ (kJ/mol)	ΔG_{II} (kJ/mol)	ΔH_{II} (kJ/mol)	$T\Delta S_{II}$ (kJ/mol)
NOM	-27.1	-15.2	11.9	-25.6	19.3	44.9
FA	-29.8	-2.8	26.9	-25.6	15.5	41.1
HA	-27.8	-2.1	25.7	-21.0	19.3	40.3

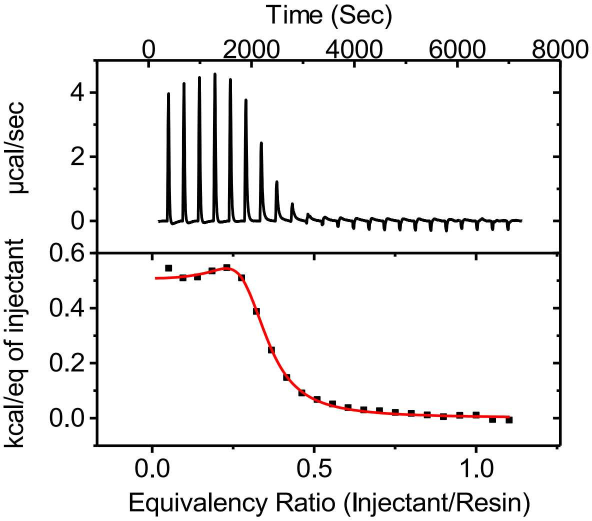
In presence of sodium sulphate, the results are contradictory to those in presence of nitrate. As shown in Table 6.3 and Figure 6.4, both ΔH and ΔS values increases, demonstrating the overwhelming contribution of positive entropy change to the removal of organic matter. In other words, in presence of sulphate, the overall ion exchange removal of organic matter is an entropy-driven process and electrostatic attractions are suppressed. This observation is consistent with the findings of Newcombe and Drikas (1997) about the effect of sulphate on the contribution of electrostatic and non-electrostatic interactions to the adsorption of NOM onto activated carbon. For the high affinity adsorption where both enthalpy and entropy have positive contributions to the removal, presence of sulphate increases both ΔH_I and ΔS_I values, and according to ITC measurements shown in Table 6.3, this impact on three studied organic matter is in the order of HA>NOM≥FA. Two phenomena may contribute to the increase in ΔH, the reduction in electrostatic attractions between the resin and organic matter and/or the increase in the heat required for dehydration. Also, the increase in ΔS value is an indication of more freedom of water molecules and thereby more system chaos. As the HA has the less charge density compared to NOM and FA, the ion shield in presence of sulphate has the highest impact on the enthalpy change in removing HA. Moreover, HA is the most hydrophobic fraction and the presence of sulphate reduces the solubility of hydrophobic domains (i.e. more hydrogen bonds in presence of sulphate) resulting in a more positive entropy change during dehydration process which compensates the unfavourable change in the enthalpy.

a)



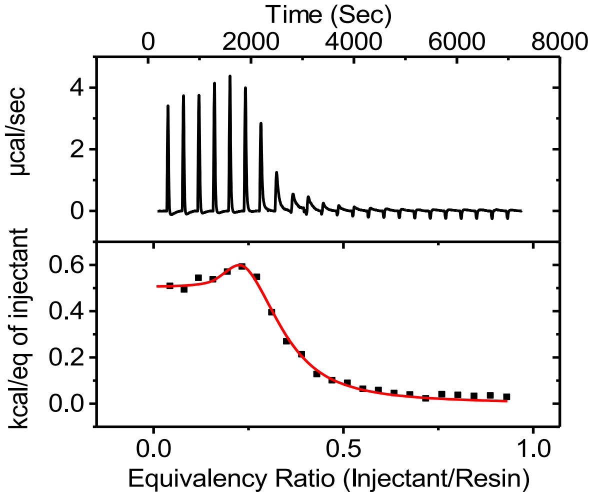
Two sites model data fitting parameters			
K_1	4.15E4	K_2	4.3E3
H_1	438 cal/eq	H_2	1.61E3 cal/eq

b)



Two sites model data fitting parameters			
K_1	2.91E5	K_2	4.77E3
H_1	504 cal/eq	H_2	982 cal/eq

c)



Two sites model data fitting parameters			
K_1	8.29E4	K_2	5.65E3
H_1	500 cal/eq	H_2	1.06E3 cal/eq

Figure 6.4, ITC data for titration of NOM (a), FA (b), and HA (c) solution containing 10 mM sodium sulphate.

Regarding ΔH_{II} and ΔS_{II} associated with the low affinity adsorption of organic matter onto ion exchange resin, as represented in Table 6.3, they increase in presence of sulphate for NOM and FA. And, the impact of sulphate on NOM is more significant compared to FA and this is attributed to the hydrophilic fraction of NOM that is only driven by electrostatic interactions, which are extremely screened in presence of sulphate. Conversely, ITC measurements revealed that the presence of sulphate reduces the contribution of entropy in removing HA and also favours a reduction in the endothermic heat required for dehydration of HA (i.e., the enthalpy change decreases). Given that HA contains the most aromatic components of high molecular weight, a possible explanation for this observation could be the structural and conformational changes in higher molecular weight aromatic compounds in presence of sulphate. Sulphate has a great ability to decrease the entropy of the system by increasing the order of water molecules (Moelbert et al. 2004; Collins & Washabaugh 1985), which is not favourable thermodynamically. Therefore, when sulphate dissolves in water containing hydrophobic compounds with low charge density, the possibility of hydrophobic interactions within the solution increases in order to stabilize the system thermodynamically. In other words, in presence of sulphate the hydrophobic compounds may aggregate or fold to exclude some water molecules structured themselves around hydrophobic domains, yielding an increase in the entropy of the system. In the case of HA studied in this work, a possible phenomenon underlying the converse impact of sulphate compared to FA and NOM is the lower charge density and the higher aromatic content of HA. Consequently, there is more possibility for intermolecular hydrophobic interactions (including pi-pi interactions) to happen, which eventually results in lower dehydration heat during the removal process.

Table 6.3, Thermodynamic data of the uptake of organic matter by anion exchange resin in presence of 0.1 mM sodium sulphate.

Organic Matter	I			II		
	ΔG_I (kJ/mol)	ΔH_I (kJ/mol)	$T\Delta S_I$ (kJ/mol)	ΔG_{II} (kJ/mol)	ΔH_{II} (kJ/mol)	$T\Delta S_{II}$ (kJ/mol)
NOM	-26.4	12.5	38.9	-20.7	46.1	66.8
FA	-28.1	16.1	44.2	-21.4	34.2	55.6
HA	-31.2	17.7	48.9	-21.0	34.5	55.5

Overall, from the ITC results obtained in presence of inorganic anions, it is concluded that the solute-solvent interactions and the conformational changes of component molecules are of great contributions to the removal process. However, this change in water molecules behaviour (i.e. solute-solvent interactions) may favour the removal of some NOM molecules over others, which requires other experiments and analytical analysis. It is worth mentioning that some researchers reported the change in ion exchange selectivity towards some specific fractions of NOM in presence of inorganic anions (Tan & Kilduff 2007; Croué et al. 1999).

6.4. Conclusions

The intricate structure of NOM has been always a difficulty in detailed understanding of its removal mechanism. This research was an attempt to facilitate the study of the interactions involving in NOM removal by ion exchange resins. ITC studies were carried out for NOM and its isolates, and the results indicate the contribution of different molecular interactions to the retention of NOM onto the ion exchange resin. The overall removal process was shown to be an entropy-driven with dehydration heat being an important factor especially for fractions with low charge density and higher aromatic content. It is also proposed, not proven, that pi interactions between aromatic organic compounds and the resin matrix may take place. Moreover, thermodynamic studies in presence of different inorganic anions have shown that the NOM-water (solute-solvent) interactions significantly contribute to the thermodynamics of removal process. The enthalpy-entropy compensation effect resulted from the impact of salts on solute-solvent interactions is an indicator of the importance of solvent properties and its considerable effect in thermodynamic analysis of organic isolates adsorption on ion exchange resins.

Chapter 7 : The Impact of Resin Properties in Removing Natural Organic Matter (NOM)

As discussed and demonstrated in earlier chapters, the ion exchange removal of NOM from water is influenced by different factors including the characteristics of the resin and the organic compounds. Chapters 4 and 5 reported on the impacts of NOM characteristics and inorganic anions in water. The focus of this chapter is on the impact of the resin polymeric structure. Two types of resins, one polyacrylic and one polystyrene, were investigated. All the resin properties, except the polymeric composition, were similar. Accordingly, ion exchange experiments were carried out for different model waters containing NOM isolates with the two selected resins. The results of previous chapters with the polyacrylic resin revealed the significance of hydrophobicity and its impact on the entropy as a driving force for the retention of organic compounds on the resin. However, this chapter shows that the hydrophobicity of organic compound became less important in their removal by polystyrene (hydrophobic) resin. Therefore, it is hypothesized that the difference in hydrophobicity of the water and the resin phase is the key in determining the ion exchange selectivity. To better assess the contribution of hydrophobicity, the salt effects on water structural behaviour was utilized through studying the ion exchange process in the presence of two different salts (i.e., sodium nitrate and sodium sulphate). The increase in the removal of UV absorbing compounds (i.e., higher molecular weight aromatic molecules) with polystyrene resin, especially in the presence of sulphate, indicates that the difference between the hydrophobicity (entropy) of the resin phase and the water is primarily responsible for the ion exchange selectivity of hydrophobic organic compounds.

7.1. Introduction

The removal of natural organic matter by different types of ion exchange resins has been investigated in the literature and the performance of the resins and its relationship with the resins structural characteristics (i.e., porosity, water content/crosslinking, charged functional groups, and polymeric composition) has been widely discussed (Bazri et al. 2016; Bolto et al. 2002; Bolto et al. 2004; Cornelissen & Moreau 2008; Graf et al. 2014; Leenheer 2007; Pürschel & Ender 2008). The resin polymeric backbone is either styrenic or acrylic. Polystyrene resins tend to possess more hydrophobic characteristics than the polyacrylic resins. In terms of NOM removal, polyacrylic resins have been reported to be more effective than polystyrene resins (Fu & Symons 1990; Bolto et al. 2002; Bolto et al. 2004; Pürschel & Ender 2008). The poorer performance of polystyrene resins is attributed to the exclusion of higher molecular weight compounds due to their rigid (hydrophobic) structure (Humbert et al. 2005; Hongve 1989; Aiken & Thurman 1979; Boyer & Singer 2008; Fu & Symons 1990; Croué et al. 1999). Fu and Symmons (1990) studied the removal of different fractions of NOM with polystyrene resins and reported the hydrophobicity of the resins as a more dominant factor than the pore size in affecting the removal efficacy of the NOM fractions with a molecular size of 1000 – 10000 Daltons. The similar removal rates for both styrene and acrylic resins obtained by Bolto et al. (2002) also confirms that the pore diffusion in not the main reason for the weak performance of styrene resins. In removing organic compounds from water by polystyrene resins, the hydrophobic effect and water-water interactions are pointed out as important interactions involved in the ion exchange process (Li & Sengupta 1998; Li & SenGupta 2004b; Semmens & Gregory 1974).

The decrease in the entropy (unfavourable change) that is associated with the presence of hydrophobic moieties in water is then considered as primary factor in the selectivity of the resin towards hydrophobic compounds. Therefore, the removal of hydrophobic organic molecules is called an entropy-driven process (Li & SenGupta 2001). Despite all these studies, there is limited information on the impact of water structure in removing NOM by anion exchange resins. Moreover, the hydrophobic nature of the polystyrene resins may increase the water structure within the resin (rigid matrix) by promoting water-water interactions, which may decrease the entropy within the resin phase (Semmens & Gregory 1974), but this was rarely considered in the literature towards the interpretation of experimental results.

The solution ionic strength is also an influential factor in the retention of biomaterials on ion exchange resins and needs to be considered (Tsai et al. 2002; Melander et al. 1989; Lin et al. 2001; Chen et al. 2007). The presence of inorganic anions in the solution impacts the water structure and thereby the contribution of electrostatic and hydrophobic interactions to the process (Melander & Horváth 1977; Chen et al. 2007). It is important to note that anions with low charge density (weakly hydrated) more likely disrupt the water structure, while anions with higher charge density (strongly hydrated) increase the water structure (Nucci & Vanderkooi 2008; Zhang & Cremer 2006). Therefore, the impact pattern of different anions in water may vary, and this makes the solution behaviour a very crucial parameter.

However, researchers who studied the removal of NOM by ion exchange resins rarely discussed or interpreted their observations from the point of solution behaviour and molecular interactions involved during the process. Among these studies, Tan & Kilduff (2007) reported an increase in the removal of higher molecular weight species with styrene resins in the presence of sulphate. Also, Croué et al. (1999) obtained greater removal of the hydrophobic fraction of NOM by adding sodium chloride to the water and attributed this to the salting out effect. Both these studies were conducted using styrene resins. And, there is no systematic study to compare the performance of acrylic and styrene resins for NOM removal under different solution conditions.

Accordingly, the objectives of this chapter were: 1) to compare the performance of polystyrene and polyacrylic resins in removing different NOM isolates with a focus on the impact of polymeric composition of the resins, and 2) to quantify the contribution of molecular interactions to the removal of NOM by ion exchange resins. The approach used for the latter objective was the structural modifications of water solution by adding different types of salts. The results shed light on the important contribution of molecular interactions and water structural behaviour in the adsorption of NOM onto ion exchange resins.

7.2. Materials and Methods

7.2.1. Ion exchange resins

Two commercially available anion exchange resins were selected considering their superior characteristics for removing organic matter according to previous research. These characteristics include water content, functional group, small bead size, and porosity. Table 7.1 shows the aforementioned characteristics for the two studied resins. To isolate the impact of resin backbone, the selected resins are similar at all aspects and the only main difference is their polymeric composition.

Table 7.1, Structural properties of ion exchange resins.

Resin	Structure	Basicity	Functional Group	Capacity (eq/L)	Porosity	Water Content (%)
Ionac Macro-T	Polyacrylic	Strongly Basic	Quaternary amine,Type I	1.1	Macroporous	60-64
Lewatit MP 500	Polystyrene	Strongly Basic	Quaternary amine,Type I	1.1	Macroporous	61-63

The resins, Sybron Chemicals Inc., were preconditioned by regenerating with 10% wt sodium chloride solution followed by rinsing with Milli-Q water to remove the excess chloride. Prior to use and to accurately weigh the resins, they were air dried in desiccator for 24 hrs after decanting the excess water.

7.2.2. Synthetic water solutions

Model waters with NOM, and its two isolates (i.e., FA and HA), were prepared by adding purchased Suwannee River NOM isolates from International Humic Substances Society (IHSS). The pH of the model water was adjusted to ~6.5. The estimates of carbon distributions of NOM isolates and the properties of the model waters are presented in Tables 5.1 and 5.2, respectively.

7.2.3. Batch experiments

Batch experiments were conducted by mixing 100 mL of model waters with various amounts of the prepared resins (200, 500, 1000, and 1500 mg/L). Samples were taken after equilibrium for DOC and UV absorptivity analyses. The required time for equilibrium was 15 hr, which was obtained from kinetic studied carried out in chapter 5.

7.2.3.1. Salt effects

The approach to evaluate the importance of water structure in removing NOM by ion exchange resins was to examine the removal efficiency in the presence of different salts.

Accordingly, batch experiments were also conducted for aforementioned model waters containing different salt concentrations. The salt concentrations used in this study were 0.1, 0.5, 1, and 2 mM of sodium nitrate and sodium sulphate. These two inorganic anions were selected based on their different effects on water structure as reported in the literature and investigated in Chapter 5.

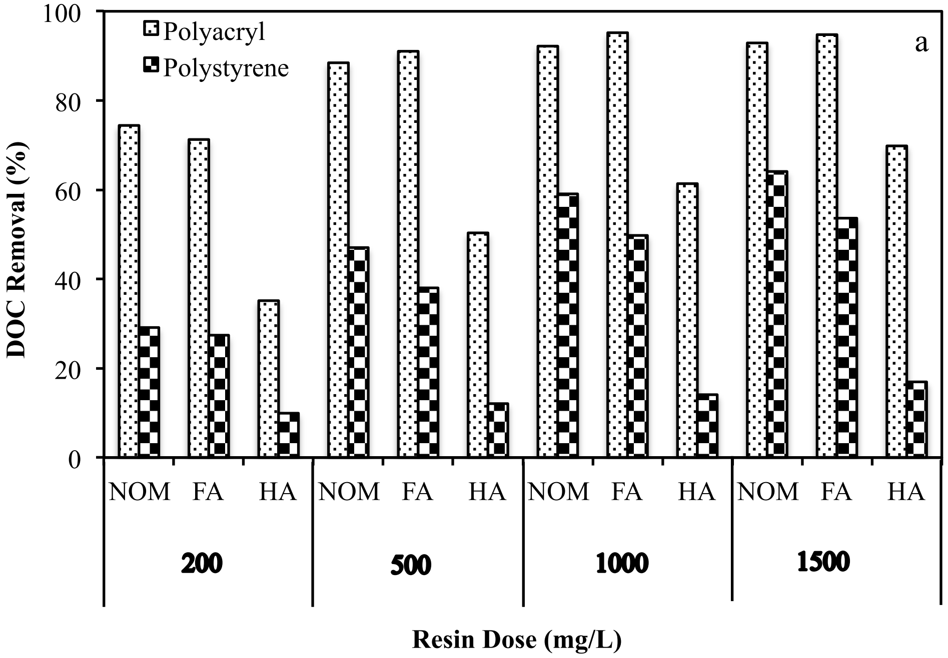
7.3. Results and Discussion

7.3.1. DOC and UV removal

The DOC and UV absorbance removal for Suwannee River NOM and its two isolates (SRFA, and SRHA) with two resins at different doses were evaluated (Figure 7.1). Figure 7.1(a) demonstrates three important features: (1) polyacrylic resin was much more effective than polystyrene resin in terms of DOC removal for all three NOM isolates; and (2) the removal of SRHA was less than those of SRNOM and SRFA for both resins. The poor removal of SRHA could be attributed to its higher molecular weight and low charge density.

