Fractionation of oil sands process water and fractions influence and degradation by advanced oxidation processes

By

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A thesis submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

Environmental Engineering

Department of Civil and Environmental Engineering

University of Alberta

Abstract

One of the most serious issues associated with the oil sands production is the generation of large volumes of oil sands process water (OSPW). OSPW is a highly complex mixture of sands, silts, salts, heavy metals, and refractory organic compounds. Currently, OSPW is retained on site in large tailings ponds and there is no active return to the regional watershed. Therefore, there is an urgent need to develop water treatment processes for the safe release of treated OSPW into the environment. In this thesis, novel separation methods were developed to isolate and fractionate OSPW inorganics and organics that allowed more accurate and comprehensive study on the characterization, influence and degradation of each OSPW fraction by ozonation or photo-oxidation.

OSPW organic fraction (OSPW-OF) was extracted by solid phase extraction (SPE) and OSPW containing only inorganic fraction (OSPW-IF) was obtained after the organic compounds were adsorbed by granular activated carbon (GAC). SPE using hydrophilic lipophilic balanced (HLB) cartridge combined with methanol elution achieved the highest dissolved organic carbon (DOC) (95.4%) and NA (90.0%) recovery as compared with other tested cartridges and liquid-liquid extraction (LLE) with dichloromethane. A recovery higher than 80.0% for each NA species was achieved using HLB cartridge with methanol elution. After passing through GAC cartridge, 96.1% of DOC in OSPW was adsorbed. The difference of pH, alkalinity, conductivity, and the concentrations of detected ions in OSPW and GAC cartridge effluent were negligible. Thus, GAC adsorption was found to be a promising method to obtain OSPW-IF representable of real OSPW.

A silver-ion SPE approach was utilized to separate OSPW NAs into 20 fractions with aliphatic O_2-NAs, aromatic O_2-NAs, O_3-NAs, and O_4-NAs dominated in different fractions. Ozonation of these fractions was conducted to study the ozonation reactivity of isolated aromatic and oxidized

NA species. The removals of aliphatic O_2−NAs fraction, aromatic O_2−NAs fraction, O_3−NAs fraction, and O_4−NAs fraction with an applied ozone dosage of 16.8 mg/L were 97.2%, 94.7%, 59.4%, and 44.7%, respectively. Aromatic and oxidized NAs (O_3−NAs and O_4−NAs) with larger carbon number were favorably removed during ozonation treatment. A comparison of the ozone utilization efficiency for different NA species indicated that the degradation of oxidized NAs consumed more ozone in molar ratio than the degradation of aliphatic and aromatic O_2-NAs, which resulted in the lower reactivity of oxidized NAs than that of O_2-NAs.

OSPW-IF adversely affected the ozonation of a model compound cyclohexanecarboxylic acid (CHA) by competitively consuming ozone. Main inorganic ions present in OSPW were separately added into CHA in buffer solution to investigate their individual influence on the ozonation of CHA. NH_4^+, Mn^{2+}, HCO_3^- and Cl^- showed slight reduction on CHA degradation. In addition, higher NA degradation was observed after the ozonation of extracted organics dissolved in buffer than the ozonation of OSPW, which demonstrated that the inorganics in OSPW inhibited the degradation of NAs during OSPW ozonation process. Moreover, ozonation of non-filtered and filtered OSPW showed that there was a negligible influence of particles on the ozonation of NAs. The results from this research suggested that ozonation would be better utilized as an intermediate or post treatment process in a treatment train for OSPW remediation and intermittent ozonation might achieve higher ozone utilization than the continuous ozonation process.

Direct photolysis of OSPW was conducted to investigate the photodegradation of NAs in OSPW without adding external catalysts. It was observed that 60 min of direct UV exposure of OSPW with the irradiance intensity of 2.92 mW/cm^2 achieved the removal of O_2-, O_3-, and O_4-NAs to be 46.4%, 11.2%, and 9.9%, respectively, which were higher than the degradation of extracted organics dissolved in buffer. This indicated that the presence of inorganics in OSPW enhanced the

photodegradation of NAs. Meanwhile, the effect of OSPW-IF on the photodegradation of model NA, 1-adamantanecarboxylic acid (ACA,) was studied. A 34% of ACA was removed in the presence of OSPW-IF, while no ACA degradation was observed in buffer solution after 60 min of UV exposure. The results indicated that OSPW-IF induced the photodegradation of ACA. Individual ions present in OSPW were added into ACA in buffer solution to clarify whether the inorganic species in OSPW could act as photosensitizers. Nitrate had demonstrated to be an active ion present in OSPW that induced the photodegradation of ACA. In the presence of nitrate, both hydroxyl radicals (•OH) and reactive nitrogen species (•NO, •NO_2) were generated, where •OH was the dominant reactive species that contributed to the degradation of ACA. Ten by-products including single and multiple hydroxyl, nitro, nitroso and carbonyl substituted by-products were proposed to be produced from the nitrate induced photodegradation process through three different pathways.

Preface

All the research conducted in this thesis was designed and conducted by myself, under the supervision of Dr. Mohamed Gamal El-Din. I designed and conducted the experiments, collected and analyzed the data, and prepared the manuscripts. Some colleagues also contributed to manuscript edits and sample analysis as follows:

Chapter 2:

- Dr. Zuo Tong How and Dr. Pamela Chelme-Ayala contributed to the manuscript revision.

Chapter 3:

- Dr. Zuo Tong How contributed to the data analysis, results discussion and manuscript revision.
- Dr. Rongfu Huang performed ultra-performance liquid chromatograph time-of-flight mass spectrometry (UPLC-TOF-MS) analysis and manuscript revision

Chapter 4:

- A version of this chapter was published in: Huang, R.[1], Qin, R.[1], Chelme-Ayala, P., Wang, C., & Gamal El-Din, M. (2019). Assessment of ozonation reactivity of aromatic and oxidized naphthenic acids species separated using a silver-ion solid phase extraction method. Chemosphere, 219, 313-320.
- Dr. Rongfu Huang contributed to the experimental planning, manuscript edits, results discussion, and UPLC-TOF-MS analysis
- Dr. Pamela Chelme-Ayala contributed to the results discussion and manuscript revision.

Chapter 5:

- Dr. Zuo Tong How contributed to the manuscript edits and revision.

- Dr. Selamawit Ashagre Messele contributed to the characteristic analysis of granular activated carbon and the running of samples on liquid chromatography mass spectrometry (LC-MS).
- Dr. Pamela Chelme-Ayala and Dr. Zhijun Luo contributed to the manuscript revision.

Chapter 6:

- Dr. Zuo Tong How contributed to the identification of by-products and possible pathways, results discussion and manuscript revision.
- Dr. Mingyu Li contributed to the analyzing of samples on liquid chromatography mass spectrometry (LC-MS).
- Dr Lingling Yang contributed to the analyzing of samples on ultra-performance liquid chromatograph time-of-flight mass spectrometry (UPLC-TOF-MS)

Dedication

This work is dedicated:

- To my beloved parents who give me love, strength, encouragement, and support me to overcome difficulties and stress.
- To my dear friends who listen and support me openly. Your companionship and support mean a lot to me.

Acknowledgement

Firstly, I would like to express my sincere and great appreciation to my supervisor, Dr. Mohamed Gamal El-Din for his academic guidance, supervision and financial support. I appreciate Dr. Gamal El-Din for offering me an opportunity to be a part of his group. His motivating guidance helped me to make progress.

My sincere gratitude goes to the postdoctoral fellow Dr. Zuo Tong How, who gave me supervision and valuable suggestions on my research work. He helped me to solve the academic problems and improve my expression in a clear manner. He revised my papers and thesis, and gave good suggestions and feedback, from which I benefited a lot.

I also would like to thank Dr. Pamela Chelme-Ayala in Dr. Gamal El-Din's research group for all her gentle help. I appreciate all her suggestions and efforts on manuscripts revision.

I appreciate all other postdoctoral fellows in Dr. Gamal El-Din's research group who helped to revise papers and analyze samples. They are Dr. Mingyu Li, Dr. Selamawit Ashagre Messele, and Dr. Rongfu Huang. I also appreciate all the help and support I received from my colleagues.

I would like to acknowledge the sponsors of my research including Natural Sciences and Engineering Research Council of Canada (NSERC) Senior Industrial Research Chair (IRC) in Oil Sands Tailings Water Treatment and Alberta's Future Energy Systems. I am grateful for a Ph.D. scholarship provided by China Scholarship Council.

Finally, I would like to thank my family and friends for their endless love.

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Chapter 1 General Introduction and Research Objectives

1.1 Background and Motivation

1.1.1 Oil Sands Process Water

In Alberta, Canada, the oil sands reserves hold estimated 165 billion barrels of bitumen within three major oil deposits covering an area of 142,200 km^2 (GOA, 2019). In the oil sands industry, bitumen is extracted from the oil sands by the Clark caustic hot water extraction process (Schramm, 2000). About 0.21-2.5 barrels of water are required for per barrel of bitumen extracted from oil sands, therefore, producing large amount of oil sands process water (OSPW). After production, OSPW is sent to tailings ponds where it is separated from solids and around 80-95% is recycled back for the bitumen extraction (NRC, 2018).

OSPW is a brackish mixture of suspended particles, inorganics and organics (Masliyah et al., 2004). The main inorganic constituents are dissolved salts with the major ions been Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-} and HCO_3^- as well as other trace metals (McQueen et al., 2017). The organic constituents in OSPW include naphthenic acids (NAs), aliphatic and aromatic hydrocarbons, heteroatomic compounds with oxygen, nitrogen or sulfur atoms, among which NAs were reported to be toxic towards microorganisms (Jones et al., 2011), aquatic organism (Bartlett et al., 2017; Hughes et al., 2017b) and mammals (Kannel and Gan, 2012; Li et al., 2017).

Naphthenic acids (NAs) is a broad term used to describe a family of saturated aliphatic and alicyclic carboxylic acids with the general chemical formula $C_nH_{2n+Z}O_x$, where “n” is the carbon number, “z” is zero or a negative even integer, representing the hydrogen deficiency resulting from rings or unsaturated bonding formation, and x represents the number of oxygen atoms ($x=2$ for classical NAs or $x \geq 3$ for oxy-NAs) (Bertheussen et al., 2017). NAs are naturally present in most oil deposits including the oil sands. When the bitumen is extracted from oil sands using alkaline hot water, NAs are released into the slightly alkaline OSPW, whose pH is greater than the pKa value of NAs (pka = 5-6) resulting in the deprotonation of portion of the NAs (Quinlan and Tam, 2015) and thus are present in OSPW in their ionic form.

1.1.2 Fractionation of Oil Sands Process Water

Studies have demonstrated that OSPW has chronic and acute toxicity towards a variety of organisms including invertebrates (Anderson et al., 2012; Bartlett et al., 2017), aquatic organisms (He et al., 2012), amphibians (Li et al., 2017), mammals (Fu et al., 2017), and microorganisms (Morandi et al., 2017). OSPW, as a whole mixture, contains unidentified components as well as interactions (potential synergistic or antagonistic reactions) among different components. It is not known whether the toxic effects of whole OSPW are due solely to some specific toxic compounds or a combination and interactions of different constituents. Research on specific species fractionated from OSPW could help to identify target pollutants (Frank et al., 2008). Thus, it is crucial to separate OSPW into different fractions to further study their toxicity effects.

In addition, sample preparation to extract organics from water samples is required for some analytical methods, such as ^{1}H nuclear magnetic resonance, Fourier transform ion cyclotron resonance mass spectrometry and Fourier transform infrared spectroscopy, which makes it necessary to develop efficient methods to extract organics from OSPW. Thus, simplification of OSPW components after separation will be of benefit to the identification of organic compounds. Meanwhile, fractionation of OSPW could be conducive to the studies of degradation reactivity and the influence of different fractions during different treatment processes.

Although several studies have been done to extract and fractionate OSPW organic components (Huang et al., 2015; Mohamed et al., 2015; Hughes et al., 2017a; Huang et al., 2019), efficient methods to separate OSPW organic and inorganic fraction have not been developed. Hereby, in this work, different separation processes were conducted to develop efficient methods to separate OSPW inorganic and organic fractions, which also provided materials for the follow-up treatment studies.

1.1.3 Treatment of Oil Sands Process Waters

Extensive research has been conducted to develop treatment methods such as physical, chemical, biological and combined processes for the reclamation of OSPW or to remove specific constituent(s) of OSPW. The following section would present the treatment methods investigated for the reclamation of OSPW.

1.1.3.1 Adsorption Processes

Adsorption process involves the equilibrium distribution of adsorbates between sorbents and the fluid phase (De Gisi et al., 2016). The interaction forces between adsorbates and sorbents include chemical interaction such as forming of chemical bonds and electrostatic forces, and physical interaction such as, van der Waals forces, hydrophobicity, dipole-dipole interaction and π-π interaction (Ali et al., 2012). The adsorbates can be retrieved, and the sorbents are easily regenerated for the physical adsorption process. Factors that influence the physical adsorption are specific surface area, adsorbent’s pore distribution, and the hydrophobic character. For example, adsorbates with high hydrophobicity are likely to be adsorbed by hydrophobic sorbents and vice versa. Chemical bonds are formed between the adsorbates and sorbents during chemical adsorption. This generation of chemicals bonds results in strong bonding between the sorbent and adsorbates but also results in chemical adsorption being selective. Because of the higher bonding strength in chemical adsorption, it is difficult to remove adsorbates and regenerate the sorbents. Chemical adsorption is influenced by the chemical properties of adsorbates and the sorbent’s surface (Gupta et al., 2009). In the actual adsorption process, the physical and chemical adsorption processes may happen at the same time.

Activated carbon (AC), a family of carbonaceous sorbents, is a good adsorbent due to its hydrophobic nature and abundant surface pores with a large surface area (Lehr et al., 2005). Surface functional groups, microporous structure and extended surface area contribute to the high adsorption capacity for organic contaminants (Hamdaoui and Naffrechoux, 2007). Research has been done to investigate the granular activated carbon (GAC) adsorption potential for the treatment of OSPW (Islam et al., 2015; Islam et al., 2018). The authors pointed out that the maximum adsorption capacities obtained from Langmuir adsorption isotherm in terms of acid-extractable fraction (AEF) and NAs were 98.5 mg AEF/g GAC and 60 mg NA/g GAC, respectively. NA species removal increased with increasing carbon number and decreasing Z number. Due to the high adsorption capacity, GAC may be a potential sorbent that could adsorb the organic compounds from OSPW and isolate OSPW inorganic fraction. In this work, GAC adsorption was conducted to adsorb organic compounds to obtain OSPW containing only inorganic fraction.

1.1.3.2 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) aim at the removal of stable and biological recalcitrant organic matter by utilizing powerful oxidizing intermediates to attack organic molecules (Andreozzi et al., 1999; Kannel and Gan, 2012). Varieties of AOPs have been studied for OSPW treatment, such as Fenton related oxidation (Zhang et al., 2016), photo-oxidation (Shu et al., 2014), and ozonation (Gamal El-Din et al., 2011; Garcia-Garcia et al., 2011; Pereira et al., 2013; Wang et al., 2016b). Sulfate radical and Ferrate (VI) based AOPs have also been studied for OSPW treatment (Wang et al., 2016a; Fang et al., 2018).

1.1.3.2.1 Ozonation

Research has shown that ozonation was potential for OSPW treatment, which could degrade NAs, attenuating toxicity and accelerating the biodegradation ability of OSPW (Scott et al., 2008; Martin et al., 2010; Garcia-Garcia et al., 2011; Anderson et al., 2012; He et al., 2012; Hwang et al., 2013; Pereira et al., 2013; Wang et al., 2013; Wang et al., 2016b). It was reported that ozonation of OSPW follows two pathways: direct ozonation and/or indirect free radical oxidation (Wang et al., 2016b; Meshref et al., 2017). At alkaline conditions, ozone decays mostly to hydroxyl radical (•OH) and other radicals (Eq. 1-7) (von Gunten, 2003) which could cause radical reactions with organic substances.

$$O_3 + OH^- \rightarrow HO_2^- + O_2, \qquad k = 70\ M^{-1}s^{-1} \qquad (1)$$

$$O_3 + HO_2^- \rightarrow \bullet OH + \bullet O_2^- + O_2, \qquad k = 2.8 \times 10^6\ M^{-1}s^{-1} \qquad (2)$$

$$O_3 + \bullet O_2^- \rightarrow \bullet O_3^- + O_2, \qquad k = 1.6 \times 10^9\ M^{-1}s^{-1} \qquad (3)$$

$$pH \leq 8 \quad \bullet O_3^- + H^+ \rightleftharpoons \bullet HO_3, \qquad k_+ = 5 \times 10^{10}\ M^{-1}s^{-1} \quad k_- = 3.3 \times 10^2\ s^{-1} \qquad (4a)$$

$$\bullet HO_3 \rightarrow \bullet OH + O_2 \qquad k = 1.4 \times 10^5\ s^{-1} \qquad (4b)$$

$$pH \geq 8 \quad \bullet O_3^- \rightleftharpoons \bullet O^- + O_2, \qquad k_+ = 2.1 \times 10^3\ s^{-1}s^{-1} \quad k_- = 3.3 \times 10^9\ s^{-1} \qquad (5)$$

$$\bullet O^- + H_2O \rightarrow \bullet OH + OH^- \qquad k = 10^8\ s^{-1} \qquad (6)$$

$$\bullet OH + O_3 \rightarrow \bullet HO_2 + O_2 \qquad k = 1 \times 10^8\ M^{-1}s^{-1} - 2 \times 10^9\ M^{-1}s^{-1} \qquad (7)$$

The efficiency of ozonation on OSPW treatment may be affected by the water matrix, which could work as •OH initiators (e.g. OH^-, Fe^{2+}) or scavengers (e.g. HCO_3^- and CO_3^-) (Staehelin and Hoigne, 1985; Lado Ribeiro et al., 2019). For example, transition metals, such as Fe(II), Mn(II), Ni(II), Co(II), Cr(III), Ag(I), Cu(II), Zn(II), and Cd(II) were reported to exhibit catalytic effect during the ozonation process (Ma and Graham, 2000; Kasprzyk-Hordern et al., 2003; Selvam et al., 2007). As OSPW is a complex mixture containing varieties of inorganic species, it is significant to investigate the influence of OSPW inorganic fraction on the oxidation treatment of OSPW to provide knowledge in order to improve the ozonation efficiency. It could also provide guidance for the design of the treatment train for the practical application of ozonation and other treatment processes for the remediation of OSPW at full scale.

1.1.3.2.2 Photo-oxidation

Relatively high operating costs and energy use are the principal drawbacks of traditional AOPs for full-scale applications (Oller et al., 2011). Thus, the utilization of renewable solar driven AOPs for OSPW remediation has drawn considerable interest (Chan et al., 2012; Shu et al., 2014; Hendrikse et al., 2018).

Photodegradation of organic contaminants can be achieved by either direct photolysis or indirect photolysis with radical reactions. Indirect photolysis happens with the generation of radicals by photosensitizing agents (e.g. H_2O_2, Fe^{2+} and humic acids) or photocatalysts such as titanium dioxide (TiO_2) (Chong et al., 2010; Liu et al., 2017; Li et al., 2018). UV-based AOPs with the generation of active radicals, such as •OH, sulfate radicals ($SO_4{\bullet}^-$), and chlorine radicals (•Cl), initiated by H_2O_2 (Afzal et al., 2012), $S_2O_8^{2-}$ (Fang et al., 2018) and HOCl (Shu et al., 2014), have been studied for OSPW treatment. Thus, in the presence of initiators in the water matrix, active radicals could be produced for the oxidization of organic contaminants.

There are a variety of inorganic ions existing in OSPW, some of which may work as radical initiators or scavengers during the photodegradation process. For example, some water matrix such as natural organic matters, humic acids, nitrite and nitrate could act as photosensitizers to adsorb UV/visible light to produce reactive radicals to achieve the indirect photolysis of organic contaminants (Liu et al., 2017; Li et al., 2018). Hereby, photodegradation of organic contaminant in OSPW may be affected by the water matrix. To date, no research has been conducted to investigate the influence of inorganics in OSPW on the photodegradation of organic contaminants. And whether there are any inorganic photosensitizers naturally present in OSPW is unclear. Understanding the influence of inorganic fraction on the photodegradation process as well as the existing of photosensitizers in OSPW could provide information about the photochemical processes upon OSPW and the possibility of photodegradation of organic contaminants by the passive solar remediation without the addition of external catalysts.

1.2 Research Scope and Objectives

The overall objective of this research was to separate OSPW organic and inorganic fractions to study the reactivity and influence of the fractions on the OSPW ozonation and photodegradation process to provide fundamental information for their future application on OSPW remediation.

The specific objectives were: 1) developing methods for the separation of OSPW organic and inorganic fractions; 2) fractionating OSPW organic components and studying the ozonation reactivity of different NA species; 3) studying the influence of water matrix in OSPW on the ozonation of NAs; and 4) investigating the influence of OSPW inorganic fraction on the photodegradation of NAs and the potential inorganic photosensitizers in OSPW which could induce the photodegradation of NAs.

1.3 Thesis Organization

This thesis consists of seven chapters. The first chapter provides a general introduction including the background information and motivations, as well as the research objectives of the thesis. More specifically, Chapter 1 provides the brief background regarding the OSPW, OSPW toxicity, isolation and extraction of OSPW fractions as well as the physical and chemical oxidation treatment processes for OSPW. Adsorption is the focus for the discussion of physical treatment while ozonation and photo-oxidation were the focus of chemical oxidation process in Chapter 1. The research objectives and the thesis organization are also listed in Chapter 1.

Chapter 2 is the literature review for the physical and chemical process on the treatment of oil and gas wastewater. Chapter 2 highlights the literature pertaining to the adsorption, ozonation and photo-oxidation processes.

Chapter 3 investigates the methods development for the separation of OSPW inorganics and organics. The organic fraction in OSPW was extracted by solid phase extraction using cartridges with different properties as well as traditional liquid-liquid extraction to compare their extraction efficiency to obtain an optimum method for the extraction of organics. OSPW inorganic fraction was obtained after the organic compounds adsorbed by granular activated carbon.

Chapter 4 shows the ozonation reactivity of different OSPW organic fractions. First, OSPW NAs were fractionated into aliphatic O_2-NAs, aromatic O_2-NAs, O_3-NAs and O_4-NAs by Ag-Ion solid phase extraction process. The isolated NA species were ozonated to study their ozonation reactivity.

Chapter 5 presents the influence of water matrix in OSPW on the ozonation of both model NA and extracted NAs. The effects of whole inorganic fraction, the individual inorganic ions, and particles in OSPW were studied to better understand their influence on OSPW ozonation process.

Chapter 6 presents the effects of inorganic fraction in OSPW on the photodegradation of NAs. The effects of individual ions in OSPW on the photodegradation of model NA were investigated to clarify if any ions could act as photosensitizers during the NA photo-oxidation process. The possible mechanism and pathway of the photodegradation of a model NA induced by the inorganic photosensitizer were studied.

Chapter 7 presents the conclusions drawn from the earlier chapters and the objective of the thesis answered. Moreover, recommendations for future works arise from this thesis are also included in this chapter.

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Chapter 2 Literature Review about The Physical and Chemical Processes for Oil and Gas Wastewater Treatment

2.1. Introduction

Oil and gas industry is an important part of modern industry. It provides large percentage of the world's energy. Nevertheless, the environmental issues caused by the oil production have gained wide attention. Like most industrial production, oil and gas production generates large amounts of wastewater, which is called oil and gas industry wastewater (OGW) in this review.

The OGW volume is affected by the production type (oil or gas), activity level or the field geographical situation. For example, oil fields of the Permian Basin in Texas, United States, produced 30 to 50 million barrels of OGW per day (Wethe and Collins, 2017). In 2017, the Alberta oil sand industry produced 0.26-3.13 barrels of oil sands process affected water (OSPW) (NRC, 2018). In 2012, the highest average discharged produced water from a single field in Norwegian continental shelf was 7.7 x 10^4 m^3/day (Bakke et al., 2013). The principal sources of OGW are drilling fluids, cuttings, cooling water, process, wash and drainage water, spills and leakage, sewerage, sanitary, and domestic wastewater (UNEP and E&PForum, 1997). OGW from different sources have different pollution levels. Most cooling water is recycled and not directly contacted with crude oil, thus it is not severely contaminated. Nevertheless, process water, produced in oil processing operations, is directly contacted with oil and becomes highly contaminated (Jafarinejad 2016).

OGW comprises of a variety of inorganic and organic contaminants. OGW would pollute surface water, groundwater and soil if discharged without treatment. Different regulatory standards have been issued all around the world to control the OGW quality before discharge. For example, the Alberta government implemented the "zero discharge approach" for the oils sands industry. Thus, plenty of research has been conducted to treat OGW to meet the regulations and reduce the damage to ecological environments.

The objectives of this review are:

(a) To introduce the oil and gas wastewater (OGW), its origin, characteristics and toxicity;

(b) To summarize the current physical adsorption processes including activated carbon adsorption and solid phase extraction (SPE) process for OGW organic contaminants removal;

(c) To summarize the studies of chemical oxidation processes for OGW treatment, including UV related oxidation processes and ozonation as well as catalytic ozonation.

2.1.1 Characteristics of OGW

OGW originates from both the water in the reservoir rocks and the additional injected water. The composition of OGW is complex and varies depending on the characteristics of the crude oil and the production process. Generally, OGW is composed of inorganics, organics and suspended solids (Jafarinejad, 2016). Table 2.1 lists some of the major OGW pollutants and their origins (Barthe et al., 2015, CONCAWE, 1999)

Table 2.1 Principal OGW pollutants and their sources.

Pollutant	Sources
Oil	Distillation units, hydrotreating, visbreaking, catalytic cracking, hydrocracking, lube oil
H_2S	Distillation units, hydrotreating, visbreaking, catalytic cracking, hydrocracking, lube oil, spent caustic
NH_3 (NH_4^+)	Distillation units, hydrotreating, visbreaking, catalytic cracking, hydrocracking, lube oil, sanitary blocks
Phenols	Distillation units, visbreaking, catalytic cracking, spent caustic, ballast water
Organic chemicals (BOD, COD, TOC)	Distillation units, hydrotreating, visbreaking, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain), sanitary blocks
CN^-(CNS^-)	Visbreaking, catalytic cracking, spent caustic, ballast water
TSS	Distillation units, hydrotreating, visbreaking, catalytic cracking, spent caustic, ballast water, sanitary blocks
Amines compounds	CO_2 removal in liquefied natural gas (LNG) plants

The main characteristics of OGW include oil, total organic carbon (TOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TSS), turbidity, alkalinity, pH, conductivity, concentrations of HCO_3^-, NH_4^+, SO_4^{2-}, Cl^-, heavy metals, etc. (Ishak et al., 2012). Table 2.2 presents the principal characteristics of different types of OGW.