Moreover, a lower DOC removal of SRFA was obtained with polystyrene resin in comparison with SRNOM. Note that both SRFA and SRNOM were removed nearly to the same extent with polyacrylic resin. According to Table 5.1, the principle difference between SRFA and SRNOM is the higher aliphatic carbon content and higher charge density of SRFA compared to SRNOM. The lower removal of SRFA (compared to that of SRNOM) by polystyrene resin, despite its higher charge density, reveals the importance of non-polar moieties of the organic matter in their selectivity with polystyrene resin. Additionally, considering the higher aromatic carbon content of SRHA (Table 5.1), it can be concluded that polystyrene resins have lower selectivity for the compounds with higher hydrophobicity.

The DOC removal increased with resin dose, even though this effect was not significant for the removal of SRHA with polystyrene resin and only 5% increase in SRHA removal was achieved by increasing the resin dose from 200 mg/L to 1500 mg/L. However, according to Figure 7.1(a), 35% of SRHA was removed with 200 mg/L of polyacrylic resin. This observation suggests that the interaction between the resin backbone and the organic matter is more dominant than the interaction between their ionic functional groups in influencing the retention of the organic compound on the ion exchange resin. Note that both studied resins were the same with respect to their functional groups, counter ion, and water content.



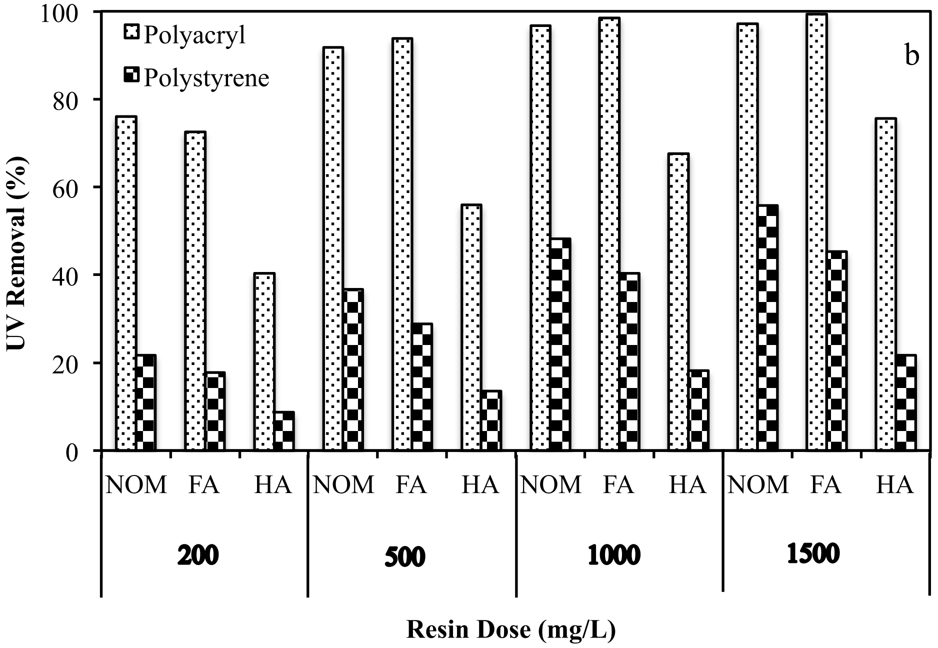


Figure 7.1, DOC (a) and UV (b) uptake at various resin doses for three water models containing Suwannee River organic matter isolates.

Figures 7.1(a) and 7.1(b) represent the percentage removal of DOC and UV absorption from three model waters by two studied resins at different doses. Comparing the date on Figures 7.1(a) and 7.1(b) indicates the preferential removal of UV absorbing compounds by polyacrylic resin. The obtained DOC and UV absorption removals with polyacrylic resins are nearly the same, while the percent UV uptake is smaller than that of DOC with polystyrene resin. To better assess the relative reduction of UV absorption and its proportional changes with DOC, the specific UV absorbance (SUVA) for treated water was analyzed (Figure 7.2). As shown, a significant decrease in SUVA was observed after treatment with polyacrylic resin; whereas, the opposite was obtained with polystyrene resin and the SUVA slightly increased after treatment. Given that SUVA is correlated with aromaticity and molecular weight of organic matter (Chin et al. 1994; Weishaar et al. 2003), these findings suggest the exclusion and/or rejection of higher molecular weight/aromatic organic matter by the polystyrene resin while they are preferentially removed by polyacrylic resin. In other studies, the weak performance of polystyrene resins in removing DOC is attributed to size exclusion phenomena (Aiken et al. 1979; Croué et al. 1999; Fu & Symons 1990; Boyer & Singer 2008). However, the findings of this research demonstrate the significance of the resins polymeric structure in the selectivity of the organic compounds for ion exchange. As polystyrene resins have more hydrophobic characteristics, it is hypothesized that the hydrophobic effect they impose to the water solution influences the removal efficiency and the selectivity of the ion exchange resin. One approach to assess this hypothesis is to study the removal in the presence of inorganic salts i.e., imposing changes in solution structure and the behaviour of the water molecules. This approach along with its associated results is discussed in the following section.

It was also interesting that the SUVA value increased with the resin dose for the polystyrene resin. The more resin dose means the more available exchange sites for organic matter and thereby a better removal was expected if electrostatic interactions are the dominant forces. But, the results demonstrate that the resin's polymeric structure is the governing factor in influencing the removal of NOM isolates by polystyrene resins. In other words, the hydrophobic effect of the polystyrene resin is more dominant than the electrostatic attraction between the resin's functional group and the organic compound's ionic charge. With respect to SRHA, the ion exchange treatment did not have any significant impact on the SUVA value and this can be explained by the homogeneous structure of SRHA, meaning that both DOC and UV absorptivity changed proportionally.

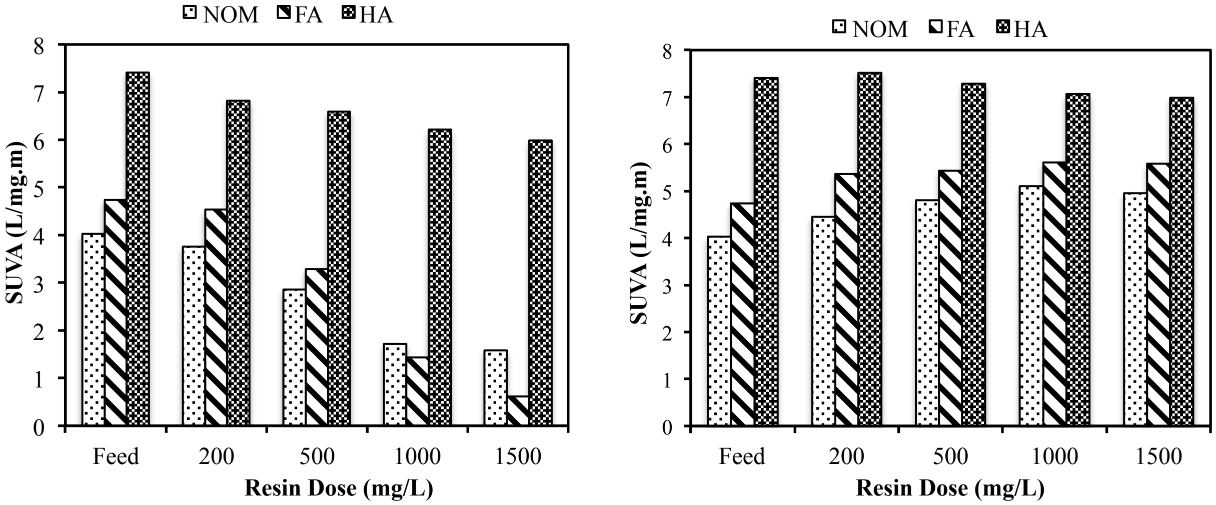


Figure 7.2, The change in the SUVA value of water samples after ion exchange with different amount of resins, Polyacrylic (a), and Polystyrene (b).

7.3.2. Impact of inorganic anions on the removal performance

The removal of NOM isolates in the presence of different inorganic salts was also investigated. This was to better evaluate the role of the resin polymeric structure in NOM removal and to understand the molecular interactions involved in the process. In this research the removal of NOM isolates with polystyrene (hydrophobic) and polyacrylic (hydrophilic) resins in the presence of sodium nitrate (low charge density) and sodium sulphate (high charge density) was examined. In this regard, experiments conducted for model waters containing various concentrations of sodium nitrate or sodium sulphate. The change in percent DOC and UV absorption with salt concentration are plotted in Figure 7.3. As Figure 7.3 represents, no change in NOM and FA removal with polyacrylic resins was observed after adding nitrate. 13% increase in HA removal on DOC basis (Figure 7.3(a)) obtained by the polyacrylic resin was more interesting. When the electrostatic interactions are the only responsible driving force for the retention of organic compounds on ion exchange resins, the presence of competing inorganic anions in the solution is expected to reduce DOC removal. While, the results confirm the involvement of other factors than electrostatic attraction between the resin and the organic matter in the removal process. Given that HA is the most aromatic isolate used in this study and thus possess more hydrophobic characteristics, hydrophobic effect is hypothesized to be a key factor in removing organic matter. Li and Sen Gupta have also reported that hydrophobic interactions play an important role in removing hydrophobic organic acids by ion exchange resins (Li & SenGupta 2004b; Li & Sengupta 1998; Li & SenGupta 2004a).

Moreover, with respect to the polystyrene resin, as Figure 7.3(a) illustrates, the removal of all three NOM isolates were enhanced in the presence of nitrate. Increasing the concentration of sodium nitrate to 2 mM, resulted in an increase of 7% for NOM removal and 10% for FA and HA removal on DOC basis. The increase in HA removal is nearly the same with respect to both resins. However, the increase in NOM and FA removal by polystyrene resin (hydrophobic) is another indication of the importance of the resin’s polymeric structure.

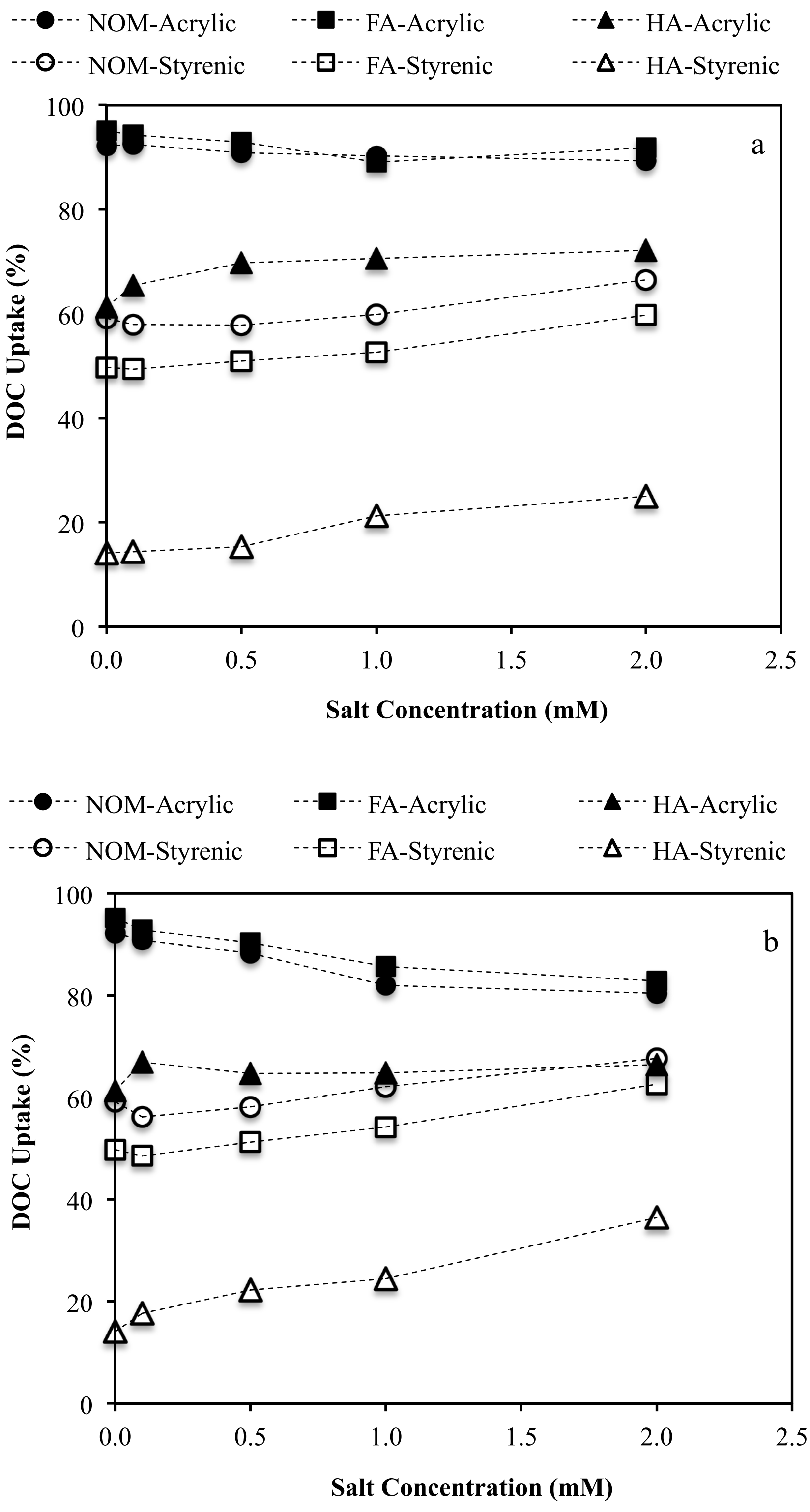


Figure 7.3, DOC uptake from different model waters with 1000 mg/L of the resin either polystyrene or polyacrylic in the presence of various salt concentrations, sodium nitrate (a), and sodium sulphate (b). See Appendix F for standard error values of the data points, which range between 0.09 and 2.88.

The percent DOC removal in the presence of sulphate is shown in Figure 7.3(b), and as demonstrated, sulphate competes with the organic compounds for ion exchange sites on the polyacrylic resin and results in a reduction in NOM and FA removal with increasing the salt concentration. However, the competition effect was not observed for HA, but a 6% increase in HA removal was obtained with the polyacrylic resin in the presence of sulphate. The results for the polystyrene resin reveals an increase of 8%, 13% and 22% for NOM, FA, and HA, respectively with increasing the salt concentration to 2 mM. The interesting point is that this observation is consistent with the hydrophobicity order of the NOM isolates. Comparing these values with those of the polyacrylic resin indicates the importance of the resin's hydrophobicity as well (i.e., polymeric structure). According to the previous studies, increasing the solution ionic strength promotes the DOC removal due to the contraction of the NOM molecules and thereby the lower size exclusion by ion exchange resins (Croué et al. 1999; Humbert et al. 2005). Moreover, it is reported that the size exclusion phenomena is more influential in removing DOC by polystyrene resins due to their rigid (hydrophobic) structure (Fu & Symons 1990). However, considering our finding in which the increase in ionic strength promoted DOC removal with the polystyrene resin more than that with the polyacrylic resin, indicates that the hydrophobicity of the resin is more dominant than size exclusion. According to the findings of Li and Sen Gupta, the removal of hydrophobic organic acids by ion exchange resins is an entropy-driven process (Li & SenGupta 2001) because their removal is followed by the release of free water molecules to the solution and results in an increase in the entropy of the system, which is thermodynamically favourable. Therefore the poor removal of DOC with polystyrene resin can be attributed to its hydrophobic structure and water-water interactions within the resin. The hydrophobicity of the resin polymer may increase the water structure within the resin (this was also confirmed by ITC tests, pleases see Appendix D, section D.2 for more details), which then reduces the differences in water structure (entropy) between the resin and the external water solution (Semmens & Gregory 1974). Thus, the decrease in the entropy of the water solution associated with low charged hydrophobic organic matter becomes less important in determining selectivity. This also explains the increase in DOC removal with the polystyrene resin in presence of sulphate, because sulphate increases the water structure within the solution, which tends to promote the transfer of hydrophobic organic compounds to the resin phase. The possibility of hydrophobic interactions between the resin matrix and the non-polar moieties of the organic matter will be discussed later in this paper.