Table 2.2 Main characteristics of different types of OGW

OGW type	Natural gas produced water[a]	Oilfield-produced water[b]	Petrochemical wastewater[c]	Petroleum refinery water[d]	Oil sands process affected water[e]
Parameters					
pH	4.2-9.7	4.3-10	6-9	8.48	8.4±0.2
Alkalinity *	28-684	n/a	n/a	990	776.9±7.6
TOC *	n/a	0-1500	n/a	n/a	56.3 ± 6.0
BOD *	n/a	n/a	150-350	3378	n/a
COD *	11.2-45.9	1220	10-15	622	211.0 ± 8.0
O&G *	7-500	2-565	<50	n/a	n/a
TSS *	24.5-1,337.4	1.2-1000	n/a	n/a	n/a
NH_4^+*	0-0.4	n/a	15	13.5	n/a
HCO_3*	n/a	77–3990	n/a	n/a	n/a
SO_4^{2-} *	n/a	<2–1650	n/a	n/a	274.7± 40.0
Cl^-*	57-220,000	80–200,000	n/a	n/a	641.0 ± 27.4

* concentration unit: mg/L
**O&G: oil and grease
n/a: Not available
[a] (Johnson et al., 2008),[b](Fakhru'l-Razi et al., 2009), [c](Ma et al., 2009),[d](Gasim et al., 2012),[e](Wang et al., 2015)

The main OGW organic pollutants are dissolved and dispersed oil compounds. Dissolved oil comprises water soluble organic compounds including hydrocarbons, phenols, carboxylic acids, and low molecular weight aromatic compounds (Fakhru'l-Razi et al., 2009). For example, in OSPW, the principal dissolved organic pollutants are naphthenic acids (NAs). NAs are a group of acyclic, monocyclic, and polycyclic carboxylic acids (Giesy et al., 2010). Dispersed oil is composed of oil droplets suspended in OGW. The principal components of dispersed oil are nonpolar compounds including polyaromatic hydrocarbons (PAHs) and large molecular weight alkyl phenols (Ekins et al., 2007).

2.1.2 Toxicity of OGW

OGW was reported to have both acute and chronic toxicity towards organisms. For freshwater animals, the most toxic compounds are hydrogen sulfide and hydrocarbons (Elias-Samlalsingh and Agard, 2004, Fakhru'l-Razi et al., 2009). Other reports have demonstrated the DNA damaging potential and genotoxicity of OGW (Fazili and Ahmad 2014, Gupta et al., 2015). Besides toxicity towards animals, OGW also presents potential toxicity towards plants. da Costa Marques et al. (2015) reported that the untreated oil field-produced water intensely decreased the sunflower seedling percentage and seedling vigor.

OSPW showed adverse effects on organisms' immunological function, developmental delays, impaired reproduction, disrupted endocrine system, and tissue-specific pathological manifestations (Li et al., 2017, Marentette et al., 2015). Early observations of OSPW toxicity indicated that NAs are considered as the major toxic components in OSPW, exhibiting toxic effects through multiple modes of action including narcosis and endocrine disruption (Frank et al., 2008, Frank et al., 2009). Oxidized NAs, aromatic NAs and NAs with N and S also exist in OSPW and have high toxicity (Frank et al., 2008, Grewer et al., 2010, Jones et al., 2012, Reinardy et al., 2013, Scarlett et al., 2013). With the advancement of research, some studies showed that other pollutants, such as polycyclic aromatic hydrocarbons (PAHs), metals, and ions may also contribute to the overall OSPW toxicity (Li et al., 2017, Morandi et al., 2017).

2.1.3 Fractionation of OGW

Solid-phase extraction (SPE) is widely used for samples clean-up, extraction, fractionation and preconcentration of trace pollutants from environmental, clinical biological, food, and beverage samples. The Environmental Protection Agency (EPA) recommends SPE for pretreatment of organic pollutants and regarded SPE as the alternative sample preparation method to Liquid-liquid extraction (LLE) in many EPA methods for organic compounds analysis (Andrade-Eiroa et al., 2016a, b).

The basic SPE procedure consists of conditioning cartridges, loading solution, washing away undesired components and eluting the desired analytes (Camel, 2003). The mechanism of SPE could be generally described as the partition of analytes between the solid support and the liquid sample. Literature has reported that the partition of analytes on the sorbents can be attributed to intermolecular forces between analytes and sorbents, such as electronic/electromagnetic forces, van der Waals forces, π–π bonds and H-bond interactions (Huck and Bonn, 2000, Marczak et al., 2006). The most widely used SPE cartridge packings are alkyl-bonded silicas such as C8 and C18; copolymer sorbents such as cross-linked polystyrene divinylbenzene (Isolute ENV+， hydrophilic lipophilic balanced polymers (Oasis HLB) and ion exchange resins (Oasis WCX, MAX) (Simpson, 2000).

Ag-Ion SPE cartridges were reported to separate methylated OSPW extracts by elution with various solvents (Jones et al., 2012, Scarlett et al., 2013). Huang et al. (2016) reported that classical, aromatic, oxidized, and sulfur-containing NAs could be separated by the Ag-Ion SPE process without being pre-methylated. The organic fraction in OSPW was pre-extracted with dichloromethane LLE and then dissolved into hexane and loaded onto the Ag-Ion SPE cartridge. The SPE fractions were achieved by eluting the cartridge with various composition solvents (various ratios of hexane and acetone). The NA compositions of various fractions were measured by an ultra-performance liquid chromatography ion mobility time-of-flight mass spectrometry method (UPLC-IM-TOF-MS). The results showed that the classic (saturated acyclic) O_2-NAs and aromatic O_2-NAs, O_x-NAs and O_yS-NAs were separated in different fractions. In general, on a reversed phase column, the compound's retention time was reduced with higher polarity. Thus, the authors concluded that the polarity of the experimental OSPW NAs followed the order: classical O_2−NAs < aromatic O_2−NAs < O_2S−NAs < O_3−NAs < O_3S−NAs~O_4S−NAs < O_4−NAs < O_5−NAs.

Numerous studies have been carried out to compare the SPE and LLE for the extraction of organic compounds. According to the research by Telepchak et al. (2004), LLE was a general technique for extracting several compounds, whereas SPE extracted compounds with selectivity. However, this statement is controversial with that by Baggiani et al. (2007), who reported that one drawback of SPE was its lack of selectivity and the same elute would extract and fractionate different analytes. On the other hand, this could be considered as an advantage with specific SPE objectives. For example, simultaneous extraction of large number of organic compounds using SPE was economical considering the time and solvents saved. Oasis HLB sorbent is an example of SPE lacking selectivity arising from its capability of both hydrophobic and hydrophilic interactions (Blahová and Brandsteterova, 2004).

As mentioned before, an important reported advantage of SPE over traditional LLE was that SPE can extract a wide range of organic analytes (from nonpolar to very polar analytes) from a variety of samples (Bohn and Walczyk, 2004, Li et al., 2007, Obando et al., 2008, Zhou et al., 2012). Table 2.3 lists some of the SPE applications in OGW separation and fractionation

Table 2.3 Application of SPE for OGW separation and fractionation

Cartridges	Sorbents materials	Extraction compounds	Eluents	Reference
Oasis HLB, C8 and ENV+	Poly N-vinylpyrrolidone-divinylbenzene (hydrophilic lipophilic balance polymer), Octadecyl phases silica, and Hydroxylated polystyrene-divinylbenzene non-polar resin	NAs in OSPW	Mixture of hexane, DCM, and 2-propanol	Samanipour et al (2019)
Isolute ENV+	Hydroxylated polystyrene-divinylbenzene non-polar resin	NAs; ten phenolic acids compounds	acetonitrile; ethanol	Headley et al. (2002) Ferri et al. (2011)
Discovery Ag-ion	Silver counter-ions anchored on to an SCX support	Classical, aromatic, oxidized, and sulfur-containing NAs of OSPW	hexane/acetone mixture	Huang et al. (2016)
Oasis MAX	Mixed-mode anion-exchange, water-wettable, polymeric sorbent	Oxy-NAs	ethyl acetate saturated with hydrochloric acid (2 M HCl : ethyl acetate = 1:10, v/v)	Wang et al. (2013)
Oasis HLB	Poly N-vinylpyrrolidone-divinylbenzene (hydrophilic lipophilic balance polymer)	NAs in OSPW	ethyl acetate	Bataineh et al. (2006)

2.2 Physical and Chemical OGW Treatment Process

Because of the high mineral and organic content as well as the toxicity, it is necessary to treat OGW before discharging into the environment. There have been many studies focusing on OGW treatment so far, including physical, chemical, biological and combined technologies. This review focuses on physical adsorption and chemical oxidation processes.

2.2.1 Physical Adsorption Processes

The adsorption process is achieved when some substance stays on a sorbents surface owing to the unbalanced molecular or atomic forces on sorbent's surface. The adsorbed substance is called the adsorbate. The adsorption process results in the accumulation of adsorbates on the sorbent's surface and a decrease of the surface force. Adsorption technology is extensively used to remove color, odor, organic and inorganic pollutants.

The adsorption process involves the equilibrium distribution of adsorbates between sorbents and the fluid phase. Two factors could contribute to the adsorption. One factor is the adsorbate solubility. Adsorbates with high hydrophobicity are likely to be adsorbed by hydrophobic sorbents and vice versa. The other factor is the interaction forces between adsorbates and sorbents including electrostatic forces, van der Waals forces and chemical bond forces. Van der Waals forces attribute to physical adsorption which is reversible and unselective with unfixed adsorption sites. The adsorbates can be retrieved, and the sorbents are easily regenerated. Factors that influence the physical adsorption are specific surface area and adsorbent's pore distribution. Chemical bond forces forming strong chemical bond contribute to chemical adsorption, which is selective. Because of the higher bonding strength in chemical adsorption, it is difficult to remove adsorbates and regenerate the sorbents. Chemical adsorption is influenced by the chemical properties of adsorbates and the sorbent's surface (Gupta et al., 2009). In the actual adsorption process, the physical and chemical adsorption processes may happen at the same time. Table 2.4 lists some recent research about OGW treatment by using different sorbents.

Table 2.4 Research about OGW treatment by different sorbents

Sorbents	Adsorbates	Adsorption mechanism	Reference
Carbon xerogel	Naphthenic acids and acid extracted fraction from oil sands process water	Weber and Morris intraparticle diffusion	Benally et al. (2018)
Granular activated carbon	Naphthenic acids and acid extracted fraction from oil sands process water	Intraparticle diffusion	Islam et al. (2018)
Chemical modifications hollow silica microspheres	Crude oil from simulated produced water	Presence of π-π and cation-π interactions (silica derivative containing aromatic functional groups); van der Waals forces; hydrophobic interactions	Torano (2017)
Lignite activated coke (LAC)	Bio-refractory DOC; Organic pollutants containing –COOH and –NH_2 functional groups; hydrophobic compounds	Chemical adsorption attributed to the functional carboxylic, phenolic, and lactonic groups on the surface of the LAC	Tong et al. (2016)
Carbon-based adsorbent prepared by oily scum; Activated carbon (AC)	COD; Oil	The mesoporous property contributed to the adsorption of macromolecular materials	Tang et al. (2016)
Agricultural residues: sugarcane bagasse (SB) and banana pith (BP)	Oil and grease	Monolayer, homogenous adsorption	Abdul Hamid et al. (2016)
Powdered activated carbon (PAC); Commercial organoclay (OC); Lab synthesized organoclay (BTMA)	Phenol; naphthalene	Adsorption by PAC occurred via surface adsorption mechanism; organoclay adsorption occurred by hydrophobic or pi electron interactions	Younker and Walsh (2015)
petroleum coke (PC)	Naphthenic acids	hydrophobic interactions	Pourrezaei et al. (2013)
Immobilized flaxseed gum gel beads	Oil	Chemisorption	Long et al. (2012)

2.2.1.1 Activated Carbon Adsorption

Activated carbon (AC) is a generic term to describe a family of carbonaceous sorbents. Most commercial AC is derived from coal and other cheap materials with high carbon content (Simate et al., 2016). The physical and chemical properties of AC, such as surface area, porosity, surface functional groups, pore structure, and composition, depend on the AC production processes. The hydrophobic nature and abundant surface pores with a large surface area make AC a good organic contaminant adsorbent (Lehr et al., 2005). The adsorption efficiency is determined by the AC and contaminant's physicochemical properties, such as AC surface area, surface composition, contaminant's compound structure and solution pH (Hubbe et al., 2014, Simate et al., 2016).

Niasar et al. (2016) investigated the removal of NAs and treatment of OSPW by AC. The results showed that a model NA (2-naphthoic acid) was more easily adsorbed than diphenylacetic acid and 1,4-cyclohexanedicarboxylic acid was the least adsorbed. Aromatic compounds were adsorbed more by AC, which was attributed to π-π interaction between benzene rings and the AC surface. The adsorption capacity of model compounds and the reduction of OSPW total organic carbon were influenced by pH. Model compounds were favored to be adsorbed at pH 4 rather than at pH 8. At pH 8, most of the compounds were expected to be deprotonated and negatively charged. The AC surface was positive as the measured AC pH_{pzc} was larger than 8.0. Thus, lower molecular weight model compounds adsorbed at pH = 8 rather than at pH = 4, which indicated that model NAs were adsorbed mainly by hydrophobic interaction rather than by electrostatic interaction. Increasing the pH also reduced the OSPW TOC removal by AC. AC removed almost 99% of the TOC in OSPW at pH 3.5, while only 50% TOC removal occurred at pH 8. The authors also reported that for the adsorption of model NAs, the Freundlich model fit well, which implied that the adsorption process was non–homogeneous and multi-layer.

Hubbe et al. (2014) reported that phenolic compounds were favored to be adsorbed by AC at low pH. There were two explanations for this result. One was the increasing repulsion between phenols and AC at high pH. Generally, the AC surface was negatively charged arising from the carboxylic acid function group. At higher pH, the phenolic hydrogens were dissociated and the phenols were converted to phenolates, which are negative charged. Thus, increasing pH results in strong repulsion between AC and phenols and decreases the adsorption. The other explanation was that increasing pH enhanced the phenol's hydrophilicity and weakened the adsorption. The phenolate was more soluble in the aqueous phase and therefore less prone to be adsorbed.

However, other research found that pH did not present any significant influence on the AC adsorption. A study by Simonović et al. (2009) investigated the influence of pH on the adsorption of mineral oil from industry wastewater by hard coal. Their results showed that the initial pH did not have a significant effect on the adsorption process. The removal differences in oil removal between pH 3.0 and 10.5 were under 15%. This may be because the mineral oil is composed mainly of alkanes, without enough ionizable or hydrophilic groups, and were chemically stable and should not be influenced by pH (Zeledón-Toruño et al., 2007).

In summary, organic compounds with higher carbon numbers are more hydrophobic and nonpolar. Those compounds are preferred to approach AC surface and pores and are more readily adsorbed on the AC surface (Islam et al., 2015, Scarlett et al., 2013, Zubot et al., 2012).

2.2.2 Chemical Oxidation Processes

The aim of chemical oxidation in water and wastewater treatment is to convert organic pollutants into less toxic or relatively harmless compounds. Chemical oxidation is widely applied in water and wastewater treatment, such as in the treatment of industrial and municipal wastewater, taste and odor removal and water disinfection. One advantage of the chemical oxidation process is the ability to degrade recalcitrant organic contaminants (Fakhru'l-Razi et al., 2009, Hasan et al., 2012). The strength of oxidants is determined by their oxidation potential. Table 2.5 shows the oxidation potential of some conventional oxidants (Parsons, 2004). Hydroxyl radical (•OH) is the most powerful oxidant after fluorine and it is a non-selective oxidant. The symbol "•" means a single unpaired electron and indicates that the radical is unstable.

Table 2.5 Oxidation potential of common oxidants

Oxidants	Oxidation Potential (v)
Fluorine	3.03
Hydroxyl radical	2.80
Sulfate radical	2.60
Atomic oxygen	2.42
Persulfate anion	2.12
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Permanganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Chlorine	1.36

Advanced oxidation processes (AOPs) are highly promising water treatment technology aimed at the removal of stable and biological recalcitrant organic matter. AOPs involve the production of powerful oxidizing intermediates, such as •OH, that can attack most organic molecules (Andreozzi et al., 1999, Kannel and Gan, 2012). •OH is a short-lived and extremely potent oxidizing agent, oxidizes organic compounds primarily by either by hydroxylation or hydrogen abstraction. During this process, organic radicals are generated and continuously react with •OH radical to produce the final products (Tang, 2004).

Varieties of AOPs have been used to treat OGW, such as Fenton related oxidation (Al-jibouri et al., 2015, Coelho et al., 2006, Diya'uddeen et al., 2015, Hasan et al., 2012, Zhang et al., 2017, Zhang et al., 2016b), photodegradation (Shu et al., 2013, Shu et al., 2014, Souza et al., 2011, Stepnowski et al., 2002, Zhang et al., 2016a), and ozonation (Gamal El-Din et al. , 2011, Garcia-Garcia et al., 2011, Pereira et al., 2013, Souza et al., 2016, Wang et al., 2016b). Oxidants such as $Na_2S_2O_8$, $KMnO_4$ and Ferrate (VI) were also studied for OGW AOPs treatment (Sohrabi et al., 2013, Wang et al., 2016a, Wang et al., 2016b).

The disadvantages of AOPs are that they involve expensive combinations of strong oxidizing agents such as ozone, UV rays, and hydrogen peroxide. In addition, the efficiency of AOPs can be influenced by the solution characteristics. The presence of anions such as carbonate and chloride can act as radical scavengers and compromise the efficiency of AOPs (Liang et al., 2011). The performance of UV-based AOPs could also be hindered by suspended particles that have the potential to attenuate UV light (Brandi et al., 2000).

2.2.2.1 Ozonation

Ozonation has been widely studied for the treatment of OGW compounds (Gulya et al., 1994; Wang et al., 2004). To date, much research has been carried out to investigate the effectiveness of the ozonation of OSPW. The results have shown that ozonation is efficient in degrading NAs in OSPW (Wang et al., 2016b), in attenuating its toxicity (Anderson et al., 2012, Garcia-Garcia et al., 2011, He et al., 2012a, He et al., 2011, He et al., 2012b, Mesherf et al., 2017) and accelerating its biodegradation ability (Hwang et al., 2013, Martin et al., 2010, Pereira et al., 2013, Wang et al., 2013; Lei et al., 2018).

In general, ozone reacts with aqueous organic compounds following two pathways: direct ozonation and indirect free radical oxidation. At neutral to acidic pH, molecular ozonation takes place at the electron rich parts of organic molecules such as C–C double bonds because of the electrophilic property of ozone molecule. At alkaline conditions, ozone decays mostly to •OH and other radicals by chain reactions, which cause radical reactions with organic substances (Hoigné and Bader, 1976, Kornmüller and Wiesmann, 2003, Staehelin and Holgné, 1982).

Al-jibouri et al. (2015) investigated the kinetics of direct ozonation (molecular ozone and NAs reaction) and indirect ozonation (hydroxyl radical and NAs reaction) for the degradation of NAs. The rate constants of the direct ozonation at 5, 15 and 25 $^{\circ}$C were determined to be 0.67, 2.71 and 8.85 $M^{-1}s^{-1}$, respectively, while the rate constants of the indirect ozonation of NAs were found to be 1.12×10^8, 1.78×10^8 and 2.33×10^8 M^{-1} s^{-1} at 5, 15 and 25 °C, respectively. The results showed that hydroxyl radical reacts faster with NAs than molecular ozone.

Kang et al. (2015) investigated the ozonation of oilfield wastewater with low biodegradability. The authors found that the ozonation treatment removed 79.3% of petroleum sulfonate and reduced the microtoxicity. The biodegradability increased when ozone dose was lower than 0.12 $O_{3applied}/[PS]_0$, where $[PS]_0$ was the initial concentration of petroleum sulfonate. When the ozone dose increased from 0.12 to 0.16 $O_{3applied}/[PS]_0$, the biodegradability decreased as a higher ozone dose could mineralize the biodegradable organics. Thus, an optimum ozone dose was necessary for the objective of increasing the biodegradability.

Wang et al. (2004) studied the possibility of improving the biodegradability of drilling wastewater using ozone. The biodegradability of wastewater was improved, and the molecular weight of organic compounds decreased continuously at the early stage of ozonation process. With longer ozonation times, the biochemical oxygen demand began to decrease. The biochemical oxygen demand to total organic carbon (BOD/TOC) ratio dropped to the lowest point (0.4 g/g) when wastewater was treated with ozone continuously for 15 min. The 5 min ozonation followed by biological degradation combination produced a TOC removal rate of 54.3%, which was comparable to 30 min direct ozonation under the same conditions. Thus, the authors concluded that short-term ozonation followed by biological treatment was very efficient in TOC removal.

The research of Scott et al. (2008) showed that after 50 minutes exposure of OSPW to ozonation, the effluent was non-toxic (based on the microtox bioassay) with decreased NA concentrations by approximately 70%. With 130 minutes of ozonation, GC-MS analysis showed higher molecular weight NAs ($n \geq 22$) were decreased by over 95%, while the proportion of lower molecular weight NAs ($n = 5$–13) clustering mostly with $z = 0$, -2 and -4 were decreased by over 75%.

Xue et al. (2016) investigated the ozone pretreatment on member fouling behaviors of an anoxic-aerobic membrane bioreactors (MBRs) for OSPW treatment. Their results showed that 30 mg/L ozone pretreatment enhanced the OSPW NA degradation and improved the MBR's fouling control. The authors explained that ozonation altered the water organic composition, reshaped the microbial community leading to the better fouling control. The authors concluded that low-dose ozonation is a good pretreatment option to enhance OSPW organic contaminants degradation and alleviate the MBRs membrane fouling for OSPW treatment.

Wang et al. (2016b) compared the efficiency of different oxidation processes (hydrogen peroxide/UV, potassium ferrate (VI), ozone) at the same dose of 2.0 mM. for OSPW treatment. The authors concluded that ozonation was the most efficient process to degrade OSPW NAs and also the most effective to transform to Ox-NAs species. O_2, O_3 species abundances decreased to 7.3% and 22%, while O_4, O_5 and O_6 species increased to 40.5%, 21.8% and 6.9%, respectively.

2.2.2.1.1 Ozone related AOPs

In aqueous solution, ozone could react with OH^- and H_2O_2 and form HO_2^-. The reaction rate to generate HO_2 by ozone and H_2O_2 is 40000 times faster than that by ozone and OH^-. •OH will then be generated after series of reactions, which will oxide organic compounds (Gulyas et al., 1994). The series of reactions are described with the following equations (Andreozzi et al., 2000):

$$\mathrm{HO^- + O_3 \rightarrow O_2 + HO_2^-} \qquad (1)$$

$$\mathrm{H_2O_2 \rightleftharpoons HO_2^- + H^+} \qquad (2)$$

$$\mathrm{HO_2^- + O_3 \rightarrow HO_2 \cdot + O_3^- \bullet} \qquad (3)$$

$$\mathrm{HO_2 \bullet \rightleftharpoons H^+ + O_2^- \bullet} \qquad (4)$$

$$\mathrm{O_2^- \bullet + O_3 \rightarrow O_2 + O_3^- \bullet} \qquad (5)$$

$$\mathrm{O_3^- \bullet + H^+ \rightarrow HO_3 \bullet} \qquad (6)$$

$$\mathrm{HO_3 \bullet \rightarrow HO \bullet + O_2} \qquad (7)$$

Photolysis of ozone generates H_2O_2, thus O_3/UV involves all the organic destruction mechanisms present in H_2O_2/UV process. In addition, the presence of UV radiation increases the decomposition rate of the ozone that generates the superoxide anion radical ($\bullet O_2^-$) and the hydroperoxyl radical

($HO_2\cdot$); this can cause a significant rise in the pollutant removal (Andreozzi et al., 1999, Glaze, 1987).

Souza et al. (2016) studied the treatment of oil refinery wastewater by UV, O_3 and a UV/O_3 combined method. The wastewater used in their study was biological treatment effluent. The TOC (12-19 mg/L) in the effluent indicated that there was biological recalcitrant organic matter remained after biological treatment. The oxidation results showed that since most compounds in the wastewater were not photosensitive, UV treatment alone (photolysis) was not effective to remove the TOC and to reduce the specific UV absorption (SUVA). Compared with photolysis, a small decrease of the TOC was observed using ozone treatment alone. However, the SUVA decreased dramatically. It was evident that the ozone treatment could effectively cleave aromatic compounds (the SUVA can be correlated with the organic matrix aromaticity). However, the low TOC removal revealed that the degree of mineralization was still low after ozone treatment alone. The combination UV/O_3 treatment achieved a higher TOC removal at an ozone dose greater than 20 mg/L as compared with ozone treatment alone.

Gulyas et al. (1994) found that the addition of H_2O_2 did not exhibit obvious effects on the OGW treatment. The authors conducted experiments to study the efficiency of ozonation and O_3/H_2O_2 treatment of biologically treated oil reclaiming wastewater. Ozonation resulted in a about a 17% reduction of the COD. The addition of H_2O_2 did not markedly influence the COD removal. The authors supposed two reasons. One was that radical mechanisms may be not be vital for the degradation of their type of wastewater. The other one was that H_2O_2, which also acts as an $\cdot OH$ scavenger, was generated during the process (Arslan et al., 1999).

2.2.2.1.2 Catalytic Ozonation

Although ozone is a powerful oxidant, it is selective and reacts less efficiently with some organics (e.g., saturated aliphatic acid) and inorganic (e.g., NH_4^+) compounds. In order to accelerate the mineralization efficiency, O_3/UV, O_3/H_2O_2, and other catalytic ozonation processes are widely studied as they could generate stronger radical species (Wei et al., 2017).

Homogeneous catalytic ozonation

Transition metals, such as Fe(II), Mn(II), Ni(II), Co(II), Cr(III), Ag(I), Cu(II), Zn(II), and Cd(II) have exhibited catalytic effects during the ozonation process (Kasprzyk-Hordern et al., 2003, Ma and Graham, 2000). The principal catalytic mechanism is the production of hydroxyl radicals. Take the Fe^{2+} as an example.

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \qquad (8)$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad (9)$$

Ma and Graham (2000) investigated the degradation of atrazine by manganese Mn(II)-catalyzed ozonation. It was found that a small amount of Mn(II) (0.3–1.2 mg/L) greatly increased the atrazine degradation rate with the formation of by-product compounds of lower molecular weight and greater polarity. Either bicarbonate or *tert*-butanol had a negative effect on the atrazine degradation rate for both ozonation alone and Mn(II)-catalysed ozonation. The decomposition of ozone was greatly retarded, resulting in a higher residual ozone. These results confirm that atrazine degradation by Mn(II)-catalyzed ozonation follows a radical mechanism. The authors also observed that Mn(II) catalyzes the ozone decomposition through the formation of intermediate manganese species, such as Mn(IV), leading to the generation of hydroxyl radicals.

Heterogeneous catalytic ozonation

Diverse heterogeneous catalysts such as MnO_2, TiO_2, Al_2O_3 and mixed metal oxides have been developed to offer high-efficiency catalytic ozonation of organic pollutants (Delanoë et al., 2001, Einaga and Ogata, 2009, Ernst et al., 2004, Gracia et al., 2000).