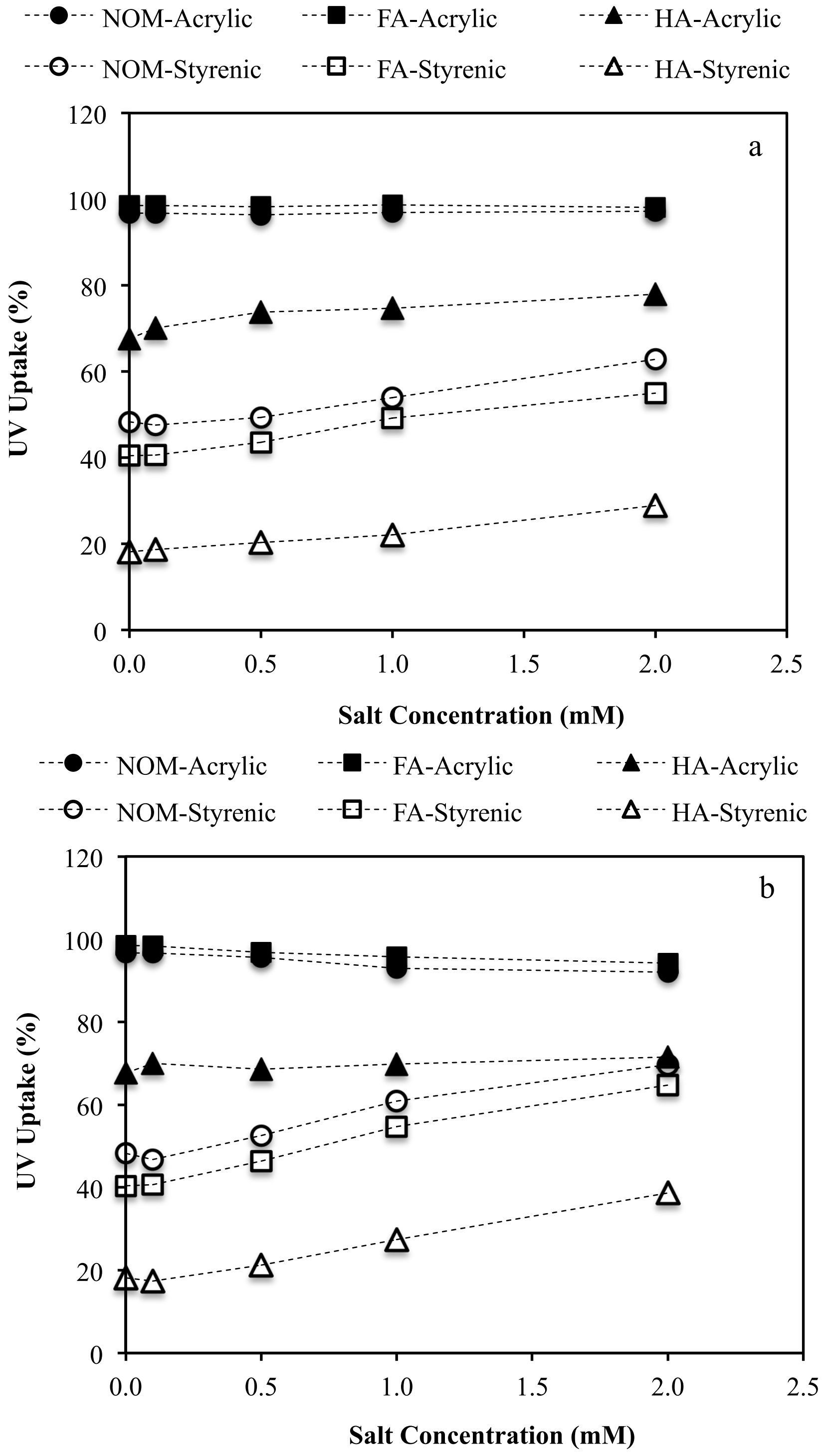


Figure 7.4, UV uptake from different model waters with 1000 mg/L of the resin either polystyrene or polyacrylic in the presence of various salt concentrations, sodium nitrate (a), and sodium sulphate (b). See Appendix F for standard error values of the data points, which range between 0.35 and 2.87.

To better evaluate the impact of sulphate/nitrate on the removal of NOM isolates with both resins, the change in the UV absorptivity of the water was studied and the results are represented in Figure 7.4(a) and (b) as the percent UV uptake at different salt concentrations. The change in DOC and UV uptake in the presence of salts is nearly the same except for NOM and FA removal with the polystyrene resin in the presence of sulphate (Figure 7.4(b)) in which the increase in UV removal is greater than the DOC removal with an increase in the concentration of sulphate. This observation suggests that the presence of sulphate and its impact on water structure promotes the transfer of UV absorbing compounds from the water to the resin phase. SUVA values were also calculated from the corresponding DOC and UV absorptivity of the water samples and data are shown in Figure 7.5(a) and 7.5(b). In the presence of nitrate, no significant change in the SUVA was observed, however, the SUVA decreased for NOM and FA with polystyrene resin in the presence of sulphate, confirming the increase in the selectivity of the resin towards the higher molecular weight and aromatic organic compounds. The constant SUVA value for HA can be attributed to its homogeneous structure as discussed before. It is also worth to note that all batch experiments in the presence of nitrate/sulphate were conducted at different resin doses, but the pattern achieved for the removal of DOC and UV for polystyrene resin was nearly the same at any resin dose (see Appendix E, E.1). However, in the case of polyacrylic resin, the removal efficiency increased with resin dose and this is attributed to the competition effect from inorganic anions at low resin doses. For a detailed discussion on the impact of resin dose see Appendix E, E.1.

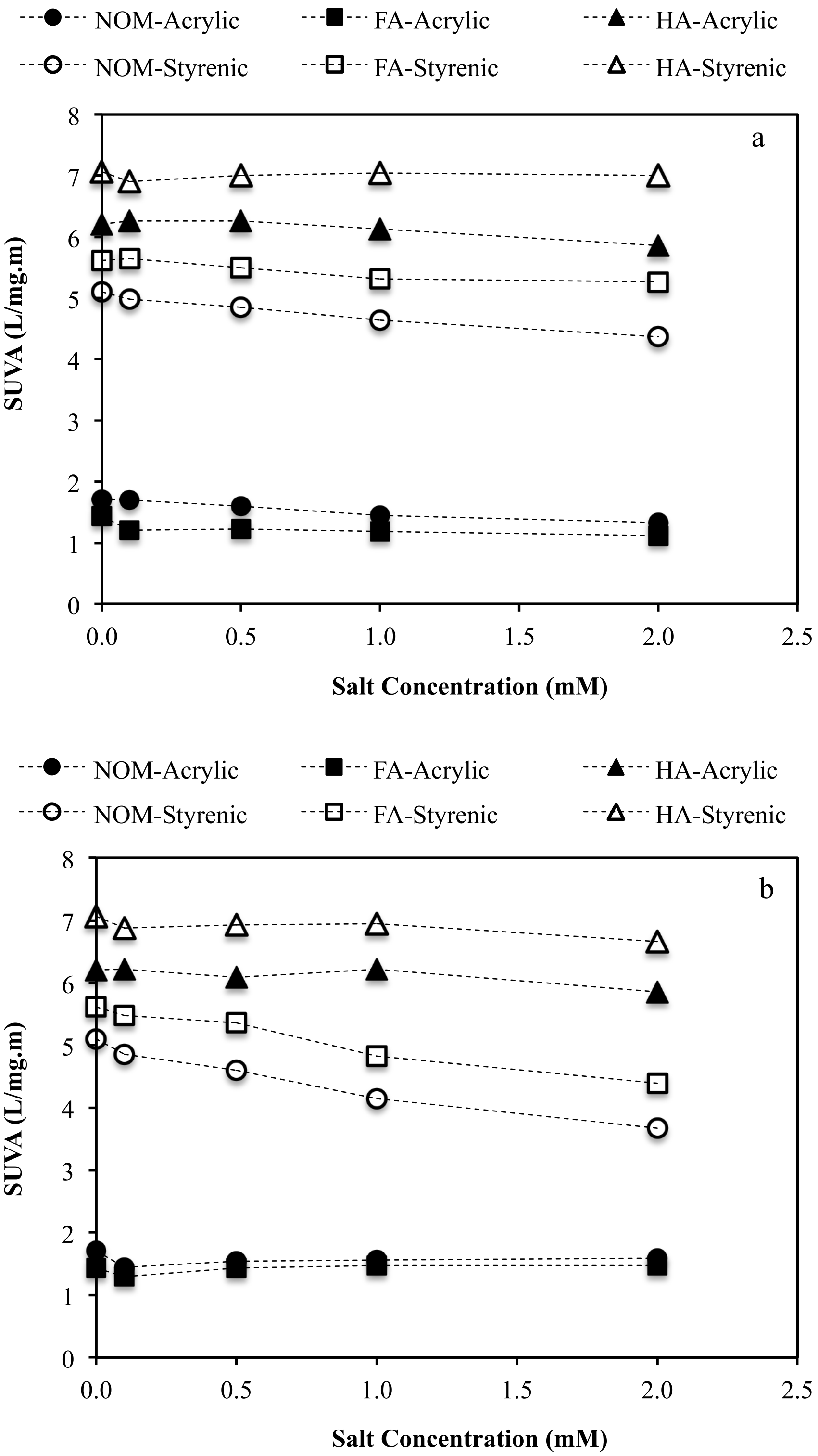


Figure 7.5, The change in SUVA with salt concentration, sodium nitrate (a), and sodium sulphate (b); resin dose: 1000 mg/L.

7.3.3. Nitrate/sulphate removal

The removal of nitrate and sulphate with ion exchange resins was also studied. Regardless of the type of NOM isolate, the same amount of nitrate/sulphate removal was achieved with a certain resin dose. The percent removal of nitrate/sulphate from a model water containing NOM with 1000 mg/L of the ion exchange resin is shown in Figure 7.6. Overall, the polystyrene resin exhibited a better performance than the polyacrylic resin in removing both nitrate and sulphate. At low salt concentrations a higher percent of sulphate was removed compared to nitrate, while the opposite was observed at high salt concentrations. This is due to the difference in the number of charges that nitrate and sulphate contain. For every sulphate molecule that is adsorbed on the resin, two ion exchange sites are occupied. This means that for the removal of a certain amount of sulphate and nitrate molecules, twice more ion exchange sites are required for sulphate than nitrate, therefore the percent removal of sulphate decreases more than nitrate with salt concentration. To confirm our interpretation, the removal of nitrate/sulphate on equivalent (i.e., meq/L) basis was also calculated (data are shown in Appendix E, E.3), and greater amount of sulphate than nitrate was removed in terms of equivalent removal even at high salt concentrations. Moreover, increasing the resin dose from 200 mg/L to 1500 mg/L gave a ≈50% rise to nitrate removal and ≈70% to sulphate removal, indicating the importance of the number of the available exchange sites in removing inorganics with higher ionic charges. The data for other resin doses are presented in Appendix E, E.3 as the same pattern was observed in terms of comparing the nitrate/sulphate removal. The ternary equilibrium between nitrate/sulphate, DOC, and chloride for NOM isolates with both studied resins is also reported in Appendix E.

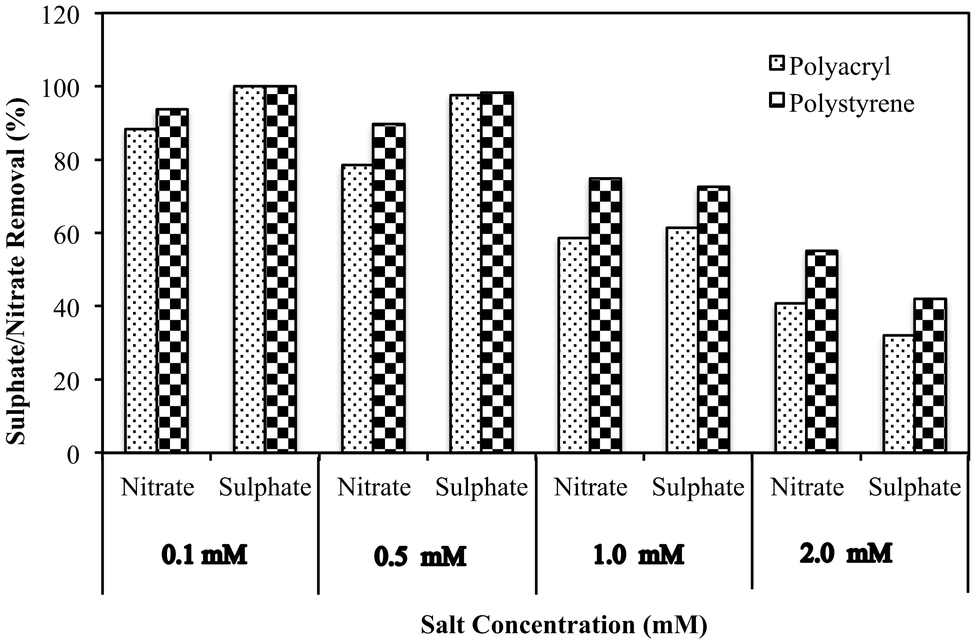


Figure 7.6, The removal of sulphate/nitrate from model waters containing SRNOM and various concentrations of sodium sulphate/sodium nitrate (Resin dose: 1000 mg/L of either polystyrene or polyacrylic).

7.3.4. Removal stoichiometry

In the literature, the possibility of the occurrence of physical adsorption (hydrophobic interactions/hydrogen bonding) between polystyrene resins matrix and non-polar moieties of hydrophobic organic compounds is proposed (Bolto et al. 2002; Croué et al. 1999; Fu & Symons 1990; Li & SenGupta 2004b). If hydrophobic interactions are happening during the removal, then the expectation is to remove more hydrophobic/aromatic organic compounds by the polystyrene (hydrophobic) resin than the polyacrylic (hydrophilic) resin, however, the opposite was observed in this work. Therefore, to investigate the removal mechanism, the adsorption stoichiometry for the removal of NOM isolates with both resins in the presence/absent of salts was studied. The studied resins in this work were in chloride form, meaning that for an ion exchange that might happen between the resin and the organic matter, a certain amount of chloride ion on equivalent basis released to the water for the adsorption of the same equivalent of the organic compounds. For this reason, the amount of net chloride release to the water after treatment was measured and the values are plotted versus the adsorbed DOC and inorganic anions in terms of meq/L (Figure 7.7). For both resins and under any salt conditions, the data points are clustered around the diagonal line (dashed line in Figure 7.7); the same behaviour was also obtained for FA and HA (the data are not presented here). This demonstrates that ion exchange is the predominant mechanism in removing NOM from water by the polyacrylic/polystyrene resins. However, physical adsorption (e.g., hydrophobic interactions and/or hydrogen bonding) may also take place concurrent with ion exchange but the results confirmed that physical adsorption is not the primary removal/adsorption mechanism. Combining this with other findings, it is concluded that hydrophobic interactions are not the dominant interactions between the resin and the organic matter, but hydrophobicity and its subsequent impact on water structure is the key factor in determining the ion exchange selectivity. That is to say, the difference in entropy of the water solution and the resin phase is the principle driving force for the adsorption of hydrophobic organic compounds onto ion exchange resins. Thereby manipulating the water structure by spiking different types of salts may promote the selectivity towards specific fractions of NOM.

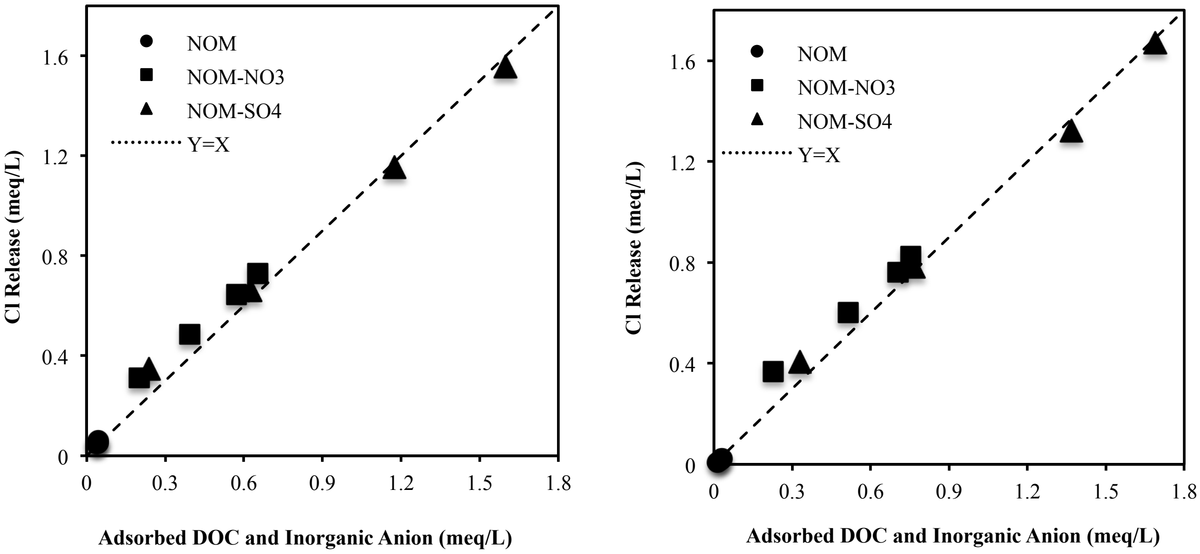


Figure 7.7, Stoichiometry of the removal by ion exchange (resin dose: 1000 mg/L, and sodium sulphate/sodium nitrate concentration: 1 mM).

7.4. Conclusions

This research aimed to investigate the impact of the resin polymeric structure in the ion exchange of NOM isolates. It is found that hydrophobicity is the very important factor in the ion exchange of organic compounds as a driving force. Hydrophobic characteristics within the solution can change the water molecules structure (i.e., entropy reduction) and this might be a consequence of the hydrophobicity of either the organic matters non-polar moieties or the resin's polymeric structure. Collectively, the difference in the hydrophobicity of the water (i.e., organic matter) and the resin phase is of a great importance and is the dominant factor in the selectivity and retention of the organic compounds on ion exchange resins. The contradictory performance of the polyacrylic resin and the polystyrene (more hydrophobic) resin in removing UV absorbing compounds (i.e., compounds with higher SUVA value) is an evidence for this conclusion. Moreover, the presence of inorganic anions/salts in water promoted the removal of UV absorbing compounds with polystyrene resin due to their impact on the water structural behaviour. The results obtained from this work can yield in a better design of ion exchange process by understanding the molecular interactions and analyzing the water molecules behaviour under different conditions.

Chapter 8 : Conclusions and Recommendations

The removal of organic compounds from water by ion exchange resins involves the contribution of various interactions. This work studied the removal efficiency of three organic compounds as well as different NOM isolates. Studying the removal of model compounds was very valuable in understanding the role of hydrophobicity, as it is very challenging to distinguish the effect of hydrophobicity from so many other factors that involve in NOM removal.

The better removal of compounds with more hydrophobic nature indicated the importance of hydrophobic effects. Moreover, the overall process of ion exchange for NOM removal was endothermic and entropy-driven which was evidenced by ITC studies. The large positive entropy change was an indication of the dominant contribution of the dehydration effects to the driving force for binding. The presence of other anions in water that may impact the water molecules structure and thus the dehydration effects has to be also taken into account in examining the ion exchange performance with respect to removing different fractions of NOM. Given the paramount role of hydrophobic effects in driving the ion exchange removal of NOM, it is very crucial to consider the hydrophobic characteristics that may be posed to the system by the resin phase as well. According to the findings of this research, it is concluded that the main driving force for transferring NOM molecules from water phase to the resin phase is the difference in hydrophobic character (entropy) of the water and the resin. Specific conclusions and highlights of this work are classified and discussed more in detail below.