Chen et al. (2014) investigated heavy oil refinery wastewater treatment by activated carbon-supported manganese oxides (MnOx/GAC) catalytic ozonation. Three catalysts were prepared with three different $Mn(NO_3)_2$ concentrations. MnOx/GAC prepared with 0.25 M $Mn(NO_3)_2$ exhibited greater COD reduction efficiency in the catalytic ozonation process. The system of MnOx/GAC (prepared using 0.25 M $Mn(NO_3)_2$) combined with ozone promoted COD reduction efficiency, improved biodegradability and decreased microtoxicity for oil refinery wastewater under the conditions of 30 °C, 80 min treatment, 2.025 g/h O_3 dose and pH 7.36. ESI FT-ICR MS analysis revealed a pronounced increase of H/C and O/C (atomic ratios) in the organic pollutant molecules after the treatment. The authors investigated the changes for O-compounds in negative-ion mode by the two-dimensional modified van Krevelen diagram. The results showed that the sum of O_x, O_xS, N_xO_x and $N_xO_xS_x$ compounds decreased from 2962 to 2643 after treatment. However, the number of O_x compounds increased from 847 to 973 during the treatment. The results showed that the dominant catalytic ozonation mechanism was oxidation via hydroxyl radicals. The results suggested that high molecular weight pollutants with high toxicity and low biodegradability were first degraded to small molecular-weight oxidation products with low toxicity and high biodegradability. Afterward small molecular pollutants and oxidation products were further oxidized or mineralized.

Chen et al. (2016) reported that iron-loaded AC could enhance ozone decomposition and produce more •OH radicals. Furthermore, the catalytic ozonation process improved the oil-field wastewater COD removal and the BOD_5/COD ratio. The catalyst dose influenced the catalytic effect. The COD removal efficiency and the BOD_5/COD ratio increased dramatically when the catalyst dose range was from 0 to 1.0 mg/L, while little change was observed when the catalyst dose increased from 1.0 to 3.0 mg/L. This may be explained by the following two reactions:

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \qquad (10)$$

$$\bullet OH + O_3 \rightarrow O_2 + HO_2^{\bullet} \qquad (11)$$

The excess hydroxyl radicals were consumed by itself or O_3 so that the catalytic effect was weakened.

There was research proving that some heterogeneous catalytic ozonation processes can be achieved by the adsorption effect of the catalyst rather than the generation of •OH. Carbajo et al. (2007) tested the ozonation of different types of phenolic wastewater in the presence of a perovskite catalyst. Wastewater A (a mixture of syringic, pyruvic and gallic acids in water) was first ozonated without catalyst for 30 min, then the catalyst was added to the solution. The result showed that catalyst concentration did not show appreciable influence with concentrations higher than 0.1 g/L. Thus, from the economic point of view, some savings can be attained by reducing the amount of catalyst used. Wastewater with higher initial COD exhibited a higher removal rate. The degree of mineralization was favored by higher temperature and higher pH. The addition of free radical scavengers did not influence the COD depletion. This indicated that the catalytic effects arose from to the adsorption of reactants to facilitate the reaction rather than the generation of free radicals. Wastewaters B (from wine distillery), C (from olive debittering) and D (from olive oil production) showed different behaviors depending on their nature. No differences were observed between catalytic and non-catalytic runs for easily oxidized wastewaters. Activity of perovskites in the ozonation process was only experienced for those effluents showing a certain refractory character to the direct ozonation process without catalysts.

2.2.2.1.3 Effect of water matrix on the ozonation process

As it was discussed in the section 2.2.2.1.2, some transition metals could initiate the decomposition of O_3 to produce •OH and contributed to homogeneous catalytic ozonation process to improve the oxidation efficiency. However, some anions such as Cl^- and CO_3^{2-} act as scavengers during the AOP. They can scavenge •OH radicals and thus inhibit the oxidation efficiency (Abdullah et al., 1990). Lu et al. (1997) explored the effect of inorganic ions on the efficiency of Fenton oxidation, where their results showed that $H_2PO_4^-$ and Cl^- suppress Fenton reagent's decomposition effect for dichlorvos. Liang et al. (2006) evaluated the influence of carbonate and chloride ions on persulfate oxidation of trichloroethylene and observed that a high level of chloride and carbonates resulted in scavenging effects on the oxidation of trichloroethylene by persulfate. De Laat and Le (2006) investigated the effect of chloride ions on the Fenton-like oxidation process, which the results also showed that the presence of chloride decreased the decomposition of H_2O_2 and the probe compound oxidation rate.

Ma and Graham (2000) investigated how the bicarbonate influences the Mn(II)-catalyzed ozonation of atrazine. The authors found that with an increase of the bicarbonate concentration, the atrazine oxidation rate by Mn(II)-catalyzed ozone was substantially reduced and a correspondingly higher residual ozone was observed.

Afzal et al. (2012) showed that, although the UV/H_2O_2 process contributed to a high CHA degradation rate in ultrapure water, Cl^-, CO_3^{2-} and a real OSPW matrix decreased the degradation efficiency. This indicated that in the real application of AOPs, radical scavengers existing in the water matrix should be considered.

Grebel et al. (2010) studied the effect of halide ions and carbonates on the degradation of organic contaminants by AOP. Their results showed that the inhibiting effect varied depending on the target contaminants. Some intermediate halogen radicals reacted more selectively with electron-rich organic compounds, which to some extent compensated the impact of •OH radical scavenging.

2.2.2.2 Photodegradation

Photodegradation can be achieved either by direct photolysis where the pollutants degradation is due to their absorbance of UV irradiation, or by radical reactions (indirect photolysis). Radical reaction happens with the generation of radicals by photosensitizing agents such as H_2O_2, TiO_2 or chlorine. Aromatic compounds are easily degraded by direct photolysis as those compounds themselves absorb UV irradiation.

Gulyas et al. (1994) studied the efficiency of UV/TiO_2 system for the treatment of biologically treated oil reclaiming wastewater with 300 mg/L of COD. The results showed that at pH 3, after 5 hours UV/TiO_2 treatment, the COD was reduced by 70% and the biodegradation ability of the wastewater was enhanced. For the UV/TiO_2 system, TiO_2 is irradiated by UV light with electrons transferred from the valence band to the conduction band. Dissolved oxygen molecules are reduced to superoxide anion radicals (O_2^-.) by TiO_2. O_2^- suffers a disproportionation reaction to form molecular oxygen and hydrogen peroxide. The hydrogen peroxide is then further reduced to hydroxide ions and hydroxyl radicals by additional electrons. Organic molecules are attacked by ·OH and transferred to organic radicals and degraded in further radical reactions.

Wang et al. (2016b) compared the efficiency of different oxidation processes (UV/H_2O_2, ferrate (VI), and ozonation) on OSPW treatment. In the UV/H_2O_2 process, •OH was generated arising from the cleavage of the O-O bond in H_2O_2 by UV radiation. UV/H_2O_2 oxidation achieved 42.4% removal of classical NAs at 2.0 mM H_2O_2 and 950 mJ/cm^2 UV dose with medium pressure mercury lamp. One-ring and multiple-ring fluorescing aromatics were transformed simultaneously. The oxidation occurred through both radical reaction and direct photolysis. Classical NAs with high hydrogen deficiency were very likely to be aromatic compounds, which can adsorb UV and be transformed through direct photolysis process.

Headley et al. (2009) studied the photocatalysis of oil sands NAs and model-NAs irradiated with TiO_2 suspension under fluorescent and natural sunlight conditions. Under natural sunlight condition, approximately 75% of NAs were degraded within 8 hours. Molecules with z values between 0 to −6 were observed more readily to be degraded. The varied degradation efficiency appeared to be linked to differences in the molecular weights and the cyclic degree of the compounds.

Shu et al. (2014) studied the application of UV/chlorine process for the remediation of OSPW in both laboratory-scale and under actual sunlight. The researchers observed that at the laboratory-scale using the UV/chlorine treatment, the NA degradation was •OH-based and structure-dependent. The pseudo-first-order rate constants increased with increasing carbons numbers. This was consistent with other research (Afzal et al., 2012). The enhanced reactivity could be related to the increment of hydrogen atoms and/or alkyl groups with more carbon introduced, resulting in higher reactivity toward •OH. For each carbon group, the pseudo-first order rate constants also increased with the increasing number of cyclic rings, which was consistent with the other study (Perez-Estrada et al., 2011). This may be explained by the increased tertiary carbon with the increased in number of rings. The higher tertiary carbon also related to more H atoms at the tertiary carbon positions, which are more reactive than those on secondary or primary carbons. In terms of the pH influence on NA degradation rate, higher NA degradation rate in raw OSPW (pH 8.3) was observed than those at an alkaline condition (pH = 10). Under actual sunlight, direct solar photolysis partially degraded fluorophore organic compounds, but did not degrade NAs. However, the solar/chlorine process effectively removed OSPW NAs and fluorophore organic compounds in the presence of 200 or 300 mg/L OCl^-. After solar/chlorine treatment, the acute toxicity of OSPW toward *Vibrio fischeri* was reduced, while the toxicity toward goldfish primary kidney macrophages showed no reduction.

2.3 Conclusion

With the continuous improvement in environmental requirements, the quality of OGW effluents is strictly required. Physical adsorption and chemical oxidation have been widely studied for the OGW treatment.

Physical adsorption is a widely used traditional water treatment technology and the current and future research emphasis is on the development of inexpensive and more efficient adsorbents. AC adsorption has been reported to be a promising process for the removal of organic compounds from OGW.

Chemical oxidation has been widely applied for OGW treatment. An obvious advantage of chemical oxidation is the degradation of recalcitrant organic compounds, which is important component in OGW. The development of AOPs focuses on improvement of the treatment and economic efficiency. However, some compositions in the OGW may present side effects on the AOPs efficiency and the high cost of AOPs is still a challenge for the application of AOPs on the OGW treatment. Thus, an in-depth study of the OGW degradation mechanism and catalytic AOPs are vital to improve the OGW treatment efficiency and reduce the process cost.

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Chapter 3 Separation of Oil Sands Process Water Organics and Inorganics

3.1 Introduction

In 2017, approximately 1.25 million barrels of bitumen was produced per day in Alberta oil sands industry and 0.21-2.5 barrels of water are required for per barrel of bitumen extraction (NRC, 2018). After the bitumen extraction, all process water is stored in tailings ponds and is known as oil sands process water (OSPW) (Hughes et al., 2017). Although around 3/4 of OSPW is recovered from tailings ponds and recycled back for the bitumen extraction process (NRC, 2018), the volume of remaining OSPW would accumulate due to constant input of fresh OSPW from the bitumen extraction process, which results in environmental concerns.

During the bitumen extraction process, dissolved organic matter, consisting mainly of organic acids, is dissolved into OSPW (Hughes et al., 2017). The main organic contaminants in OSPW are reported to be a mixture of aliphatic and (poly-) alicyclic carboxylic acids known as naphthenic acids (NAs) (Zhao et al., 2012). In addition to NAs, OSPW also contains other organic compounds such as aliphatic hydrocarbons, heteroatomic compounds with nitrogen or sulfur atoms, phenolic compounds, polycyclic aromatic hydrocarbons (PAHs), and BTEX (benzene, toluene, ethylbenzene, and xylene) (Frank et al., 2016; Huang et al., 2018). As bitumen in oil sands is extracted by alkaline water, this results in the OSPW to be a brackish mixture containing different inorganic salts where the major ions are Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-} and HCO_3^- and also trace level of other metal ions (Allen, 2008; Masliyah et al., 2004; McQueen et al., 2017; Puttaswamy and Liber, 2012).

NAs in OSPW have received great attention as they were reported to be responsible for the acute toxicity of OSPW towards microorganisms (Zhao et al., 2012; Klamerth et al., 2015), aquatic organisms (Marentette et al., 2015; Morandi et al., 2015) and mammals (Fu et al., 2017; Li et al., 2017). At present, the principal toxic composition of OSPW towards tested organisms have not been fully identified mainly due to the complex components of OSPW. It is not clear whether the toxic effects of whole OSPW are due solely to NAs, a combination of NAs and other organic toxic compounds or a combination of the organic and inorganic fractions of OSPW. Although research has been done to extract and separate OSPW organics (Bartlett et al., 2017; Bauer et al., 2017; Jie et al., 2015; Scarlett et al., 2013; Yue et al., 2015), methods for the isolation of OSPW organic and inorganics are barely reported. Meanwhile, the toxicity of OSPW inorganic fraction and inorganic-organic complex are unclear.

As OSPW is composed of complex organic mixture, it is difficult to analyze and identify the organic compounds individually. Extraction is required before the organic composition analysis using methods such as ^{1}H nuclear magnetic resonance (Wang et al., 2016b), Fourier transform ion cyclotron resonance mass spectrometry (Wang et al., 2016a), Fourier transform infrared spectroscopy (Gamal El-Din et al., 2011) and gas chromatography coupled with mass spectrometry (Jie et al., 2015). Extraction process simplifies the composition of OSPW with saline matrix removed, which could facilitate the characterization of organic compounds (Huang et al., 2016a). Liquid-liquid extraction (LLE) (Huang et al., 2016b) and solid phase extraction (SPE) (Huang et al., 2016a, Frank et al., 2016) have been widely used for the extraction of OSPW organics for compositions measurement and species-specific studies. LLE using dichloromethane as solvent is commonly used for the extraction of NAs from OSPW. However, in the work by Hughes et al. (2017a) where the authors compared the extraction of NAs from OSPW using LLE and SPE showed that SPE demonstrated better recovery of NAs from OSPW. An additional disadvantage of LLE was that it consumed more organic solvent that is harmful to the environment and experimenter (Yang et al., 2017). Thus, SPE using different sorbents materials were studied in this paper as to further improve the extraction efficiency of SPE in the extraction of OSPW organic matter and to reduce the use of the harmful organic solvent.

Developing efficient methods to separate OSPW inorganics and organics will be conducive to the identification of OSPW organic components and allow the toxicity study of different fractions. Moreover, the separation of OSPW organic and inorganic fraction would assist in the study of OSPW inorganic matrix influence on the removal of organic contaminants by different technologies, which would provide valuable information for the improvement of OSPW treatment efficiency. In the present study, copolymers consisting of specific components, and porous carbon-based sorbent granular activated carbon (GAC) were used to develop optimum methods to efficiently extract OSPW organic fraction (OSPW-OF) and isolate inorganic fraction (OSPW-IF). This is the first study that almost exclusively separate OSPW inorganic and organic fractions and the results of the research could be applicable for the separation of other process water.

3.2 Materials and Methods

3.2.1 Regents and Materials

OSPW was collected from Fort McMurray, Alberta and stored at 4 °C and was allowed to be warm to room temperature before used. Sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium bicarbonate ($NaHCO_3$), optima-grade water, methanol, dichloromethane (DCM), and hexane were purchased from Fisher Scientific Co. Canada. Discovery® DSC-18 (6 mL, 1 g) cartridge was obtained from Sigma-Aldrich Co. Canada. OASIS HLB (5 mL, 200 mg) and MAX (6 mL, 150mg) cartridge was obtained from Waters Co., ON., Canada. Isolute ENV+ cartridge (6 mL, 200 mg) were purchased from Biotage®, NC, USA. Bond Elut PPL cartridge (3 mL, 200 mg) was purchased from Agilent Technologies Canada Inc., ON, Canada. Granular activated carbon (GAC) was purchased from Calgon Carbon Corporation, PA, USA. Empty cartridge used to pack GAC was purchased from Biotage®, NC, USA.

3.2.2 Separation Approaches

The properties of SPE sorbents are listed in Table 3.1. Prior to SPE process, OSPW was filtered using 0.45 μm nylon membrane (GE Healthcare Whatman™) to remove suspended particles. Since the dominated organic species in OSPW is organic acids especially NAs which have estimated pk_a values of 3.5, 4.8, and 6.8 for O_2-, O_3-, and O_4-NAs. At the natural pH of OSPW around 8.5, NAs would be present as anions (Huang et al., 2016b; Huang et al., 2015). Thus, acidizing of OSPW to protonate organic acids into their neutral form was conducive to achieve higher extraction efficiency for SPE process using HLB, ENV+ and C18 cartridges. The pH of OSPW was adjusted to 2 using concentrated HCl. For ion-exchange resin MAX, no pH adjustment was applied. Each extraction process was conducted in duplicate. SPE cartridges were placed on a vacuum manifold and the cartridges were conditioned with 10 mL methanol followed by 50 mL ultrapure water. 40 mL OSPW was passed through cartridges with a flow rate of 1 mL/min. Organic compounds in OSPW was retained on the sorbents and the effluent was collected for the composition determination. After the cartridges were dried at 40 °C under nitrogen, the retained organics were eluted by 20 mL methanol. For MAX cartridge, 20 mL methanol was used to elute the nonacid compounds absorbed in the cartridge due to hydrophobic sorption. The cartridge was then eluted by 20 mL acidify methanol (2 M HCl: methanol = 1:10, v/v). All the eluent was collected and evaporated to dryness under air at room temperature to obtain the dry organics. The dry organics were re-dissolved in 40 mL of $NaHCO_3$ (300 mg/L, pH = 8.7) for analysis. Figure 3.1 shows the schematic of the SPE process. LLE with DCM was conducted to compare with SPE for the extraction of organic fraction. 20 mL of DCM was used to extract 40 mL of OSPW (pH =

2) twice. The DCM extracts were collected and combined together. Similar with the SPE procedure, after evaporating to dryness, the residue extracted organic fraction was re-dissolved in 40 mL of $NaHCO_3$ for analysis

Table 3.1 Properties* of solid phase cartridges used in this study

Cartridge	**Sorbent structure**	**Sorbent mode**	**Interaction Mode**	**Average particle size (µm)**	**Average pore size (Å)**	**Specific surface area (m^2/g)**	**Bed mass (mg)**	**Volume (mL)**
HLB	Divinylbenzene-vinylpyrrolidone (hydrophilic-lipophilic balanced) copolymer	Reversed phase polymer-based sorbent	Hydrophobic-hydrophilic interaction	60	80	800	200	5
ENV+	Hydroxylated styrene-divinylbenzene copolymer	Reversed phase polymer-based sorbent	Hydrophobic-hydrophilic interaction	120	800	1000	200	6
PPL	Styrene-divinylbenzene polymer modified with a proprietary non-polar surface	Reversed phase polymer-based sorbent	Hydrophobic-hydrophilic interaction	125	125	640	200	3
C18	Octadecyl bonded silica-based gel	Reversed phase silica-based sorbent	Hydrophobic-hydrophilic interaction	56	74	490	1000	6
MAX	Divinylbenzene-vinylpyrrolidone copolymer coated with quaternary amine groups	Anion exchange/ reversed phase mixed sorbent	Hydrophobic-hydrophilic interaction/ ionic interaction	30	80	NA**	150	6

*Properties of each individual cartridge was obtained from the manufacturer website
** Not available

OSPW containing only inorganic fraction was obtained with the organic compounds in OSPW adsorbed by GAC. The characteristics of GAC are listed in Table 3.2. The GAC was washed with 0.1 mM HCl and NaOH sequentially to remove impurities. The GAC was rinsed five times using ultrapure water (200 mL) before drying overnight at 100 °C. 3 g of clean dry GAC was packed in a 6 mL empty column with the diameter of 1.3 cm and depth of 6.5 cm. Ultrapure water (200 mL) was loaded on the GAC cartridge, with the last 40 mL effluent filtered with 0.45 µm nylon membrane and collected as blank. 40 mL of OSPW was passed through the GAC column by gravity. The effluent was collected and filtered with 0.45 µm nylon membrane for analysis. After adsorption process, the GAC was transferred into 40 mL vials. The desorption and recovery of adsorbate was achieved by ultrasonic washing the sorbent in 20 mL methanol for 30 min. The methanol extract was isolated using centrifugation. The dry organics were obtained after the evaporation of methanol and re-dissolved into 40 mL $NaHCO_3$ solution. The schematic of the separation of OSPW inorganic and organic fraction is shown in Figure 3.1.

Table 3.2 Characteristics of the GAC

Sample	**S_{BET} (m^2/g)**	**S_{meso} (m^2/g)**	**S_{micro} (m^2/g)**	**V_{micro} (cm^3/g)**	**V_{meso} (cm^3/g)**	**V_{total} (cm^3/g)**	**D_p (nm)**
GAC	976	137	839	0.386	0.213	0.599	2

S_{BET}: Total surface area; S_{meso}: Mesopore surface area; S_{micro}: Micropore surface area
V_{micro}: Micropore volume; V_{meso}: Mesopore volume; V_{total}: Total pore volume
D_p: Average pore diameter

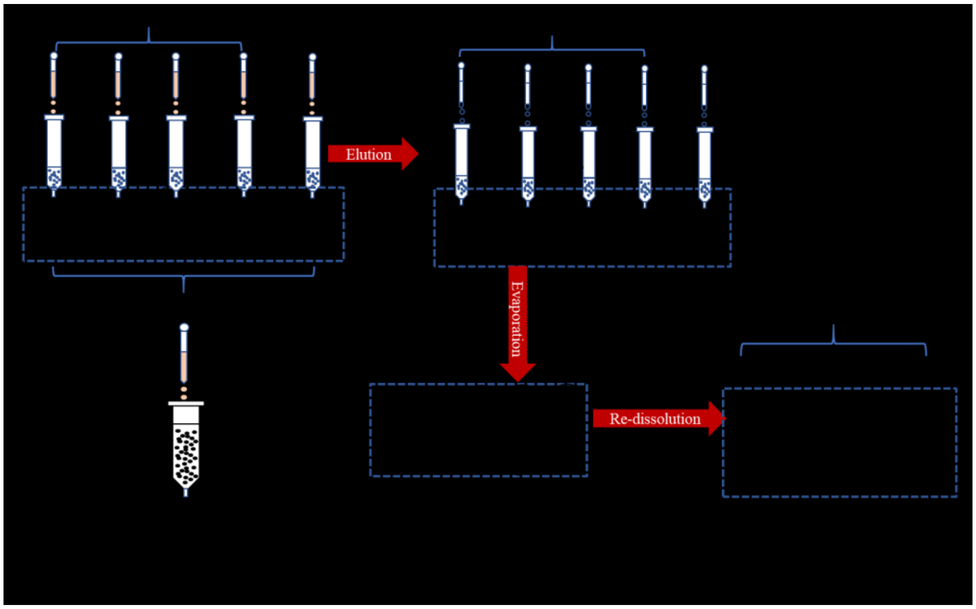

Figure 3.1 Schematic of the separation of OSPW inorganic and organic fraction.

3.2.3 Analytical Determination

The analysis of anion concentrations was conducted by ion chromatography (ICS-2000 and 2500, Dionex, Sunnyvale, CA, USA). The concentrations of metal and some non-metals ions were quantified by inductively coupled plasma mass spectrometry (ICP-MS, Elan 6000 ICP mass spectrometer, PerkinElmer, Waltham, MA, USA). Dissolved organic carbon (DOC) of the separation samples was measured by Shimadzu TOC-V CHS/CSN Model Total Organic Carbon Analyzer. The fluorophore organic compounds were monitored using a qualitative approach. Synchronous fluorescence spectra (SFS) of the OSPW were recorded with a Varian Cary Eclipse fluorescence spectrometer (Ontario, Canada) using the Cary Eclipse system. The optimized wavelength offset ($\Delta\lambda$) between the excitation and emission monochromators for synchronous fluorescence was set at 18 nm, and spectra were recorded between 200 to 500 nm excitation wavelengths with excitation and emission slits set at 5 nm and scan speed 10 nm/s. The photomultiplier tube (PMT) voltage of the detector was set at 780 V.

NA concentration was measured by an ultra-performance liquid chromatograph time-of-flight mass spectrometry (UPLC-TOF-MS) (Synapt G2, Waters, ON). 1 mL of each water sample was centrifuged at 10 000 RPM for 10 min. The injection solution was prepared with 500 μL of the supernatant, 100 μL of 4.0 mg/ L internal standard (ISTD) compound (Myristic acid-1-^{13}C) in methanol, and 400 μL methanol to reach a final sample volume of 1 mL. The samples were analyzed using UPLC-TOF-MS in high-resolution mode (mass resolution = 40000 FWHM at 1431 m/z) at mass range of 100-600 (m/z). The chromatographic separation was achieved by a method developed in our previous reports for the separation of NAs (Huang et al., 2016a; Huang et al., 2015). The electrospray ionization source was operated in the negative mode to measure NAs in the samples (Pereira et al., 2013). Data acquisition was controlled using MassLynx (Waters, ON) and data analysis was performed using TargetLynx (Waters, ON). One raw OSPW sample has been used as the quality control sample to ensure the method stability. This method was developed previously for semi-quantification of NAs based on the signal of a compound versus the signal of spiked ISTD (Huang et al., 2015; Wang et al., 2013b).

3.3 Results and Discussion

Solid phase extraction cartridges of different sorbents characteristics were used to assess the most suitable sorbent for the extraction of organic fraction from OSPW. Five SPE cartridges, HLB, MAX, C18, ENV+, and PPL, were employed in this study. HLB, C18, ENV+, and PPL are reversed phase sorbents, with various modification of the sorbents, while MAX is an ion-exchange type sorbent. HLB is a hydrophobic-lipophilic balanced sorbent, which is capable to adsorb both polar and non-polar compounds. C18 is a polymerically bonded octadecyl with high carbon loading for greater binding capacity. C18 is a commonly used reversed phase sorbent that could retain structurally diverse organic compounds from aqueous solution. ENV+, a hydroxylated styrene-divinylbenzene copolymer sorbent, could highly retain non-polar compounds and extract polar analytes that could not be retained by C18 cartridge. PPL is a styrene-divinylbenzene polymer modified by a non-polar surface, which could achieve the retention of highly polar to nonpolar compounds. MAX is a mixed-mode polymeric sorbent that could achieve higher selectivity for extracting acidic compounds by anion-exchange groups. The details of sorbents structure and the physical properties of these solid-phase sorbents are shown in Table 3.1.

3.3.1 Recovery of OSPW Organic Fraction

Organic fraction recovery efficiency was assessed by comparing the DOC recovery efficiency of different extraction methods. DOC recovery was calculated as follows:

$$\text{DOC recovery} = \frac{\text{DOC}_{\text{OB}}}{\text{DOC}_{\text{OSPW}}} \times 100\% \qquad (4)$$

where DOC_{OB} is the DOC of the extracted organics redissolution in buffer and DOC_{OSPW} is the DOC of the original whole OSPW.

DOC recovery by SPE processes using different cartridges after methanol is showed in Figure 3.2a. The highest DOC recovery of 95.4% was obtained by HLB cartridge. ENV+ achieved lower DOC recovery of 89.3% as compared to HLB. C18 and MAX recovered 53.0% and 53.5% DOC, respectively. The DOC recovery from MAX was the sum total of DOC eluted by methanol and acidified methanol, of which 9.96% DOC was eluted by methanol. Wang et al. (2013a) pointed out that methanol eluted organic compounds from MAX cartridge was regarded as the nonacid compounds. PPL recovered the least 38.8% of DOC. LLE using DCM achieved 48.8% DOC recovery, which was lower than all the SPE methods except for PPL cartridge. The lower DOC recovery observed by LLE than other SPE methods was consistent with the results of previous study (Yang et al., 2017), showing that DCM LLE had lower DOC extraction efficiency than SPE using HLB and C18. The lower organic recovery of DCM LLE may because DCM is a low-polar compound and lack of pronounced functional groups to form effective chemical interaction with organic compounds. In this case, the extraction of organic molecules from OSPW by DCM LLE was only based on the molecular distribution equilibrium between the DCM and water (Huang et al., 2016b) and the only available interaction was the hydrophilic-hydrophobic interaction (Yang et al., 2017).