8.1. Specific Conclusions

- **The role of hydrophobicity in the ion exchange removal of organic molecules**

To distinguish the impact of hydrophobicity from that of other characteristics such as ionic charge and molecular weight, the removal of two hydrophobic (NAA and BA) and one hydrophilic (GA) organic compound was investigated. It is worth noting that the selected compounds all contain one carboxylic group and nearly similar molecular weight. The results showed that the removal efficiency of the organic compounds was correlated with their hydrophobicity; the higher their hydrophobicity, the greater their removal. In addition, it was determined that the competing effect of inorganic anions (i.e., sulphate/nitrate) decreased with increasing the hydrophobicity of the organic molecules. Moreover, the experiments conducted at different resin doses indicated that decreasing the resin dose had the lowest impact (i.e., reduction in removal percentage) on the most hydrophobic compounds and the highest impact on the hydrophilic compound. It was hence concluded that the hydrophobicity of non-polar moieties of the organic compounds and their possible impact on the entropy of the system had significant contribution in driving the ion exchange removal of organic compounds.

Ion exchange experiments were also conducted for NOM isolates including SRNOM, SRFA, and SRHA. The competition from inorganic anions for ion exchange sites was less significant on SRHA, which is the most hydrophobic fraction studied in this research. This is consistent with the findings obtained from model organic molecules. Combing these findings, it can be concluded that the hydrophobic effect (i.e., the rejection of hydrophobic moieties from water due to their weak interaction with water molecules), is the predominant driving force for the removal of organic matter. Therefore, hydrophobic (entropy) contribution is more significant than the electrostatic interactions for the removal of hydrophobic organic compounds. For this reason, their removal efficiency was less affected by the occupation of the ion exchange sites by other anions in water.

In all experiments, the amount of chloride (the resin counter ion) release was measured and it was found that for every equivalent of the organic molecule that adsorbs onto the resin, the same equivalent of chloride releases to the water. This means that ion exchange is the central removal mechanism; nonetheless, the paramount driving force for the transfer of the organic molecule to the resin phase is the entropy. The positive entropy change that was obtained by ITC studies also confirms the entropy-assisted removal of NOM by ion exchange resins.

- **Salt induced effects on the selectivity of ion exchange resins**

Two inorganic salts were investigated in this research and the results showed that the solute-solvent interactions are the paramount factors in determining the ion exchange selectivity, also highlighting the important role of the hydrophobicity of the NOM. Also, the change in the background water matrices can shift the selectivity of the ion exchange resins towards some specific fractions of the NOM by affecting the solvation behaviour of the water molecules. The following conclusions have been made out of the experimental results:

  - Where both electrostatic and hydrophobic effects contribute to the removal (e.g., SRFA which consists of aliphatic structured high charge density molecules), nitrate and sulphate both promote the ion exchange selectivity towards the removal of UV absorbing compounds.
  - Where hydrophilic compounds are also present in water (e.g., SRNOM that contains both hydrophobic and hydrophilic compounds), sulphate has a better performance in enhancing the removal of the UV absorbing compounds. The suppression of electrostatic interactions by sulphate results in the dominant contribution of the hydrophobic effect and thus the preferential removal of UV absorbing compounds.
  - When the hydrophobic characteristic of the organic matter is immense (e.g., SRHA), nitrate increases the overall DOC removal by lowering the hydrophobic effect through disrupting the water structure. Moreover, increasing the electrostatic effects

for example by increasing the resin amount, slightly improves the removal of UV absorbing compounds particularly in the presence of nitrate.

Thermodynamic properties of the ion exchange process in presence of nitrate and sulphate were also quantified using isothermal titration calorimetric studies. In the presence of nitrate, a favourable reduction in the endothermic heat required for the dehydration of hydrophobic moieties was achieved, indicating the disruption of hydrogen bonds in the presence of nitrate. In contrast, the overwhelming contribution of entropy for SRFA and SRNOM was observed in the presence of sulphate, this was interpreted in two ways: i) the increase in the enthalpy change due to the suppression of electrostatic interactions, or ii) the increase in the entropy due to the more structured water molecules in the presence of sulphate. Surprisingly, the entropy contribution to the removal of SRHA decreased in the presence of sulphate and this was mainly attributed to the higher molecular weight and higher hydrophobicity of the SRHA that may lead to its structural and conformational changes in water containing sulphate. Overall, the findings of this research indicate the significant contribution of the solute-solvent interactions to the removal of the organic matter and therefore, the salt-induced alterations in the behaviour of water molecules affects the selectivity of the ion exchange process.

- **The impact of resin hydrophobic properties**

The impact of resin's polymeric structure was investigated by focusing on the contribution of the hydrophobic effect to the removal of natural organic matter. This was achieved by comparing the removal of NOM isolates with polystyrene (more hydrophobic) resin and that with the polyacrylic (more hydrophilic) resin. The polystyrene resin exhibited lower performance in removing DOC and had lower affinity for the UV absorbing compounds. Moreover, increasing the resin dose had an adverse impact on the removal of UV absorbing compounds (i.e., SUVA increased with the resin dose). Given that the central difference between the two studied resins is their polymeric backbone, it is concluded that the hydrophobic characteristic of the polystyrene resin has a negative impact on the removal performance, confirming the importance of hydrophobicity and its significant contribution to the removal either from the water or the resin phase.

It was also found that the increase in DOC removal (especially UV absorbing compounds) in the presence of sulphate was greater with the polystyrene resin than that of the polyacrylic resin. As proven by ITC studies, the presence of sulphate increases the entropic contribution by enhancing the hydrophobic characteristics in water with an increase in the order of water molecules. Therefore, it is concluded that increasing the difference in the hydrophobicity of the resin phase and the water is the dominant driving force for the transfer of the organic matter to the resin phase. The increase in the SUVA value of the treated water with the resin dose (polystyrene resin) is another indication for the predominant effect of hydrophobic contribution than the electrostatic interactions. The better performance of polystyrene resin compared to the polyacrylic one in removing inorganic anions (sulphate/nitrate) confirms the preferential removal of highly charged smaller molecules with the polystyrene resin.

Collectively, the hydrophobicity of the organic matter has a positive contribution to the removal, while the hydrophobic contribution from the resin phase plays a negative role in the retention of hydrophobic and UV absorbing compounds onto the resin. Therefore, the difference in the entropy of the resin phase and the water is the main driving force in the ion exchange removal of the organic matter. In other words, the relative hydrophobicity within the system is the predominant factor in determining the selectivity of the ion exchange process for the organic compounds removal.

8.2. Significance of This Research

This research intended to study the fundamental mechanisms governing the removal of NOM by ion exchange. The data obtained here are broadly beneficial for the selection of treatment strategies appropriate for different water treatment conditions and more specifically for an efficient utilization of the ion exchange process in order to maximize NOM removal. Moreover, the findings of this work could be beneficial in optimizing the combination of ion exchange process with other processes (e.g., coagulation) in water treatment facilities. This research has taken three approaches towards achieving the overall objectives:

Studying the ion exchange of simple model organic molecules to better evaluate the impact of the organic compound's characteristics and to avoid the limitations caused by the intricate structure of the NOM in studying the fundamentals. The findings on the importance of hydrophobicity provided a framework for the interpretation of the results and shed light on some contradictories reports in the literature, on the important factors in the ion exchange process for NOM removal.

This research took advantage of the salt effect on water molecules structure to better investigate the hydrophobic contribution to the NOM removal. This approach has been widely applied for the retention of proteins or biopolymers onto the ion exchange resins; however, to the authors' knowledge, this work is the first step in evaluating the salt mediated solvation effects on the uptake of NOM onto ion exchange resins. This approach provided a great perception of solute-solvent interactions and their paramount impact in determining the ion exchange selectivity. Also, the results yielded an insight into how the change in the background water matrices can shift the selectivity of the ion exchange resins towards some specific fractions of the NOM by affecting the solvation behaviour of the water molecules. Furthermore, the findings of this research provided a quantitative and satisfactory interpretation of the experimental results obtained for NOM removal from water solutions with high ionic strength.

The removal of NOM from water has been considered as an entropy-assisted sorption in the literature; however, it has not been quantitatively proven. Through isothermal titration calorimetric (ITC) approach utilized in this study, the thermodynamic properties associated with the ion exchange adsorption of NOM from water were measured. Note that the change in the enthalpy and entropy of the NOM removal is too small to be measured through the conventional methods; hence, ITC gives insights to the thermodynamic aspects of the process with its ability to measure very small changes in the reaction heat. Despite some limitations around the use of ITC for NOM studies, this work for the first time introduced ITC as an alternative technique for studying the thermodynamics of NOM removal, potentially opening new opportunities towards enhancing the fundamental knowledge in this area. Furthermore, the findings obtained from the ITC work conducted in this research yielded insight into the contribution of entropy/enthalpy to the retention of NOM. Such information provides the scientific and engineering community work with ion exchange process invaluable fundamental information on the molecular interactions that are involved or drive the uptake of NOM under different conditions.

8.3. Recommendations for Future Work

- Evaluation of the ion exchange process in the presence of both nitrate and sulphate is recommended. The outcomes will help to understand the interplay of their effects on the removal efficiency and could be a better simulation of natural waters containing both sulphate and nitrate together.
- Investigating the impact of the presence of phosphate ion on the removal of UV absorbing compounds and the ion exchange selectivity is suggested. This is because

phosphate is also one of the common anions that can be found in natural water sources. Moreover, according to Hofmeister series, phosphate has more kosmotropic characteristics (i.e., increasing the order of water molecules) compared to sulphate, hence, one could be expected to achieve much better removal of UV absorbing compounds in the presence of phosphate.

- Further research on the impact of resin properties using a wide range of anion exchange resins is strongly recommended. A study with gel type resins, more specifically weak based resin is suggested. The findings of such research may guide further investigations and more extensive interpretation of the results from the point of molecular interactions and their involvement in driving the removal of NOM during the ion exchange process.
- Applying ITC at different temperature and also for different ion exchange resins such as polystyrene, weak based, and gel type resins, would bring new insights into the understanding of the contribution of resin characteristics on NOM removal. For future ITC studies, the thermodynamic values obtained in this study can be used as a first guess in data fitting models.
- Regeneration of the ion exchange resins is one of the principle concerns in implementing this process. As solvent-solute interactions are of great importance during the regeneration, an investigation on the effect of inorganic anions especially sulphate on the efficiency of the regeneration is recommended. One suggestion is to increase the hydrophobic characteristics of the regenerant by adding a small amount of organic co-solvent such as methanol during the first stage of regeneration and then perform a second run of regeneration using only water as the solvent. It is believed that the outcomes can be of great value and may lead to an optimum design of regeneration parameters.

- This work was based on batch experiments in order to investigate the fundamentals. However, with having these findings as a guide for future works, continuous flow studies (e.g., fixed bed ion exchange) with a focus on the solvent-solute interactions and salt effects are recommended. This will be of great value in creating a broader database of the different molecular contributions to the selectivity of the ion exchange process. Moreover, this research showed that the removal rate of inorganic anions is quite fast compared to NOM, and it is still unknown how the continuous presence (constant concentration) of these anions in the water flow can contribute to the removal efficiency. Hence, the continuous flow operation could build more extensive knowledge to the existing understanding of the salt effects on the water molecules behaviour and thus the retention of NOM molecules onto the ion exchange resins.
- Ion exchange chromatography could also be a good approach to simulate the real fixed bed reactors for NOM removal. It can also allow for studying some factors such as the change in the flow rate. More importantly, it can be an easy approach to investigate the regeneration of the ion exchange resin through elution of the ion exchange column after removal of NOM.
- It is also encouraged that evaluation of the ion exchange process be performed with various natural water sources with a great focus on the contribution of the hydrophobic and the electrostatic effects to the removal. Applying ITC measurements for natural water sources may also bring some valuable insights. However, one obstacle with natural water sources is the interference of other factors that might mask the impact of salts or any specific contributions.

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Appendices

Appendix A: The Removal of Organic Compounds at Different Salt Concentrations

Table A.1, The percentage of DOC removal for pure organic compounds with ion exchange resin in the presence of salts at different concentrations.

BA	Resin dose\Salt		0.1 mM		1 mM		10 mM	
		No Salt	NO3	SO4	NO3	SO4	NO3	SO4
	Feed	0%	0%	0%	0%	0%	0%	0%
	20	69%	51%	15%	12%	0%	0%	0%
	50	83%	71%	50%	27%	0%	0%	0%
	100	88%	82%	68%	43%	2%	3%	0%
	150	91%	86%	78%	53%	6%	6%	0%

NAA	Resin dose\Salt		0.1 mM		1 mM		10 mM	
		No Salt	NO3	SO4	NO3	SO4	NO3	SO4
	Feed	0%	0%	0%	0%	0%	0%	0%
	20	82%	65%	23%	23%	0%	1%	2%
	50	89%	81%	65%	41%	1%	5%	3%
	100	92%	87%	80%	58%	5%	11%	3%
	150	94%	89%	85%	66%	11%	16%	3%

GA	Resin dose\Salt		0.1 mM		1 mM		10 mM	
		No Salt	NO3	SO4	NO3	SO4	NO3	SO4
	Feed	0%	0%	0%	0%	0%	0%	0%
	20	43%	20%	7%	1%	0%	0%	0%
	50	61%	36%	20%	7%	0%	0%	0%
	100	72%	52%	36%	14%	0%	1%	0%
	150	75%	61%	46%	20%	0%	1%	0%

In this work, batch experiments for GA, BA, and NAA at different salt concentrations were conducted. According to Table A.1, which represents the DOC removal percentages; no significant removal was achieved at salt concentrations of 1 mM and above. Therefore, the discussions in chapter 4 were made for the results obtained at 0.1 mM concentration of the salts.

Increasing the salt concentration negatively affected the DOC removal, and this impact had an adverse relationship with the hydrophobicity of the organic compound. In other words, the reduction in GA (hydrophilic compound) removal with an increase in the salt concentration was more significant compared to BA and NAA.

Appendix B

B.1. Relationship between UV absorptivity and DOC of the treated waters

The change in UV absorbance at 254 nm versus DOC for water samples after treatment with ion exchange resin at different resin doses was plotted in Figure B.1. A linear relationship was obtained between DOC and UV absorptivity. Moreover, the linearity was the same at any resin doses, meaning that increasing the resin does not impact the proportional changes in DOC and UV absorptivity of the water samples.

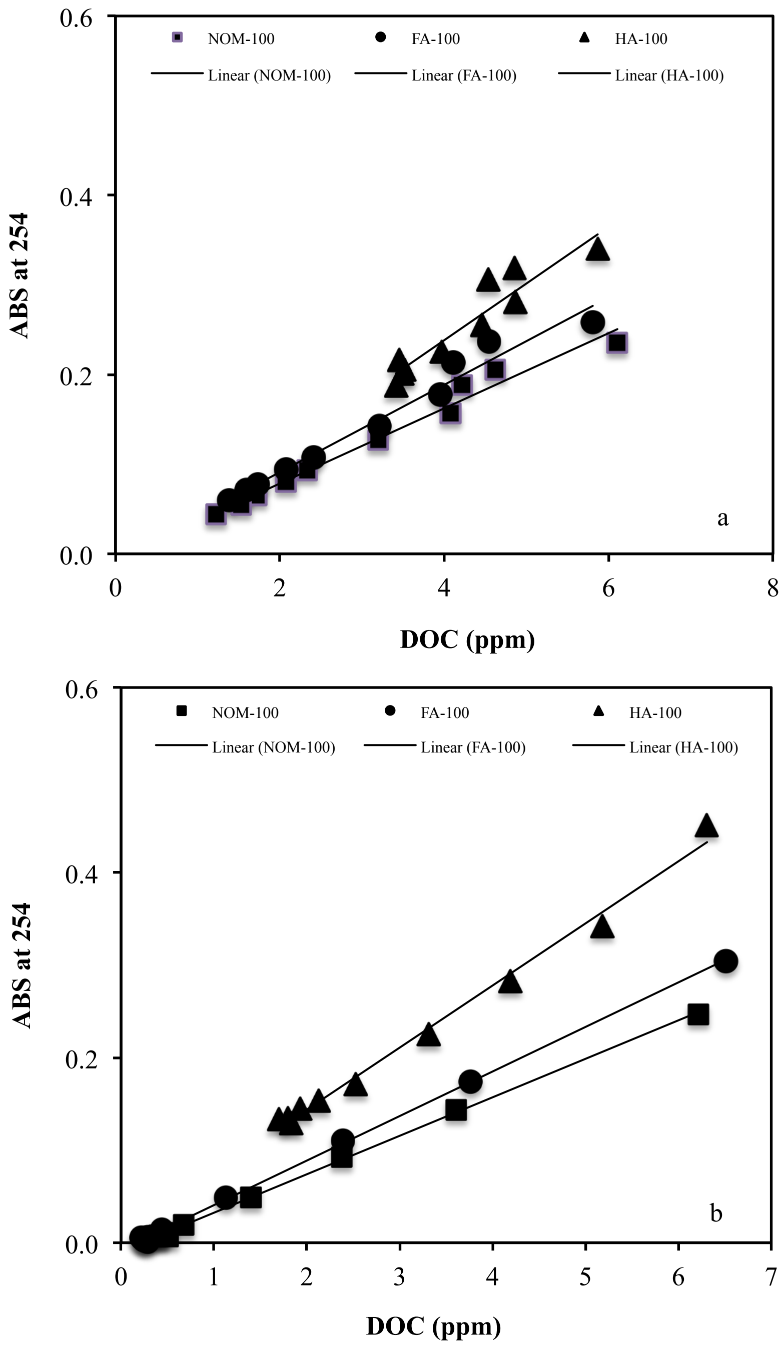
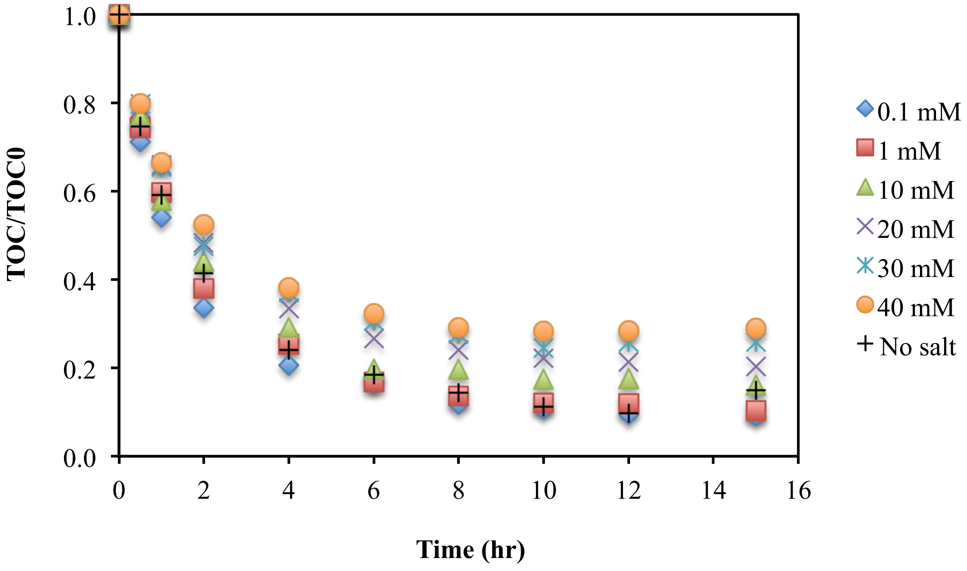


Figure B.1, UV absorptivity vs. DOC for water samples containing NOM isolates treated with resin doses of a) 200 mg/L, and b) 1000 mg/L.