For the five tested SPE cartridges, HLB followed by ENV+ achieved the highest DOC recovery. It was reported that HLB cartridge with the sorbent of hydrophilic-lipophilic balanced copolymer containing hydrophilic monomer, was better able to extract most polar compounds than the silica-based (e.g. C18) or hydrophobic polymeric sorbents (e.g. Styrene-divinylbenzene polymer) (Fontanals et al., 2005). ENV+ cartridge contains the sorbent of hydroxylated styrene-divinylbenzene copolymer, in which the hydrophobic styrene-divinylbenzene copolymer was modified and the hydrophilicity was improved. On the other hand, the sorbent of PPL cartridge is modified with a non-polar surface which improves the hydrophobicity and recovered lowest DOC from OSPW. From the above, the high DOC recovery of HLB and ENV+ cartridges may due to their higher hydrophilicity compared to other cartridges. Therefore, it was proposed that SPE cartridges with relative higher hydrophilicity was preferred to achieve higher organic matter extraction efficiency from OSPW. This result also provides the information that the OSPW organic are of hydrophilic nature, which was expected as NAs, a subset of organic acids was suggested to be the main constituent of OSPW organic fraction.

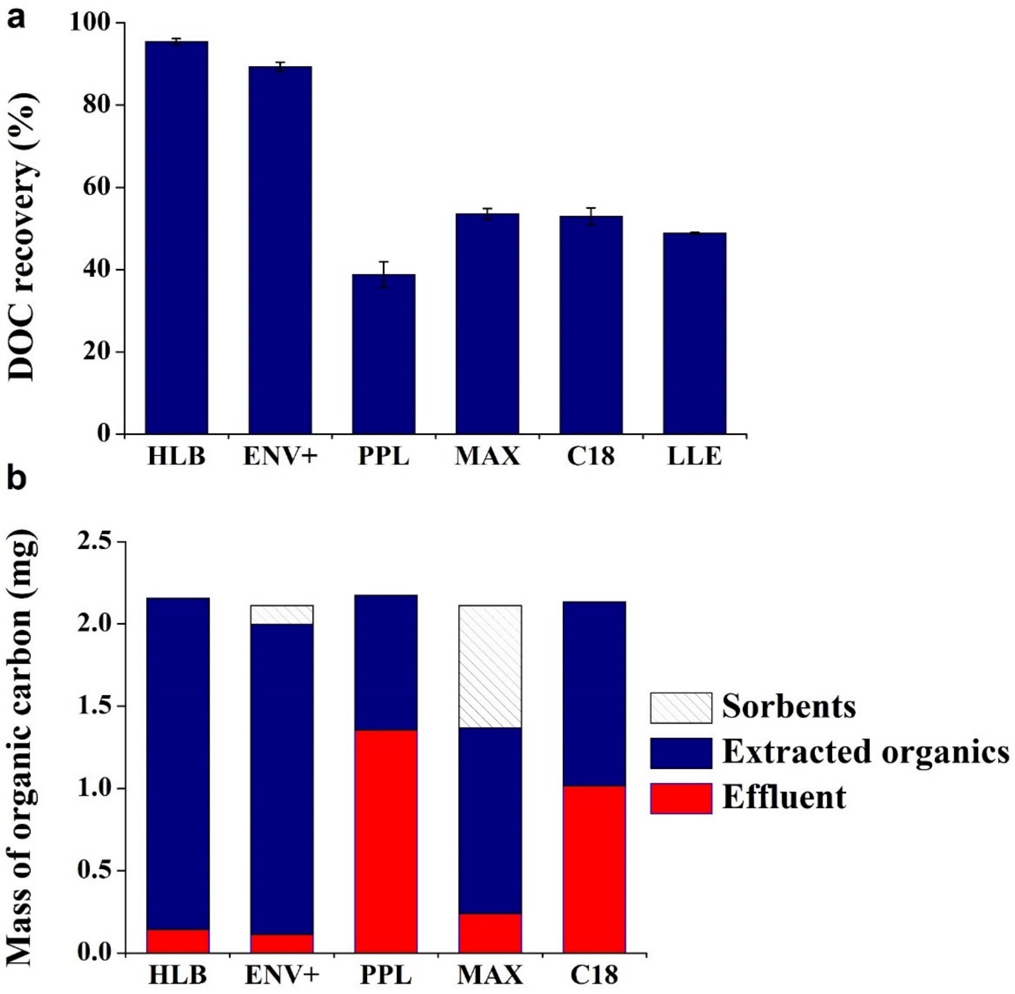

Figure 3.2 DOC recovery(a) and mass of organic carbon in effluent, extracted organics redissolution in buffer and sorbents after extraction process (b). (Note: LLE is liquid-liquid extraction by dichloromethane. $\text{DOC recovery} = {DOC_{OB}}/{DOC_{OSPW}} \times 100\%$, OB: Extracted organics redissolution in buffer).

Figure 3.2b shows the mass of the total organic carbon in effluent, reconstituted solution and cartridges after SPE process, which could exhibit the adsorption ability of the SPE sorbents and the elution ability of methanol. For HLB, PPL and C18, almost all the adsorbed organic carbon was eluted by methanol. It indicated that methanol could efficiently elute the OSPW organic carbon retained on HLB, PPL and C18 cartridges. Thus, the low DOC recovery efficiency of PPL and C18 was due to their low adsorption efficiency rather than the elution ability of methanol, which was also suggested from their low DOC removal in Figure 3.5. However, methanol could not elute all the organic matter adsorbed on both ENV+ and MAX, which resulted in lower DOC recovery, especially for MAX where around 30% of the organic DOC was not eluted by methanol.

The recovery of the NAs, which are toxic compounds of concern in OSPW, was also investigated and showed in Figure 3.3a. NA species were classified by their oxygen number, O_2-NAs to O_6-NAs. O_x-NAs were the sum of O_2-NAs to O_6-NAs. NA recovery was calculated as follows:

$$\text{NA recovery} = \frac{\text{NA}_{\text{OB}}}{\text{NA}_{\text{OSPW}}} \times 100\% \qquad (5)$$

where NA_{OB} is the concentration of NAs in the extracted organics redissolution in buffer and NA_{OSPW} is the concentration of NAs in the original whole OSPW.

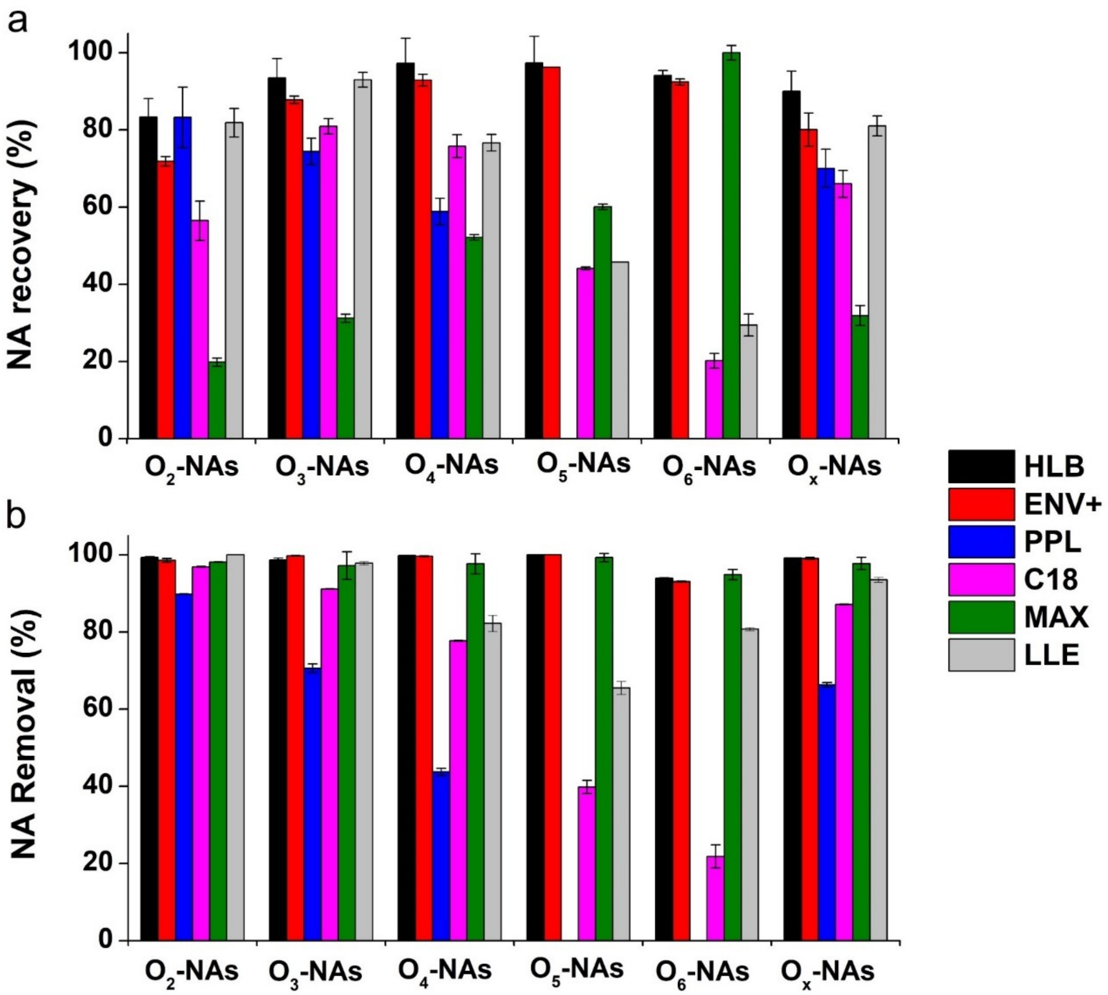

Figure 3.3 NA recovery (a), and removal (b) by SPE and LLE (Note: O_x-NAs are the sum of O_2-O_6 NAs.
NA recovery $= {NA_{OB}}/{NA_{OSPW}} \times 100\%$; $NA\ removal = {(NA_{OSPW} - NA_{EF})}/{NA_{OSPW}} \times 100\%$; , EF: Effluent, OB: Extracted organics redissolution in buffer)

Consistent with the DOC recovery efficiency, HLB cartridge achieved the highest NA recovery efficiency, with the total NA extraction efficiency of 90.0%. O_2-NAs extraction efficiency (83.3%) was lower than that of oxidized NAs (95.4%). The concentration of O_2-NAs in original OSPW, effluent of HLB cartridge and the reconstituted solution were 20.1 mg/L, 0.1 mg/L and 16.8 mg/L, respectively (Figures 3.4a, b, c). 99.3% of the O_2-NAs in OSPW was adsorbed by the HLB cartridge, while 83.3% was recovered after methanol elution. O_2-NAs recovery versus carbon number and double bond equivalence (DBE) were plotted in Figures 3.4d and 3.4e. Attenuated recovery trend for O_2-NAs with higher carbon number and hydrogen-deficiency were observed. Decreasing recovery for NAs with lower oxygen and higher carbon number indicated that methanol was not inclined to elute non-polar compounds from HLB cartridge, which was expected as methanol is considered as a polar organic solvent. Moreover, after OSPW was loaded on the HLB cartridge, 6.7% of the DOC remained in the effluent and could not be adsorbed by the HLB sorbent, while only 0.7% of NAs remained in the effluent. This indicated that some non-NA organics such as aromatic or heteroatomic compounds could not be adsorbed on the HLB sorbent and, therefore, could not be recovered by the HLB SPE process. The recovery of total NAs by DCM LLE was 81.0%, and the NA recovery attenuated with increasing oxygen number. This was likely due to the relative low polarity of DCM and thus has lower affinity with NAs that are polar. This study demonstrated that SPE method using HLB cartridge was the better alternative for the extraction of OSPW organic matter as compared to DCM LLE.

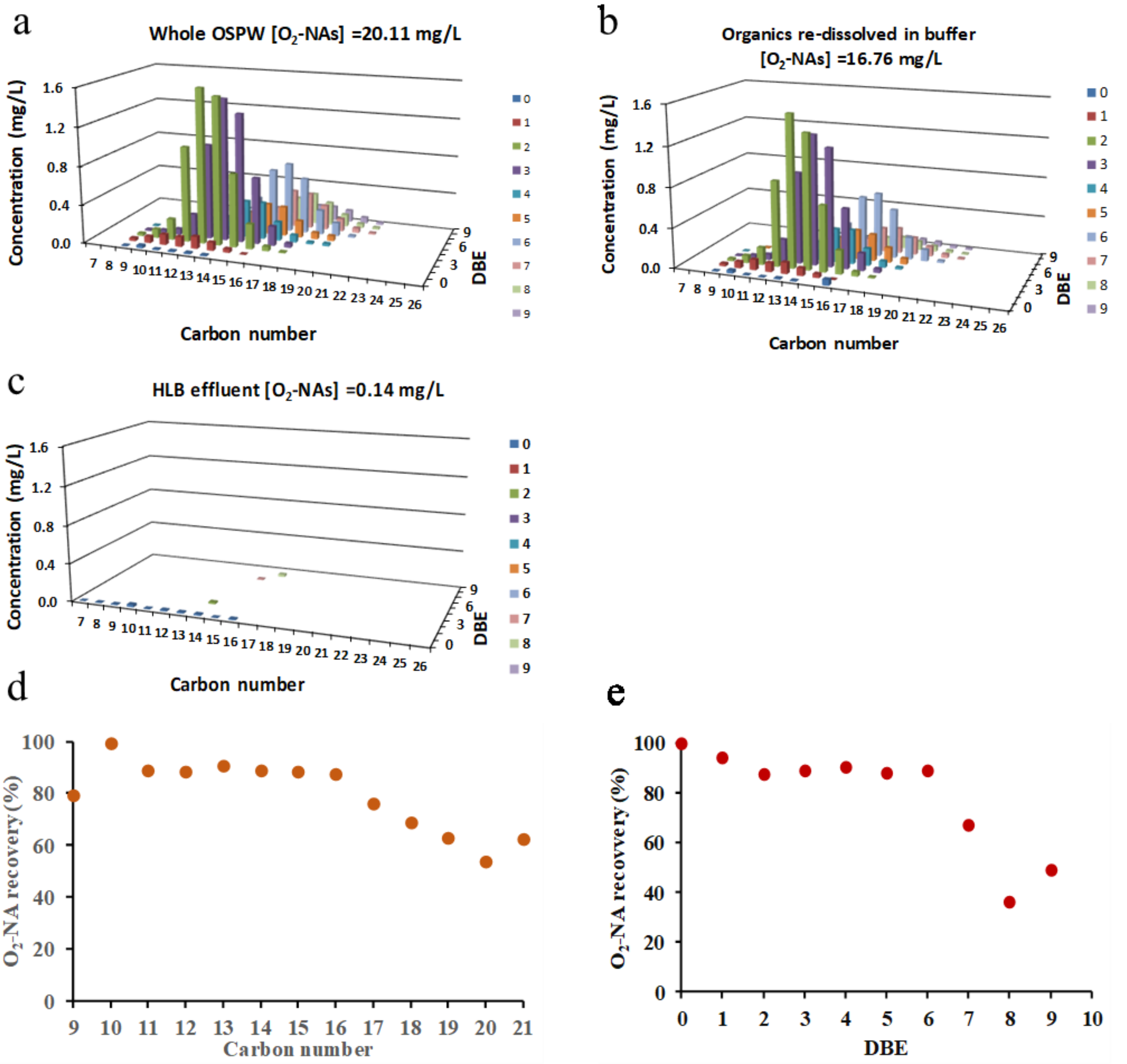

Figure 3.4 O_2-NAs distribution in (a) raw OSPW, (b) HLB extracted organics dissolved in buffer, (c) HLB cartridge effluent, O_2-NAs recovery from HLB cartridge with respect to (d) carbon number and (e) double bond equivalence (DBE).