B.2. Kinetics of NOM Isolates Removal in the Presence of Salts

In this research, kinetic studies were conducted for three NOM isolates (i.e., SRNOM, SRFA, and SRHA). The results in terms of TOC/TOC$_0$) versus time are shown in Figure B.1,

Figure B.2, and Figure B.3. The impact of inorganic anions on the kinetics of the NOM isolates removal by the IEX resin decreases with increasing the hydrophobicity of the organic matter. The presence of inorganics has the least impact on the HA removal (Figure B.3), which is the most hydrophobic isolate studied in this research. This observation confirms the importance of hydrophobicity as a driving force in removing organic matter from water by ion exchange resins, as elaborated in chapter 5. Moreover, the greater effect of sulphate compared to nitrate is attributed to its higher charge density and thereby greater affinity for the ion exchange sites.



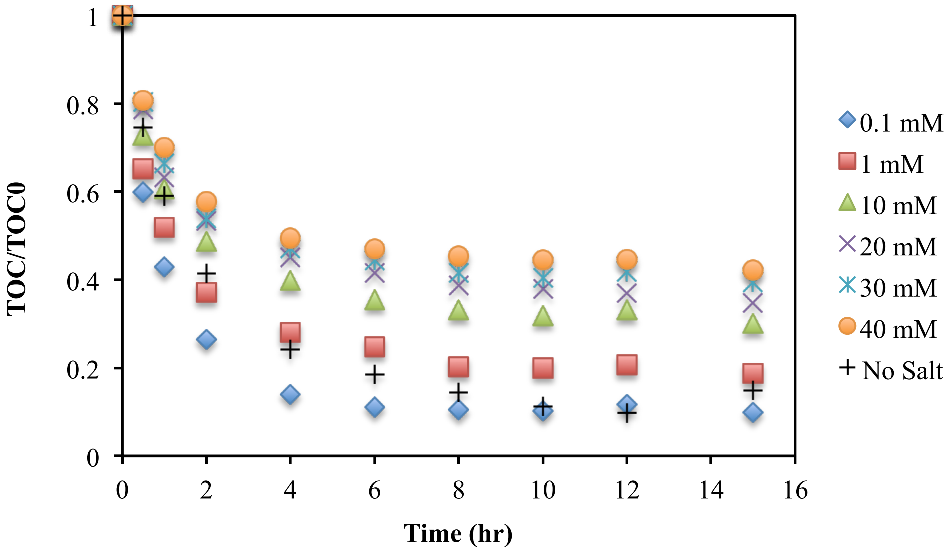


Figure B.2, TOC removal over time for SRNOM in the presence of (a) nitrate), and (b) sulphate (resin dose: 500 mg/L).

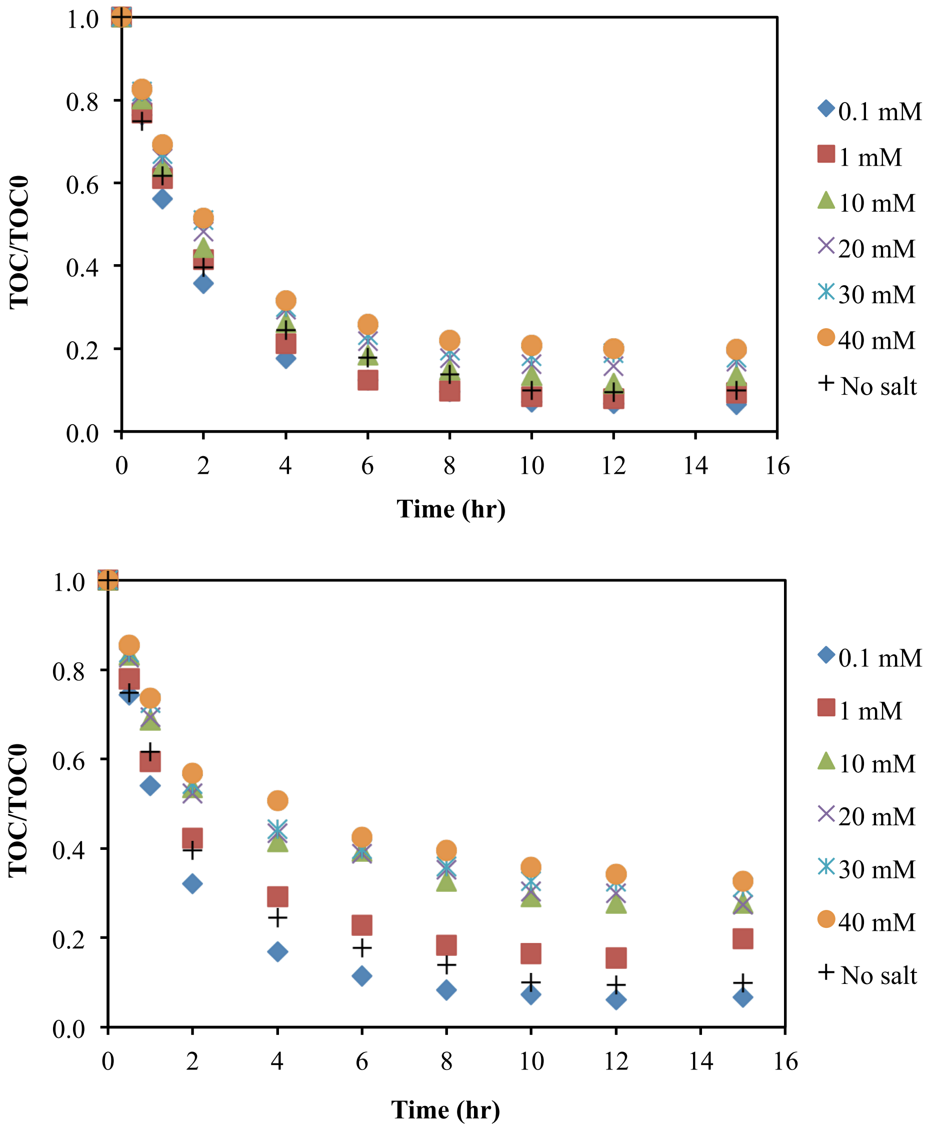


Figure B.3, TOC removal over time for SRFA in the presence of (a) nitrate), and (b) sulphate (resin dose: 500 mg/L).

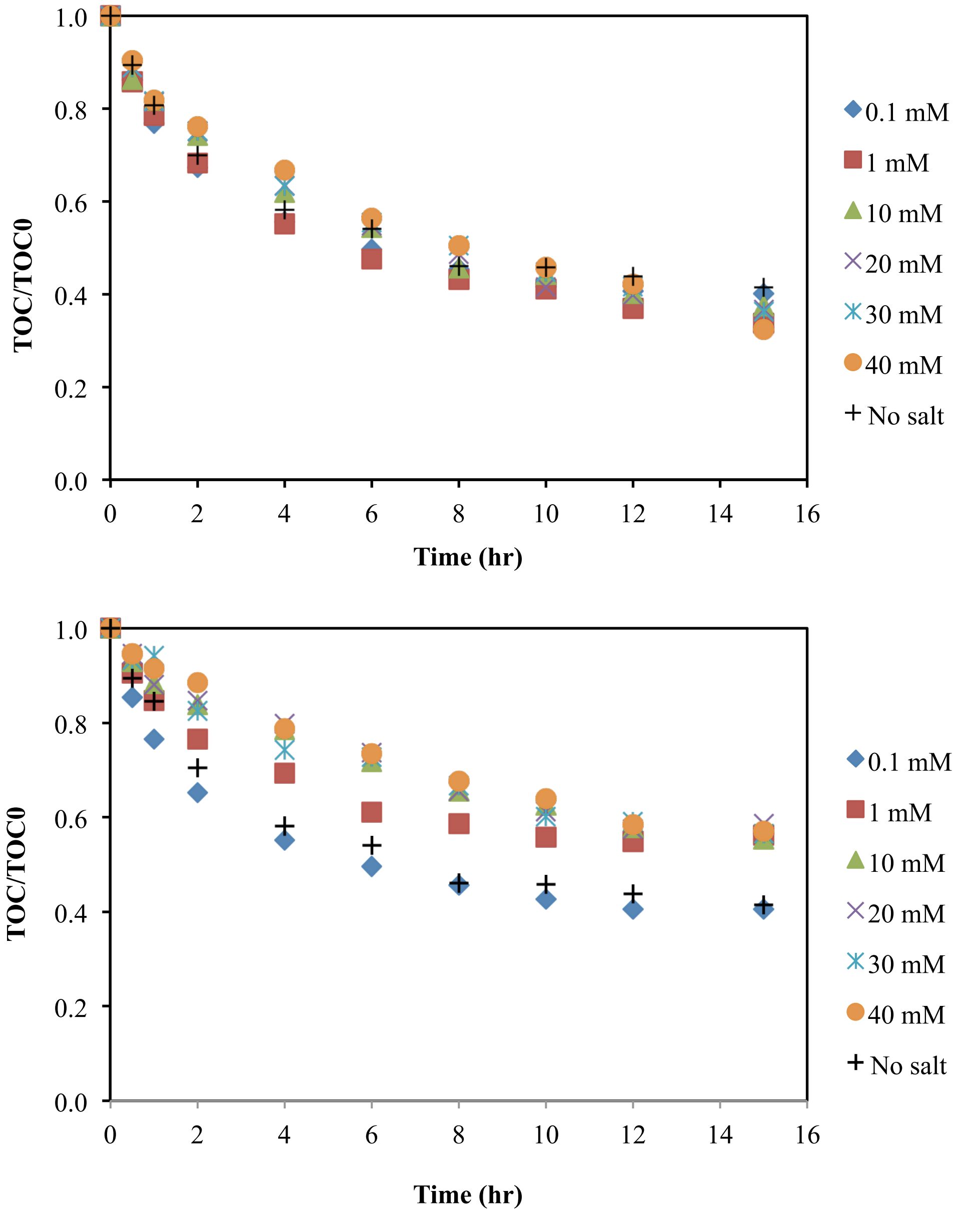


Figure B.4, TOC removal over time for SRHA in the presence of (a) nitrate), and (b) sulphate (resin dose: 500 mg/L).

B.3. Stoichiometry of the ion exchange removal of NOM isolates in presence of salts

The amount of chloride release in the experiments was measured and the results are plotted versus the total amount of adsorbed anion (i.e., DOC and inorganic anion). As shown in Figure B.5, the data points are clustered around the diagonal line. Therefore, it is concluded that regardless of the resin dose and the type of NOM isolate, the removal mechanism was entirely governed by ion exchange. However, in the case of SRFA in presence of sulphate, the amount of chloride release was slightly less than the total adsorbed anion on equivalent basis (i.e., meq/L). This can be explained by the impact of sulphate in increasing the possibility of hydrogen bonds between the resin surface and the organic matter. Thus, it can be said that at high resin dosage (i.e., 1000 mg/L), where more surface area is available, the possibility of physical adsorption increases in presence of sulphate.

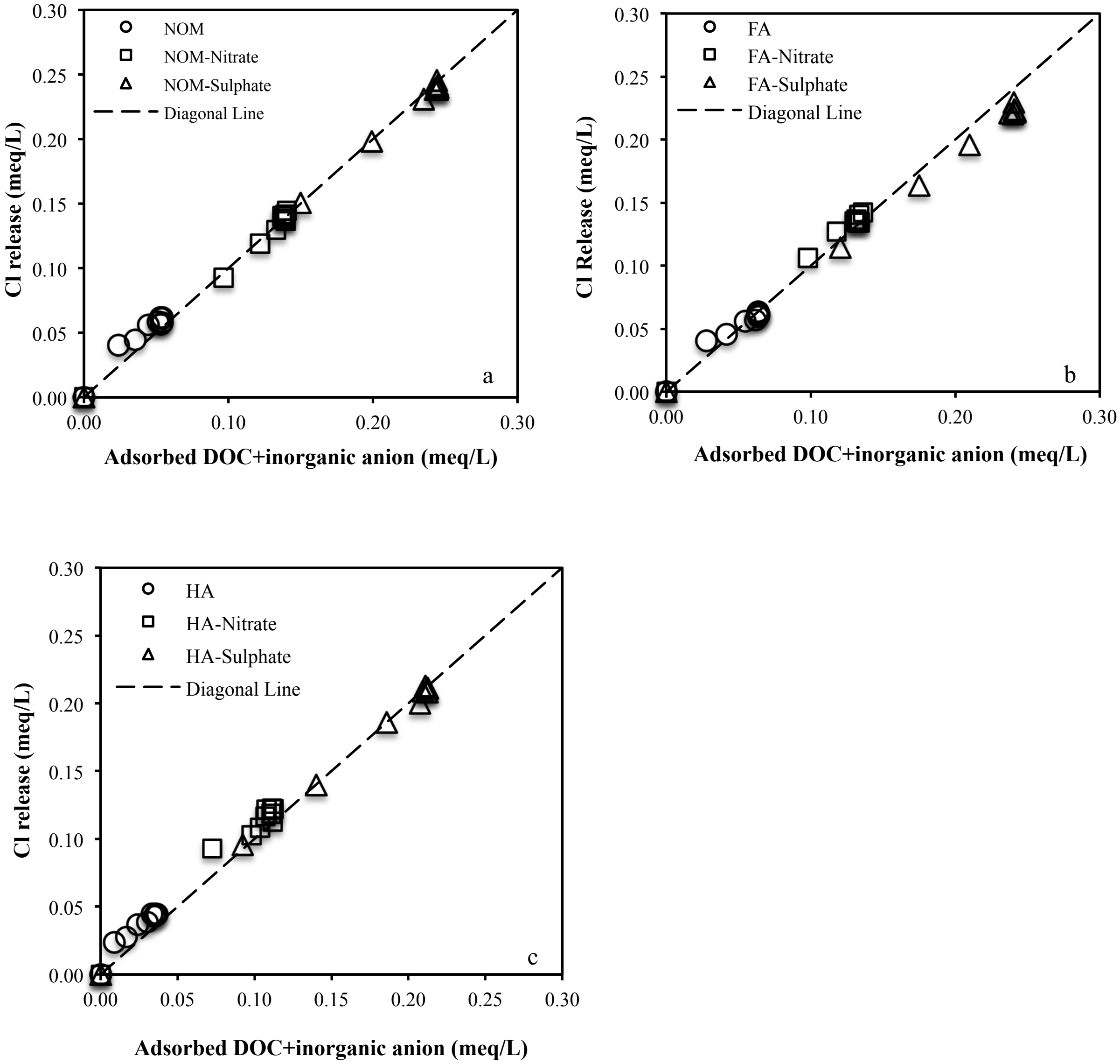


Figure B.5, Stoichiometry of the removal by ion exchange (resin amount: 1000 mg/L, and nitrate/sulphate concentration: 0.1 mM). (a) SRNOM; (b) SRFA; (c) SRHA.

Appendix C[*]

C.1. Fitting ITC data with the two sets of sites model

If the ITC test conducted for a macromolecule (i.e., NOM in this research) has binding sites with two different values of K and/or ΔH, then two sets of sites model must be applied for curve fitting.

This model uses an iteration procedure in which an initialization required, meaning that a first guess has to be applied by the user. Therefore, the involvement of the user in data fitting is important because poor initialization may not lead to a convergence to the best values. This step was a limitation in employing ITC in this research and it required a lot of guess and try steps, however, believe the values obtained in this work could be later used as initialization parameters in future ITC studies for NOM removal. After initialization procedure by the user, the software can perform iterations by hitting the “fit” button. This button in new software designs is called “1 Iter.” and/or “10 Iter.”. To reach the best fitting curve, iteration process needs to be continued to achieve the smallest chi^2 value. The software uses a basic nonlinear least square curve fitter by default.

C.1.1. Chi^2 minimization

The software uses the chi^2 minimization as a standard way of defining the best fit to find the values for the parameters that best describes the data points.

The equation used for can be simplified to:

$$x^2 = \frac{1}{n^{eff} - p} \sum [y_i - f(x_i;\, p_1, p_2, \ldots)]^2$$

---

[*] The information represented here is mainly obtained from the guide for the software users of ITC: https://www.bioch.ox.ac.uk/aspsite/services/equipmentbooking/biophysics/ITC_data_analysis.pdf (Accessed on Dec 28, 2016)

where:

p_i = fitting parameters

p = total number of adjustable parameters

y_i= experimental data point

n^{eff}= total number of experimental points used in the fitting

$f(x_i;\ p_1, p_2, \ldots)$= fitting function

$n^{eff} - p = d$ (the number of degrees of freedom)

C.1.2. Equations used for fitting ITC binding data

The cell with a volume of V_0 is initially filled with the resin solution, however, by every injection, a volume of ΔV_i is added. Therefore, the concentration of the resin slightly changes with each injection and then the average concentration can be defined as the mean of the beginning concentration (M_t^0) and the present concentration (M_t) in the active volume:

$$M_t^0 V_0 = M_t V_0 + \frac{1}{2}(M_t + M_t^0)\Delta V$$

Where

$$\Delta V = \sum_i \Delta V_i$$

then

$$M_t = M_t^0 \left(\frac{1 - \frac{\Delta V}{2V_0}}{1 + \frac{\Delta V}{2V_0}} \right)$$

With respect to injecting the solution (i.e., NOM), assuming that all of the injected NOM remains in the cell (V_0), the following expression is used by the software to correct for volume effects happening by every injection.

$$X_t^0 V_0 = X_t V_0 + \frac{1}{2} X_t^0 \, \Delta V$$

$$X_t = X_t^0 \left(1 - \frac{\Delta V}{2V_0}\right)$$

The following equations used for the two sets of independent sites:

$$\mathrm{K}_1 = \frac{\Theta_1}{(1-\Theta_1)[\mathrm{X}]} \qquad \mathrm{K}_2 = \frac{\Theta_2}{(1-\Theta_2)[\mathrm{X}]}$$

$$X_t = [X] + M_t \left(n_2 \Theta_1 + n_2 \Theta_2\right)$$

where

K = binding constant;

n = number of sites;

V_0= active cell volume;

X_t and [X] are bulk and free concentration of the NOM solution;

M_t and [M] are bulk and free concentration of the resin solution;

Θ = fraction of the occupied sites by NOM molecules.

The total heat content of the solution in V_0 is:

$$Q = M_t V_0 \left(n_1 \Theta_1 \Delta H_1 + n_2 \Theta_2 \Delta H_2\right)$$

Accordingly, the calculated heat effect for the injection i is expressed as follow after considering the displaced volume:

$$\Delta Q(i) = Q(i) + \frac{dV_i}{V_0}\left[\frac{Q(i) + Q(i-1)}{2}\right] - Q(i-1)$$

Appendix D

D.1. Selecting the best resin dose for ITC tests

In order to determine the best resin dose for ITC experiments, some tests for Suwannee River NOM with four different resin doses were conducted and the results are shown in Figure D.1. As illustrated in Figure D.1, with increasing the resin dose, first injections exhibited more exothermic process due to the more available resin sites for ion exchange, with a subsequent shift to an endothermic and entropy-driven system by increasing number of injections. Minor heat release after resin saturation, is attributed to the heat generated by dilution and mixing, which was measured through a control test. At low resin doses (i.e., 1000 and 2500 mg/L), the change in the reaction heat was quiet small and thus was not appropriate for accurate data fitting. Moreover, to increase the accuarcy of the ΔH and ΔS values, a complete process (both strong and weak affinity binding) needs to be achieved. At low resin doses, the two sets of sites (i.e., high affinity sites and low affinity sites) could not be distinguished. Therefore, fitting the data of 2500 mg/L with two sets of sites model was not as accurate as 5000 mg/L or 10000 mg/L because the initialization of the curve fitting (i.e., first guess for parameters) was unsuitable and achievement of a best convergence required more iterations and sometimes convegence did not even happen. Both, 5000 mg/L and 10000 mg/L doses were appropriate for this research, however, as mentioned in chapter 3, the cleaning procedure of the ITC cell is time-consumming and using a very high dose of the resin such as 10000 mg/L was problematic because it could attach to the walls of the cell and thereby the cleaning needed to be repeated. Considering all these facts, 5000 mg/L was selected as the best resin dose in applying ITC tests for NOM removal in this work.

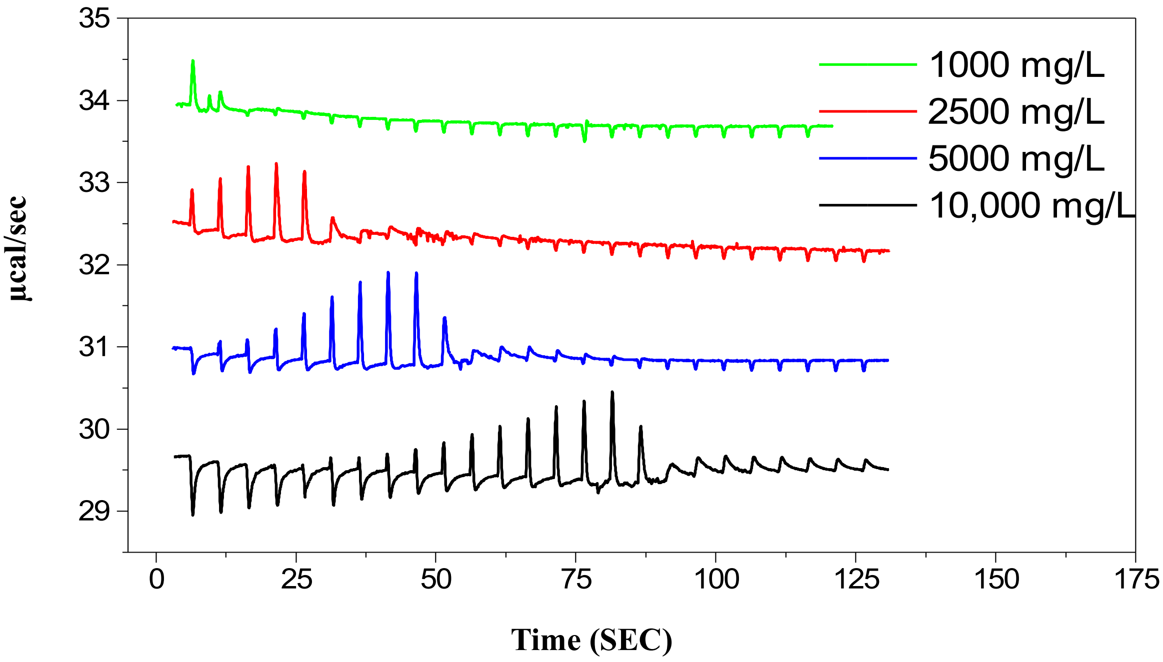


Figure D.1, ITC tests for Suwannee River NOM at different MacroT resin concentrations.

D.2. The effect of the resin matrix on thermodynamic parameters

The impact of the resin backbone structure on the contribution of the entropy and enthalpy to the NOM removal process was examined by conducting ITC experiments for both polyacrylic and polystyrene. The experimental conditions were equal for both resins. The results are represented in Table D.1. Although, both resins resulted in an increase in the system entropy, this value was significant for the polystyrene resin, which can be due to its hydrophobic characteristic and subsequent endothermic interactions involving in NOM removal through ion exchange process. Therefore, not only the hydrophobicity of the water solution is important, but also the resin structure and its hydrophobic characteristics significantly contribute to the removal process of NOM molecules and the thermodynamic properties associated with that. These ITC results confirm the achievements from batch experiments presented in chapter 7.

Table D.1, Effect of resin backbone material on removal thermodynamics.

Resin type (Backbone material)	ΔG (kJ/eq)	ΔH (kJ/eq)	TΔS (kJ/eq)
Ionac MacroT (polyacrylic)	-2.95 R*	2.3	2.95 R + 2.3
Lewatit MP500 (Polystyrenic)	-3.12 R	8.5	3.12 R + 8.5

* The gas constant (kJ/mol.K)

Appendix E

E.1. Impact of inorganic anions on the removal of NOM isolates

The impact of Inorganic anions on the removal efficiency of the NOM isolates with different resin amounts was studied. The results in terms of DOC and UV uptake are shown below for different resin doses. Figures E.1 and E.2 respectively represent the percentage of DOC and UV uptake with 200 mg/L of the resins. Figures E.3 and E.4 respectively represent the percentage of DOC and UV uptake with 500 mg/L of the resins. And, Figures E.5 and E.6 respectively represent the percentage of DOC and UV uptake with 1500 mg/L of the resins. A negative competition effect from inorganic anions was observed in removing NOM isolates by polyacrylic resin. However, this effect decreased with increasing the resin dose. Even with 1500 mg/L of the polyacrylic resin, the presence of inorganic anions resulted in an increase in SRHA removal. Comparing DOC and UV uptake by polyacrylic resin, the UV uptake was less affected by inorganic anions than the overall DOC (i.e., the reduction in UV uptake was not proportional to DOC). This observation confirms the increase in the selectivity of the polyacrylic resin towards UV absorbing compounds in the presence of inorganic anions.

It was interesting that the competition effect was not observed in studies conducted by the polystyrene resin. In addition, the presence of inorganic anions increased both DOC and UV uptake with the polystyrene resin. This can be attributed to the hydrophobic structure of the polystyrene resin in which the hydrophobic effect governs the removal process than the electrostatic interactions. It is also worth noting that, the positive impact of inorganic anions on the removal efficiency by the polystyrene resin increased with resin dose.

At very low resin doses (i.e., 200 mg/L), the DOC removal for SRNOM and SRFA in the presence of sulphate decreased and then started increasing with the salt concentration (Figure

E.1(b)). Due to the low amount of ion exchange sites at low resin doses, the competition between inorganic anions and NOM molecules is higher. However, at high salt concentrations, the salt effects are strong enough that hydrophobic behaviour governs electrostatic interactions in driving the removal process.

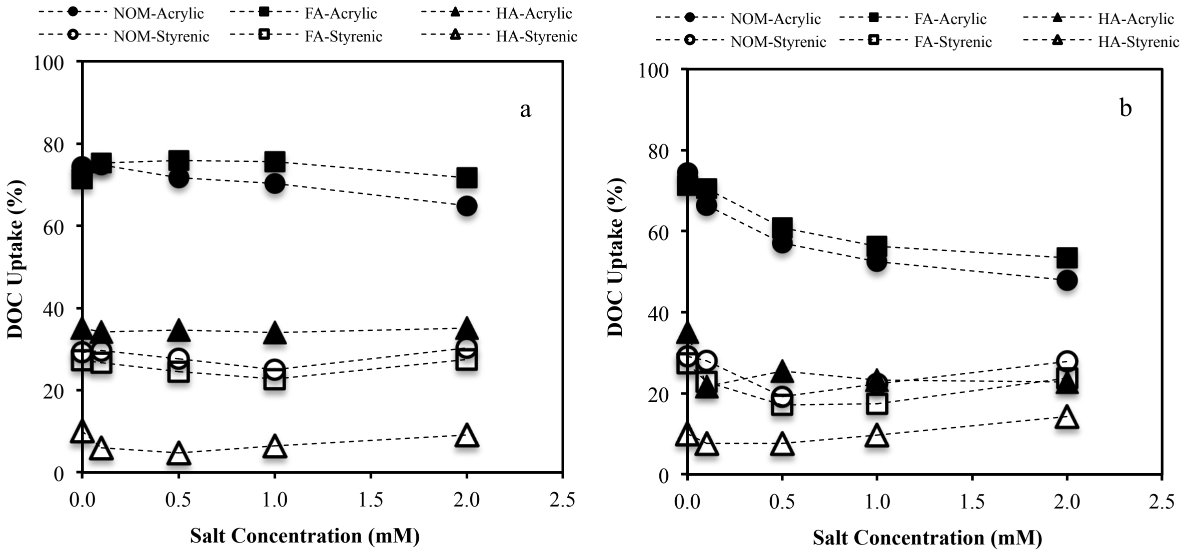


Figure E.1, DOC uptake from different model waters with 200 mg/L of the resin either polystyrene or polyacrylic in the presence of various salt concentrations, sodium nitrate (a), and sodium sulphate (b).

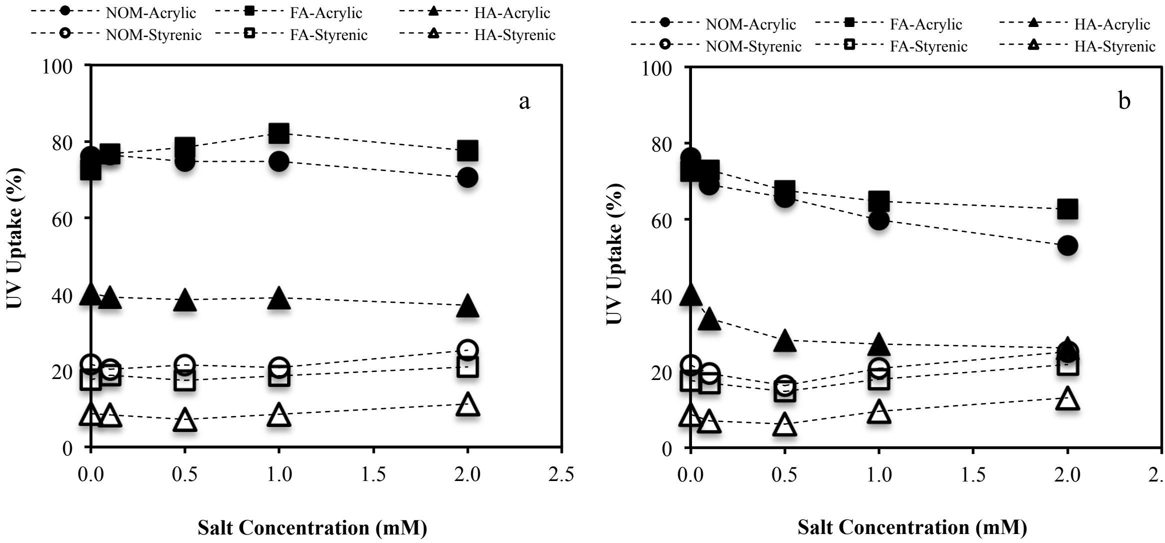


Figure E.2, UV uptake from different model waters with 200 mg/L of the resin either polystyrene or polyacrylic in the presence of various salt concentrations, sodium nitrate (a), and sodium sulphate (b).

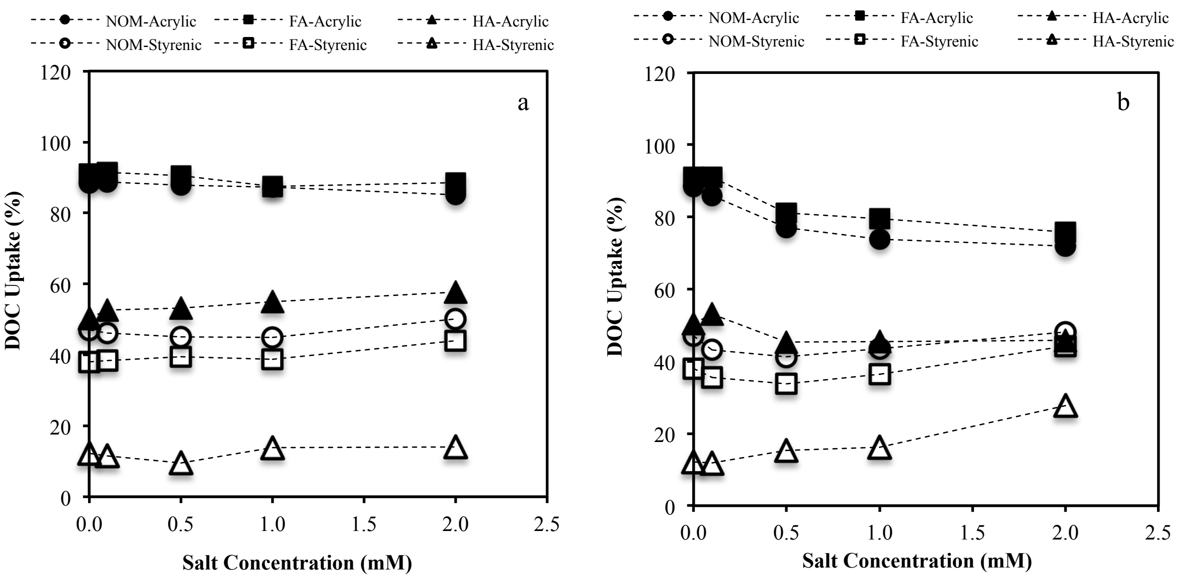


Figure E.3, DOC uptake from different model waters with 500 mg/L of the resin either polystyrene or polyacrylic in the presence of various salt concentrations, sodium nitrate (a), and sodium sulphate (b).

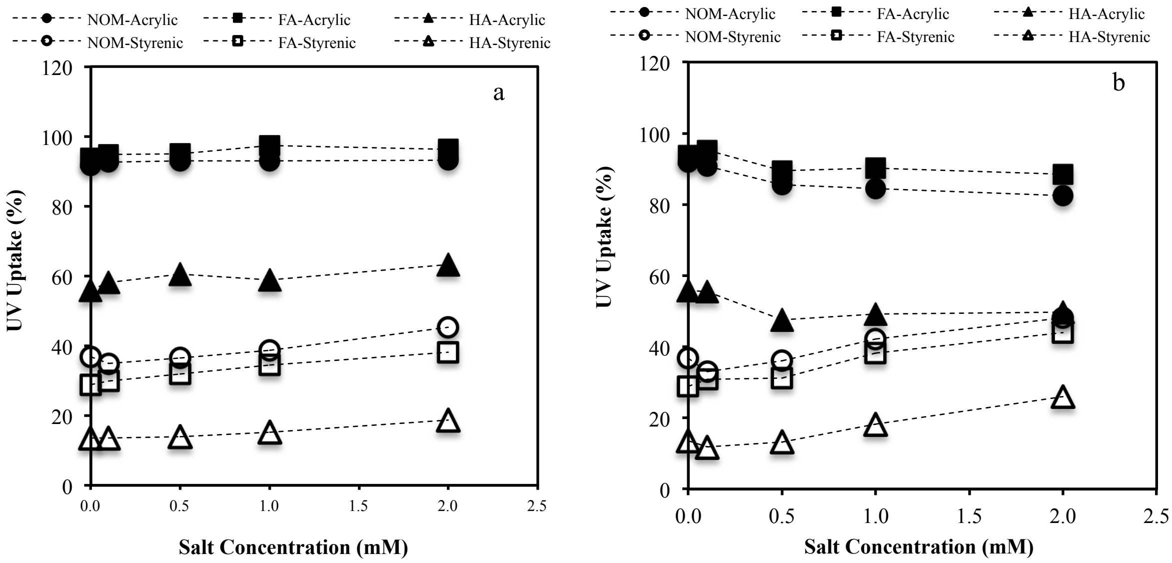


Figure E.4, UV uptake from different model waters with 500 mg/L of the resin either polystyrene or polyacrylic in the presence of various salt concentrations, sodium nitrate (a), and sodium sulphate (b).

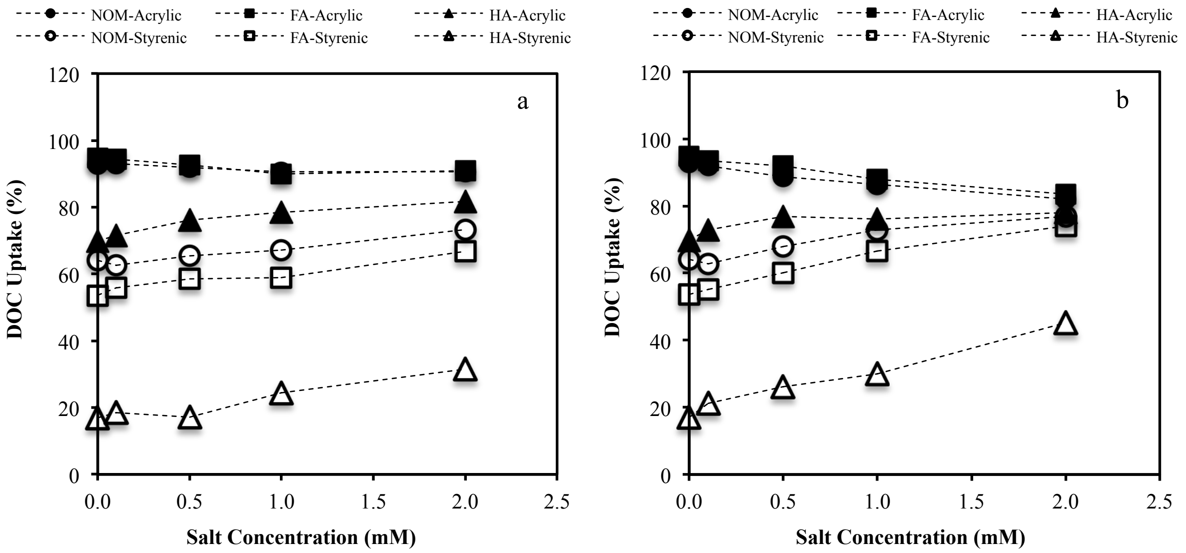


Figure E.5, DOC uptake from different model waters with 1500 mg/L of the resin either polystyrene or polyacrylic in the presence of various salt concentrations, sodium nitrate (a), and sodium sulphate (b).

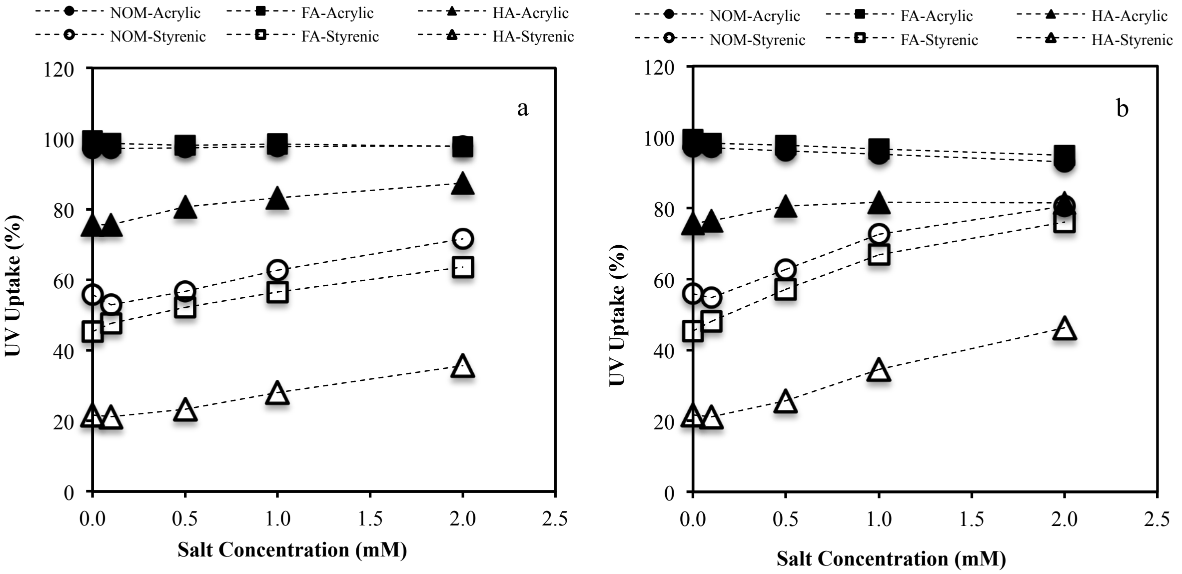


Figure E.6, UV uptake from different model waters with 1500 mg/L of the resin either polystyrene or polyacrylic in the presence of various salt concentrations, sodium nitrate (a), and sodium sulphate (b).

E.2. Ion exchange stoichiometry profiles for NOM isolates removal in the presence of salts

Figures E.1 and E.2 represent the removal stoichiometry for NOM isolates in the presence of nitrate and sulphate with the polyacrylic resin and the polystyrene resin, respectively. According to Figure E.1(a), the removal of nitrate decreased with DOC uptake and the concentration of the chloride ion within the water increased, meaning that the organic matter and nitrate were primarily removed by ion exchange process and the chloride released by the resin. However, the sulphate concentration decreased dramatically (Figure E.1(b)) and this is attributed to the higher affinity of sulphate for ion exchange change sites due to its higher charge density.

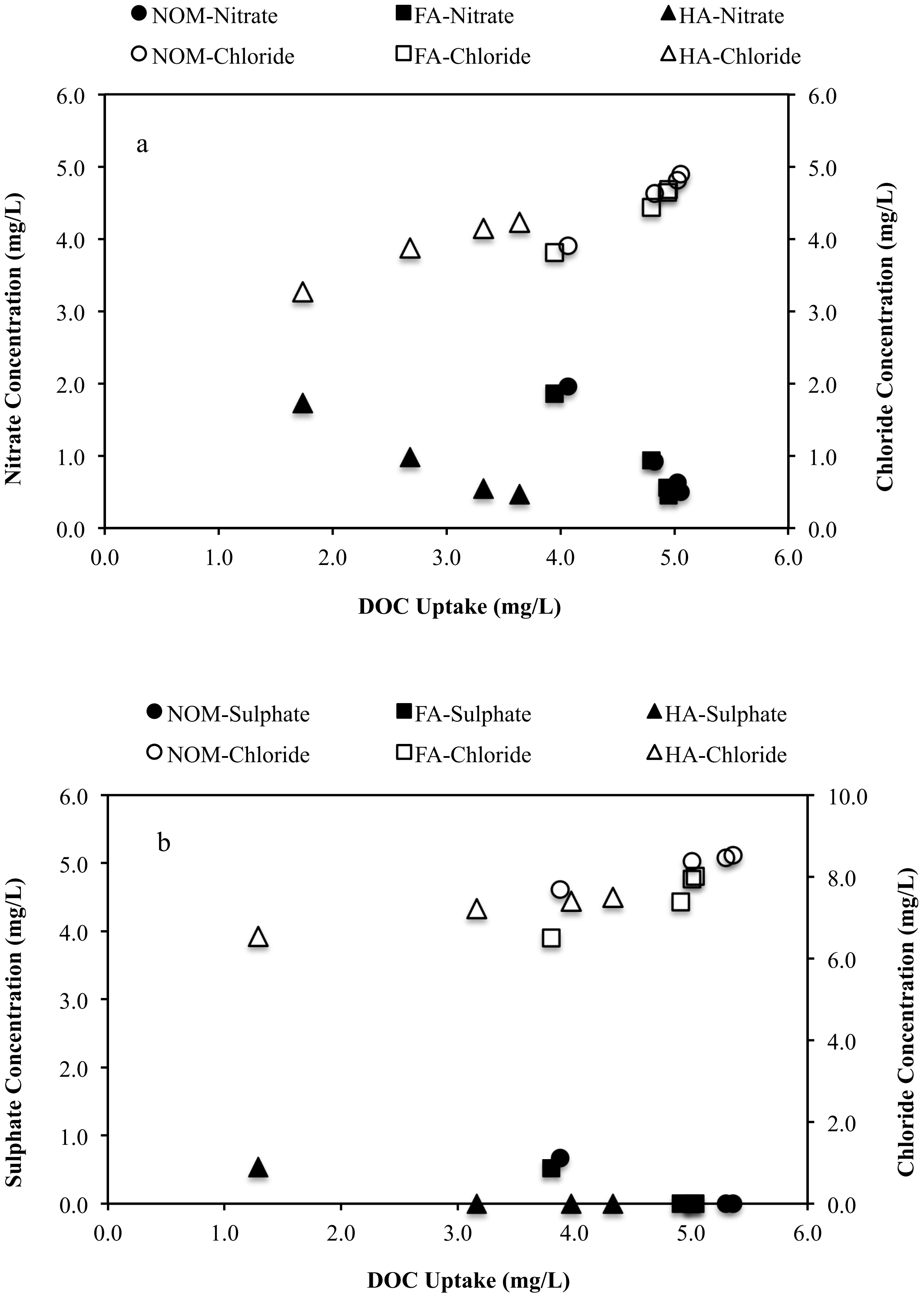


Figure E.7, The change in (a) nitrate, (b) sulphate and chloride concentration versus DOC uptake with the polyacrylic resin.

The results for the polystyrene resin are slightly different (Figure E.2). Comparing Figure E.1(a) and Figure E.2(a), demonstrates a rapid drop in the concentration of nitrate by the polystyrene resin, suggesting the superior performance of the polystyrene resin in removing nitrate regardless of the type of the organic matter. Once nitrate was depleted, chloride concentration continued increasing, confirming an ion exchange mechanism for the removal of the NOM isolates.

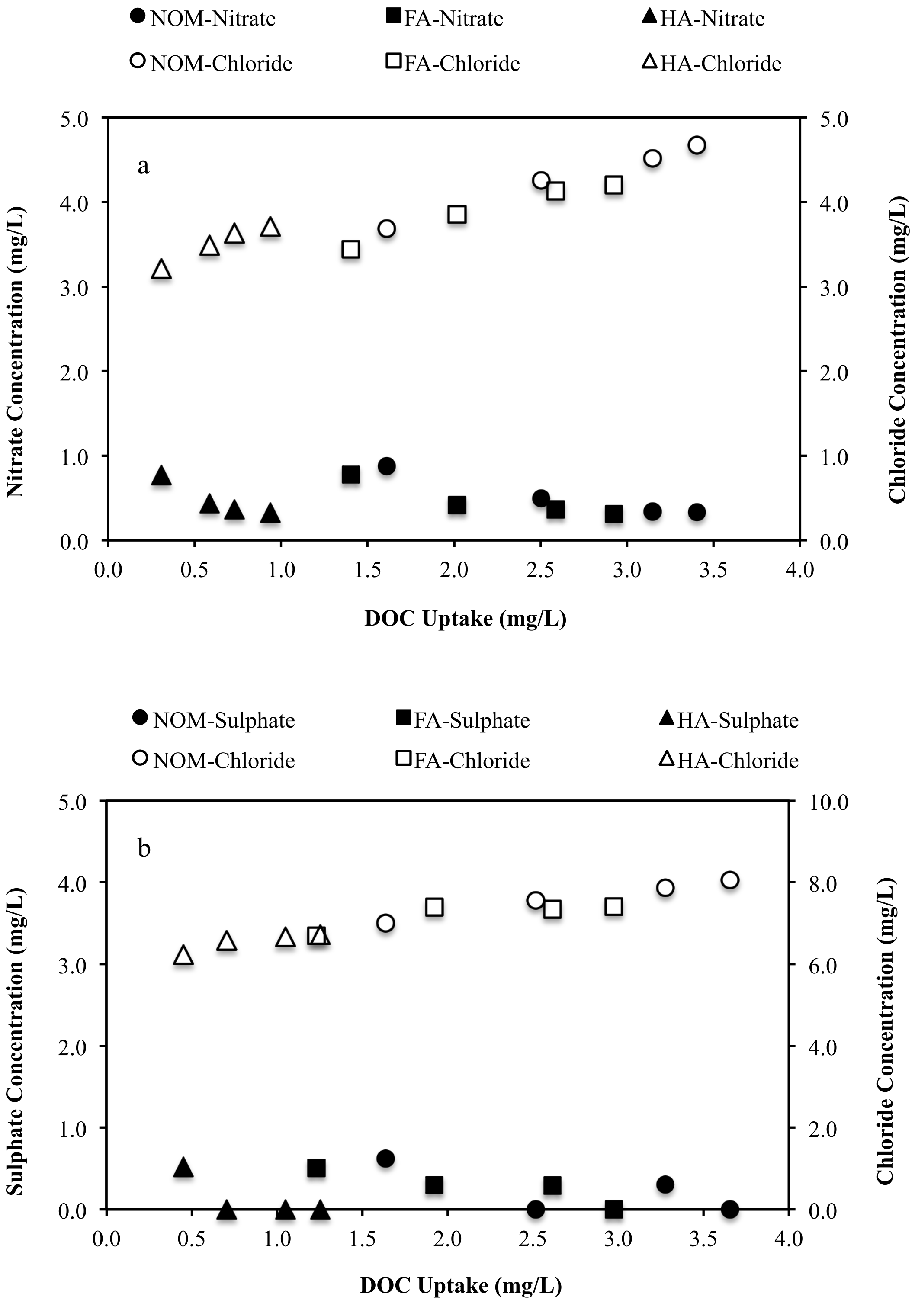


Figure E.8, The change in (a) nitrate, (b) sulphate and chloride concentration versus DOC uptake with the polystyrene resin.

E.3. The removal of nitrate/sulphate by ion exchange resins

The removal of nitrate/sulphate on an equivalent (i.e., meq/L) basis was calculated (Figure E.9), and greater amount of sulphate than nitrate was removed in terms of equivalent removal even at high salt concentrations. This indicates the preferential removal of sulphate by both polyacrylic and polystyrene resins.

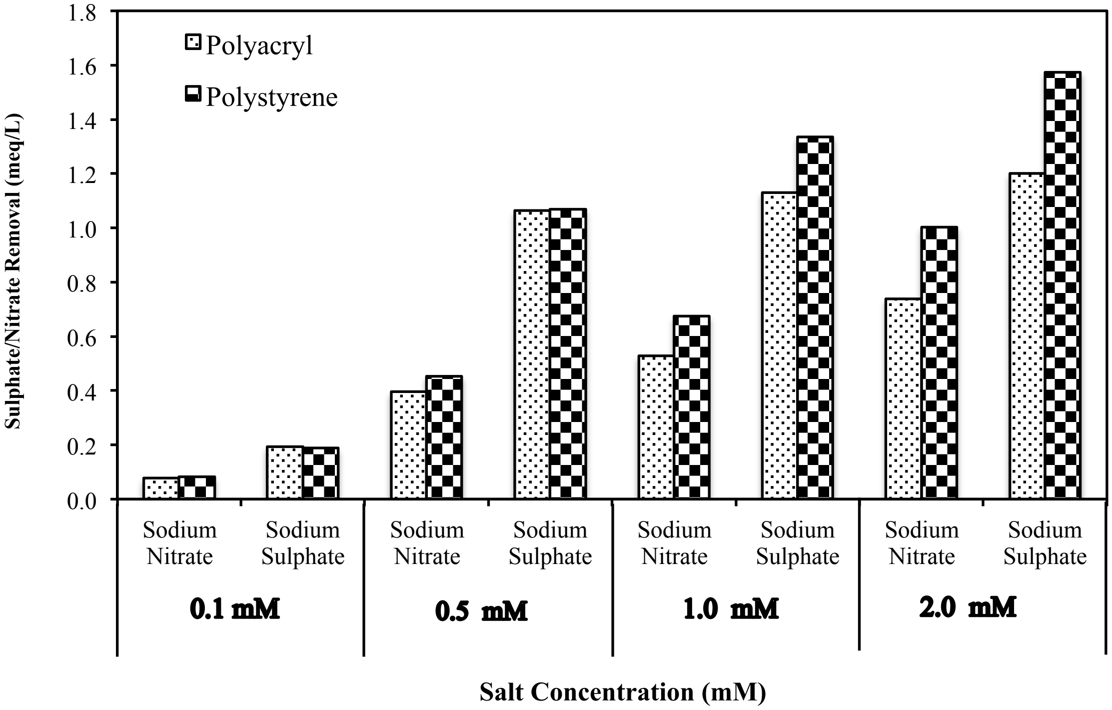


Figure E.9, The removal of sulphate/nitrate on equivalent basis (i.e., meq/L) from model waters containing SRNOM and various concentrations of sodium sulphate/sodium nitrate (Resin dose: 1000 mg/L of either polystyrene or polyacrylic).

The percent removal of nitrate/sulphate from model water containing NOM with 200, 500, and 1500 mg/L of the ion exchange resin is shown in Figure E.10, E.11, and E.12 respectively. Considering the equivalent removal and that sulphate have more ionic charges than nitrate, the polystyrene resin exhibited a better performance than the polyacrylic resin in removing both nitrate and sulphate. Moreover, ≈50% increase in nitrate removal and ≈70%

increase in sulphate removal was achieved with increasing the resin dose from 200 mg/L to 1500 mg/L. This indicates the importance of electrostatic interactions and the number of available ion exchange sites in removing high charge density inorganic anions.

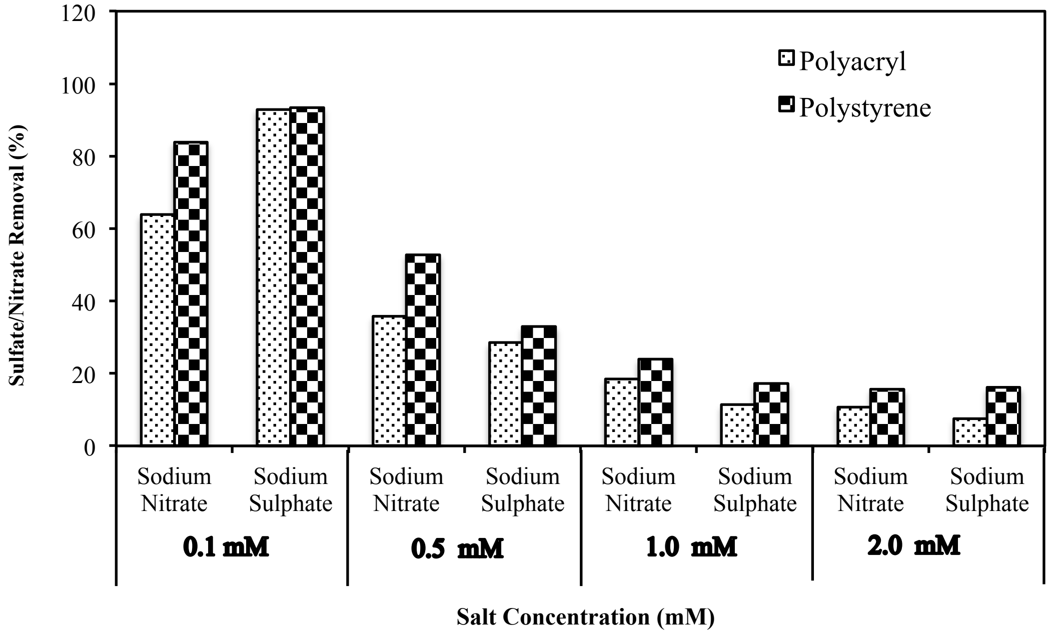


Figure E.10, The removal of sulphate/nitrate from model waters containing SRNOM and various concentrations of sodium sulphate/sodium nitrate (Resin dose: 200 mg/L of either polystyrene or polyacrylic).

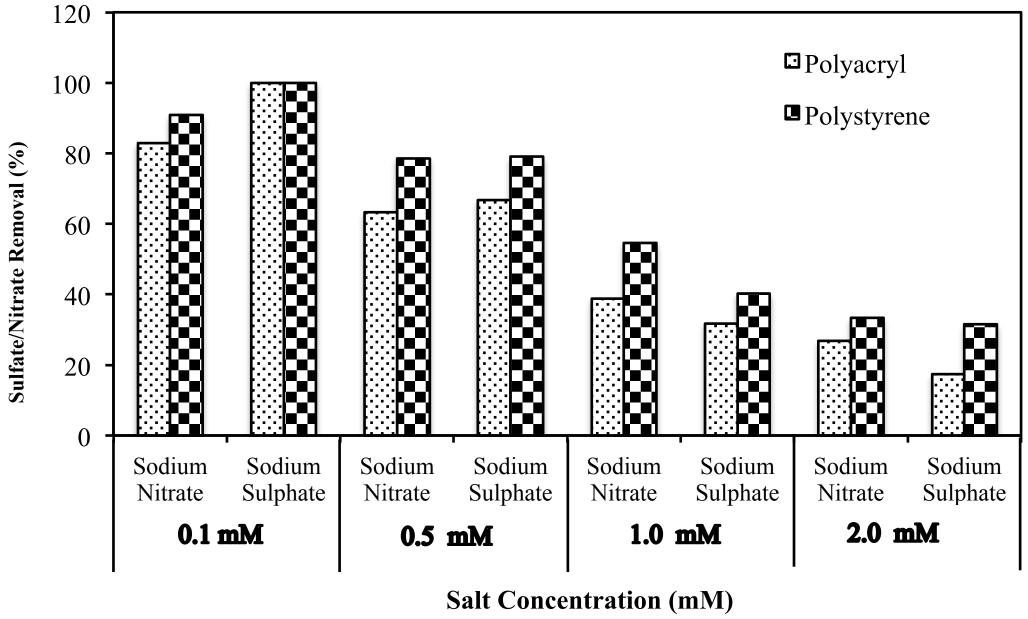


Figure E.11, The removal of sulphate/nitrate from model waters containing SRNOM and various concentrations of sodium sulphate/sodium nitrate (Resin dose: 500 mg/L of either polystyrene or polyacrylic).

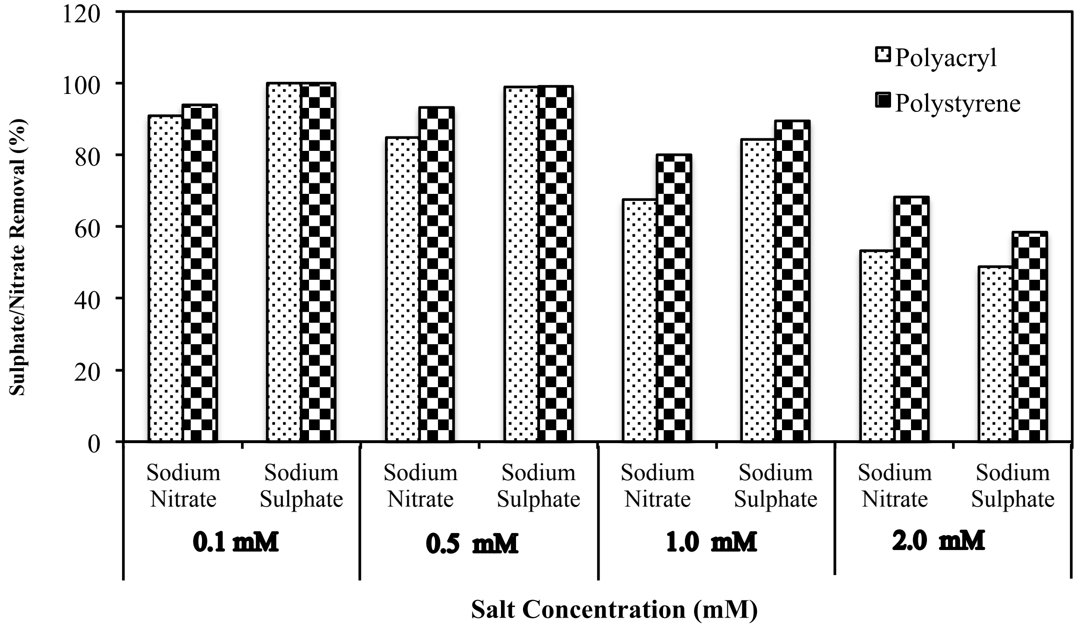


Figure E.12, The removal of sulphate/nitrate from model waters containing SRNOM and various concentrations of sodium sulphate/sodium nitrate (Resin dose: 1500 mg/L of either polystyrene or polyacrylic).

Appendix F

Experiments in this work were repeated three times and the average values were presented in the graphs. This Appendix includes the average values for presented data in some of the graphs along with the corresponding standard errors.

Table F.1, The average values and standard errors for data points presented in Figure 4.3(a).

	Nitrate Concentration (mg/L)					
	NAA_Nitrate		BA_Nitrate		GA_Nitrate	
Resin Dosage	Average Nitrate Concentration (mg/L)	Standard Error	Average Nitrate Concentration (mg/L)	Standard Error	Average Nitrate Concentration (mg/L)	Standard Error
200	1.7706	0.0480	1.9125	0.0064	1.7884	0.0491
500	0.9612	0.0636	1.1013	0.0091	1.0011	0.0327
1000	0.6415	0.0406	0.7925	0.0369	0.7086	0.0700
1500	0.5480	0.0440	0.5216	0.0016	0.5320	0.0531

	Chloride Concentration (mg/L)					
	NAA_Nitrate		BA_Nitrate		GA_Nitrate	
Resin Dosage	Chloride Release (mg/L)	Standard Error	Chloride Release (mg/L)	Standard Error	Chloride Release (mg/L)	Standard Error
200	3.29	0.0240	3.49	0.0029	3.14	0.0395
500	3.95	0.0277	4.32	0.0076	3.99	0.0287
1000	4.20	0.0120	4.79	0.0104	4.56	0.0525
1500	4.38	0.0238	4.97	0.0324	4.93	0.0605

Table F.2, The average values and standard errors for data points presented in Figure 4.3(b).

	Sulphate Concentration (mg/L)					
	NAA_Sulphate		BA_Sulphate		GA_Sulphate	
Resin Dosage	Average Sulphate Concentration (mg/L)	Standard Error	Average Sulphate Concentration (mg/L)	Standard Error	Average Sulphate Concentration (mg/L)	Standard Error
200	0.5093	0.0117	0.4486	0.0229	0.5238	0.0086
500	0.1803	0.1803	0.0000	0.0000	0.0000	0.0000
1000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1500	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

	Chloride Concentration (mg/L)					
	NAA_Sulphate		BA_Sulphate		GA_Sulphate	
Resin Dosage	Chloride Release (mg/L)	Standard Error	Chloride Release (mg/L)	Standard Error	Chloride Release (mg/L)	Standard Error
200	6.35	0.0055	6.22	0.0371	6.11	0.0052
500	7.29	0.0756	7.27	0.0004	6.71	0.1163
1000	7.49	0.0018	7.74	0.0261	7.29	0.0198
1500	7.58	0.0404	7.94	0.0126	7.50	0.1228

Table F.3, The average values and standard errors for data points presented in Figure 4.4.

	Adsorbed Organic (meq/L)					
	NAA		BA		GA	
Resin Dosage	Adsorbed NAA (meq/L)	Standard Error	Adsorbed BA (meq/L)	Standard Error	Adsorbed GA (meq/L)	Standard Error
200	0.034	0.000243	0.048	0.000047	0.034	0.000833
500	0.037	0.000204	0.058	0.000238	0.049	0.000000
1000	0.038	0.000303	0.062	0.000113	0.057	0.000000
1500	0.039	0.000349	0.063	0.000054	0.060	0.000347

	The Amount of Released Chloride (meq/L)					
	NAA		BA		GA	
Resin Dosage	Chloride Release (meq/L)	Standard Error	Chloride Release (meq/L)	Standard Error	Chloride Release (meq/L)	Standard Error
200	0.038	0.000028	0.056	0.000348	0.040	0.000298
500	0.041	0.000179	0.064	0.000570	0.048	0.000013
1000	0.044	0.001031	0.067	0.000048	0.055	0.000252
1500	0.045	0.000588	0.070	0.000175	0.058	0.001354

Table F.4, The average values and standard errors for data points presented in Figure 4.5(a).

	Adsorbed Organic and Nitrate (meq/L)					
	NAA_Nitrate		BA_Nitrate		GA_Nitrate	
Resin Dosage	Adsorbed NAA and Nitrate (meq/L)	Standard Error	Adsorbed BA and Nitrate (meq/L)	Standard Error	Adsorbed GA and Nitrate (meq/L)	Standard Error
200	0.0907	0.001149	0.0950	0.000460	0.0838	0.002388
500	0.1098	0.001338	0.1221	0.000505	0.1109	0.001397
1000	0.1175	0.000704	0.1344	0.000654	0.1289	0.001654
1500	0.1196	0.000976	0.1414	0.000134	0.1401	0.001816

	The Amount of Released Chloride (meq/L)					
	NAA_Nitrate		BA_Nitrate		GA_Nitrate	
Resin Dosage	Chloride Release (meq/L)	Standard Error	Chloride Release (meq/L)	Standard Error	Chloride Release (meq/L)	Standard Error
200	0.0929	0.000677	0.0984	0.000080	0.0887	0.001113
500	0.1113	0.000781	0.1218	0.000216	0.1127	0.000808
1000	0.1185	0.000337	0.1350	0.000295	0.1287	0.001479
1500	0.1235	0.000671	0.1402	0.000915	0.1391	0.001706

Table F.5, The average values and standard errors for data points presented in Figure 4.5(b).

	Adsorbed Organic and Sulphate (meq/L)					
	NAA_Sulphate		BA_Sulphate		GA_Sulphate	
Resin Dosage	Adsorbed NAA and Sulphate (meq/L)	Standard Error	Adsorbed BA and Sulphate (meq/L)	Standard Error	Adsorbed GA and Sulphate (meq/L)	Standard Error
200	0.1887	0.001376	0.1848	0.001191	0.1847	0.001275
500	0.2127	0.003838	0.2195	0.000119	0.2051	0.002140
1000	0.2230	0.000672	0.2323	0.001071	0.2168	0.001460
1500	0.2250	0.000584	0.2365	0.004228	0.2246	0.001355

	The Amount of Released Chloride (meq/L)					
	NAA_Sulphate		BA_Sulphate		GA_Sulphate	
Resin Dosage	Chloride Release (meq/L)	Standard Error	Chloride Release (meq/L)	Standard Error	Chloride Release (meq/L)	Standard Error
200	0.1791	0.000157	0.1755	0.001046	0.1724	0.000147
500	0.2057	0.002132	0.2049	0.000010	0.1892	0.003279
1000	0.2113	0.000052	0.2184	0.000736	0.2056	0.000560
1500	0.2138	0.001138	0.2241	0.000355	0.2114	0.003462

Table F.6, The average values and standard errors for data points presented in Figure 5.4(a).

	DOC Uptake (%) in Presence of Nitrate					
	NOM		FA		HA	
Sodium Nitrate Concentration (mM)	DOC Uptake (%)	Standard Error	DOC Uptake (%)	Standard Error	DOC Uptake (%)	Standard Error
0	90.20	1.53	90.10	0.15	58.47	1.22
0.1	90.90	0.49	93.40	0.18	59.80	0.44
1	89.60	0.54	90.70	0.43	63.00	1.34
10	83.90	0.45	86.60	0.63	62.50	1.96
20	79.70	0.55	83.10	0.33	63.40	1.42
30	74.30	0.43	82.20	0.34	63.70	2.48
40	71.00	0.23	80.30	0.33	64.00	2.86

Table F.7, The average values and standard errors for data points presented in Figure 5.4(b).

	DOC Uptake (%) in Presence of Sulphate					
	NOM		FA		HA	
Sodium Sulphate Concentration (mM)	DOC Uptake (%)	Standard Error	DOC Uptake (%)	Standard Error	DOC Uptake (%)	Standard Error
0	90.20	1.53	90.10	0.15	58.47	1.22
0.1	90.00	0.54	93.30	0.32	59.40	0.70
1	81.20	0.53	80.20	1.31	43.80	0.39
10	69.90	0.90	72.20	0.47	44.60	2.11
20	65.20	0.92	70.78	0.35	41.30	1.10
30	60.50	0.65	68.60	0.40	43.50	1.09
40	57.80	0.80	67.40	0.93	43.00	2.12

Table F.8, The average values and standard errors for data points presented in Figure 5.4(c).

	UV Uptake (%) in Presence of Nitrate					
	NOM		FA		HA	
Sodium Nitrate Concentration (mM)	UV Uptake (%)	Standard Error	UV Uptake (%)	Standard Error	UV Uptake (%)	Standard Error
0	93.49	1.28	95.22	0.63	55.87	0.58
0.1	96.35	0.67	97.70	0.41	64.14	1.38
1	95.70	0.66	97.07	0.41	65.62	1.54
10	91.05	0.77	94.91	0.45	65.05	2.78
20	86.94	0.48	95.86	0.56	64.23	0.84
30	82.35	0.70	93.53	0.30	66.28	2.44
40	75.02	0.75	90.61	0.33	65.24	2.66

Table F.9, The average values and standard errors for data points presented in Figure 5.4(d).

	UV Uptake (%) in Presence of Sulphate					
	NOM		FA		HA	
Sodium Sulphate Concentration (mM)	UV Uptake (%)	Standard Error	UV Uptake (%)	Standard Error	UV Uptake (%)	Standard Error
0	93.49	1.28	95.22	0.63	57.69	0.58
0.1	99.46	0.35	98.29	0.40	61.28	0.93
1	95.13	0.46	92.82	0.51	48.96	1.13
10	89.03	0.69	83.76	0.80	47.47	2.87
20	84.78	0.80	83.49	0.41	44.47	0.93
30	82.39	0.21	81.76	0.33	45.65	1.51
40	81.22	0.37	81.76	0.96	48.90	3.14

Table F.10, The average values and standard errors for data points presented in Figure 7.3(a).

	DOC Uptake (%) in Presence of Nitrate with Polystyrene Resin					
	NOM		FA		HA	
Sodium Nitrate Concentration (mM)	DOC Uptake (%)	Standard Error	DOC Uptake (%)	Standard Error	DOC Uptake (%)	Standard Error
0	59.13	0.65	49.75	0.32	14.10	0.63
0.1	57.91	0.29	49.36	0.53	14.36	0.09
0.5	57.79	0.47	50.90	0.86	15.27	0.73
1	59.88	0.39	52.67	0.39	21.19	1.55
2	66.55	0.28	59.72	0.42	24.97	1.52

Table F.11, The average values and standard errors for data points presented in Figure 7.3(b).

	DOC Uptake (%) in Presence of Sulphate with Polystyrene Resin					
	NOM		FA		HA	
Sodium Sulphate Concentration (mM)	DOC Uptake (%)	Standard Error	DOC Uptake (%)	Standard Error	DOC Uptake (%)	Standard Error
0	59.13	0.65	49.75	0.32	14.10	0.63
0.1	56.18	0.32	48.48	0.44	17.65	0.86
0.5	58.22	0.52	51.28	0.83	22.29	1.84
1	62.09	0.51	54.19	2.01	24.46	2.88
2	67.67	0.29	62.57	1.02	36.43	2.35

Table F.12, The average values and standard errors for data points presented in Figure 7.4(a).

	UV Uptake (%) in Presence of Nitrate with Polystyrene Resin					
	NOM		FA		HA	
Sodium Nitrate Concentration (mM)	UV Uptake (%)	Standard Error	UV Uptake (%)	Standard Error	UV Uptake (%)	Standard Error
0	48.27	1.28	40.42	0.63	18.17	0.58
0.1	47.53	0.67	40.63	0.41	18.65	1.38
0.5	49.39	0.66	43.60	0.41	20.33	1.54
1	54.02	0.77	49.19	0.45	22.18	2.78
2	62.83	0.48	54.99	0.56	29.00	0.84

Table F.13, The average values and standard errors for data points presented in Figure 7.4(b).

	UV Uptake (%) in Presence of Sulphate with Polystyrene Resin					
	NOM		FA		HA	
Sodium Sulphate Concentration (mM)	UV Uptake (%)	Standard Error	UV Uptake (%)	Standard Error	UV Uptake (%)	Standard Error
0	48.27	1.28	40.42	0.63	18.17	0.58
0.1	46.76	0.35	40.69	0.40	17.34	0.93
0.5	52.58	0.46	46.39	0.51	21.22	1.13
1	60.86	0.69	54.74	0.80	27.42	2.87
2	69.67	0.80	64.78	0.41	38.70	0.93