Recently, Samanipour et al. (2019) compared the extraction recovery and distribution of NAs from oilfield produced water by SPE using HLB and the combination of ENV+ and C8 cartridges (ENV) with the solvent of hexane, DCM and 2-propanol mixture, as well as DCM LLE. Their results showed that for the ENV method achieved the best recovery of O_2-NAs, while LLE extracted the least O_2-NAs. Meanwhile, ENV method provided a more complete chemical diversity of extracted O_2-NAs. Their results were consistent with our finding that DCM LLE was not an efficient method to extract NAs compared to SPE using HLB and ENV+. However, the authors concluded that ENV method achieved a higher recovery efficiency than HLB cartridge, which was inconsistent with our results. For the ENV method by Samanipour et al. (2019), a C8 cartridge was combined with ENV+ cartridge, which enhanced the retaining of O_2-NAs. The solvent used to elute the retained organics in their study (mixture of hexane, DCM and 2-propanol) was different from what was used in our work (methanol). Their eluting solvent was relatively less polar than our eluting solvent. Moreover, the type and source of produced water used in the work by Samanipour et al. (2019) was different from what was used in our work, which may result in different characteristics and distribution of O_2-NAs and, therefore, lead to different extraction efficiency. Thus, various types of produced water originated from extensive sources could be conducted for the future research to obtain a more comprehensive results about the most efficient methods for the extraction of NAs.

Figure 3.3b shows the NA removal after SPE and LLE. NA removal was calculated as follows:

$$\text{NA removal} = \frac{\text{NA}_{\text{OSPW}} - \text{NA}_{\text{EF}}}{\text{NA}_{\text{OSPW}}} \times 100\% \quad (6)$$

where NA_{EF} is the concentration of NAs in the effluent. For LLE, NA_{EF} is the concentration of NAs in the aqueous phase after the extraction process. NA_{OSPW} is the concentration of NAs in the original whole OSPW.

The results showed that PPL removed the least of NAs (66.3%) compared with other SPE cartridges. Moreover, PPL was inclined to adsorb NAs with lower oxygen number (Figure 3.3b). This may because that the polymer PPL sorbent is modified by a non-polar surface, which enhanced the adsorption ability for non-polar compounds. Similarly, C18 preferentially retained NAs with decreasing oxygen numbers, which could be explained by the preferentially adsorption of nonpolar compounds by C18 (Yang et al., 2017). The attenuated adsorption ability of NAs with higher oxygen number by PPL and C18 also explained their lower extraction efficiency.

SFS of extracted organics redissolution in buffer by SPE and LLE provided information for the extraction efficiency of fluorescing compounds (Figure 3.5). Peak at 270 nm (I) is assigned to be one-ring aromatics or aromatics containing two or more unfused aromatic rings, peaks at 310 nm (II) and 330 nm (III) are associated with aromatics with two and three fused rings, respectively (Wang et al., 2016b). The recovery for one ring aromatics was similar for all methods with the lowest recovery of 85% by ENV+ and highest of 100% by PPL (Figure 3.5). Difference in the recovery of aromatic with two and three fused rings were observed with MAX recovered the least two and three fused rings aromatic compounds. ENV+, PPL and C18 achieved higher recovery as compared to MAX, while HLB and LLE achieved the highest recovery for both two and three fused rings aromatics. Therefore, both HLB and LLE were overall the most effective for the extraction of aromatics from OSPW. In conclusion from the organic extraction results, SPE using HLB was the most suitable method for the extraction of organic from OSPW as it has the highest recovery of overall DOC, NAs and aromatics.

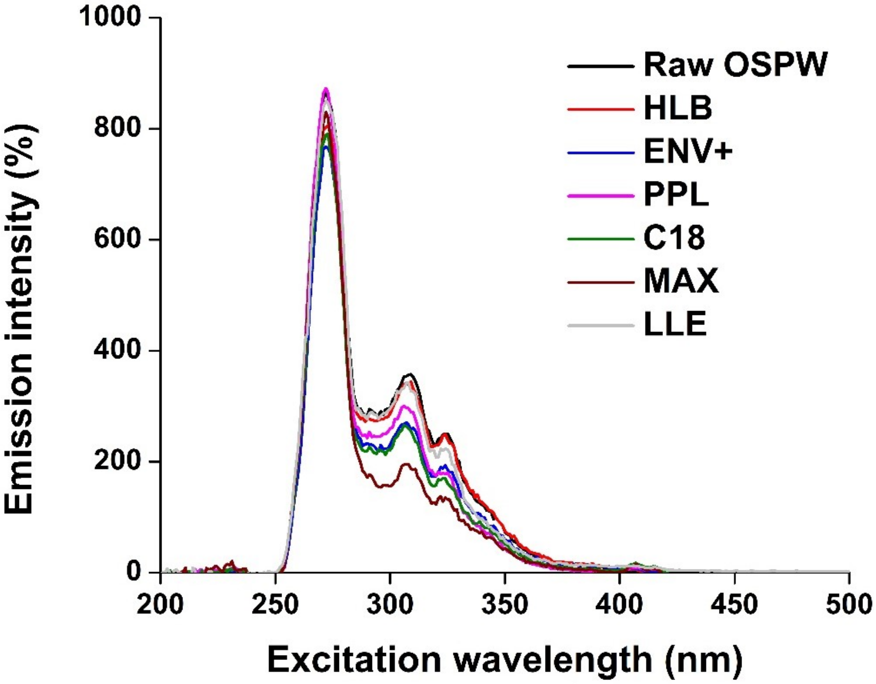

Figure 3.5 Synchronous fluorescence spectra of extracted organics redissolution in buffer by SPE and LLE

3.3.2 Isolation of OSPW Inorganic Fraction

For the adsorption of organic matter by GAC and MAX cartridges, no pH adjustment was necessary. Thus, MAX or GAC could potentially be used to isolate OSPW inorganic fraction by retaining the organics in their sorbents. As shown in Figure 3.6, GAC achieved 96.1% DOC removal, while MAX removed 88.7% of the DOC, indicating that GAC was more efficient to adsorb OSPW organic matter than MAX. The microporous structure, high interconnected porosity, high surface area, and potential functional groups of carbonaceous materials GAC would have contributed to the high organic adsorption ability from OSPW without the need of pH adjustment (Fakhru'l-Razi et al., 2009; Islam et al., 2018; Mohamed et al., 2015). The difference in properties such as pH, alkalinity, conductivity, ions concentration between original OSPW and the GAC effluent were insignificant and the adsorption and leaching of ions after the GAC adsorption were negligible (Table 3.3). Thus, GAC adsorption was able to isolate OSPW-IF that was representative of real OSPW.

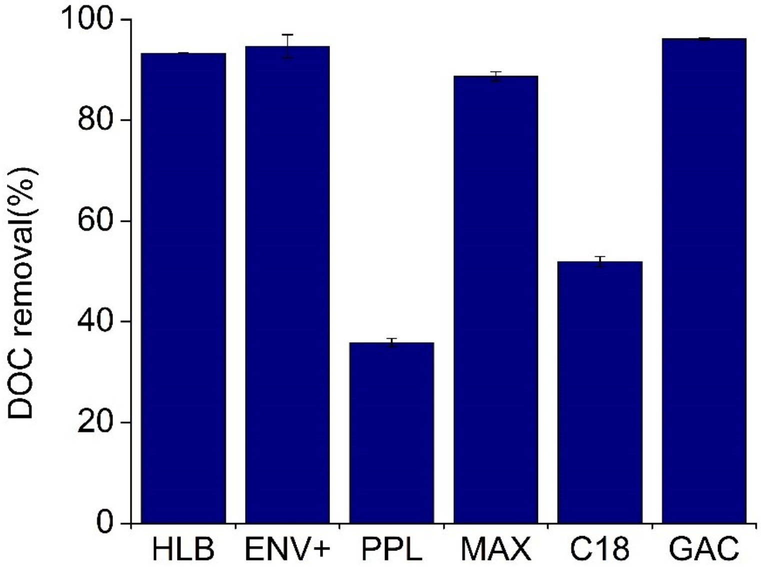

Figure 3.6 DOC removal of by SPE cartridges and GAC.

(Note: $DOC\ removal = \frac{TOC_{OSPW} - TOC_{EF}}{TOC_{OSPW}} \times 100\%$, where DOC_{OSPW} is DOC of the original OSPW and DOC_{EF} is DOC of the effluent.)

Table 3.3 Properties analysis of OSPW and the GAC effluent

Properties	OSPW	GAC effluent
pH	8.74±0.03	8.79±0.05
Alkalinity (mg/L)	485±2	482±5
DOC (mg/L)	52.78±1.21	2.04±0.11
Conductivity (μS/cm)	2.714±0.015	2.798±0.017
Analytes / Ions (mg/L)		
Lithium (Li)	0.214±0.001	0.222±0.001
Boron (B)	2.08±0.035	1.151±0.025
Sodium (Na)	695.752±8.704	723.038±9.206
Magnesium (Mg)	25.664±0.181	24.406±0.214
Aluminum (Al)	0.027±0.001	0.091±0.000
Silicon (Si)	2.755±0.113	3.619±0.427
Potassium (K)	27.006±0.061	29.316±0.433
Calcium (Ca)	16.054±0.034	14.936±0.025
Titanium (Ti)	0.008±0.000	0.01±0.000
Vanadium(V)	0.009±0.000	0.018±0.000
Chromium (Cr)	0.028±0.001	0.03±0.001
Manganese (Mn)	0.002±0.000	0.002±0.000
Nickel (Ni)	0.007±0.000	0.002±0.000
Copper (Cu)	0.023±0.000	0.015±0.004
Zinc (Zn)	0.001±0.001	0.001±0.000
Arsenic (As)	0.004±0.000	0.009±0.00
Selenium (Se)	0.003±0.000	0.003±0.000
Rubidium (Rb)	0.035±0.000	0.037±0.000
Strontium (Sr)	0.869±0.002	0.823±0.001
Molybdenum (Mo)	0.001±0.000	0.002±0.000
Antimony (Sb)	0.09±0.000	0.101±0.003
Barium (Ba)	0.003±0.000	0.004±0.000
Tungsten (W)	0.060±0.000	0.090±0.003
Uranium (U)	0.006±0.000	0.005±0.000
Anions (mg/L)		
Fluoride (F^-)	3.058±0.160	4.286±0.116
Chloride (Cl^-)	366.918±2.706	389.664±3.149
Sulfate (SO_4^{2-})	432.372±2.874	443.868±3.230
Nitrate (NO_3^-)	16.796±0.134	12.747±0.109

Figure 3.7a showed the proportion of organic carbon in effluent, organic redissolution in buffer solution and sorbent after the organic matter was adsorbed by GAC followed by the methanol elution. It showed that only 3.87% of the organic carbon was detected in the effluent after OSPW was passed through the GAC cartridge, with the DOC of the effluent to be 2.0 ± 0.1 mg/L (Table 3.3). While 96.1% organic carbon adsorbed on the GAC, only 10.1% of the organic carbon was

recovered after methanol elution. This indicated that GAC was efficient for the isolation of OSPW-IF, but not applicable to extract organic matter due to the low elution efficiency. As shown in Figure 3.7b, the recovery of all the NA species after methanol elution was relatively low with around 10%. Figure 3.7c showed that for O_2 to O_5-NAs, the recovery decreased with increasing carbon number. This is likely to be explained by the strong hydrophobic interaction between NAs with larger carbon number and the GAC (Moreno-Castilla, 2004). NAs with more carbon number is more hydrophobic, which increased their affinity on the surface of GAC. The strong affinity, in turn, made it hard for the NAs to be eluted (Pourrezaei et al., 2013). Moreover, NAs with higher carbon number contributed to relatively larger molecular size, thus they would be easily trapped by the pores but were hard to be recovered. Similarly, NAs with higher DBE had lower recovery (Figure 3.7d). Aromatic compounds can form a strong π- π dispersion interaction with the GAC surface (Moreno-Castilla, 2004), NAs with more DBE indicated an increase in aromaticity. Thus, the low recovery of NAs with increasing DBE may due to the increase in π- π dispersion interaction between the NAs and GAC.

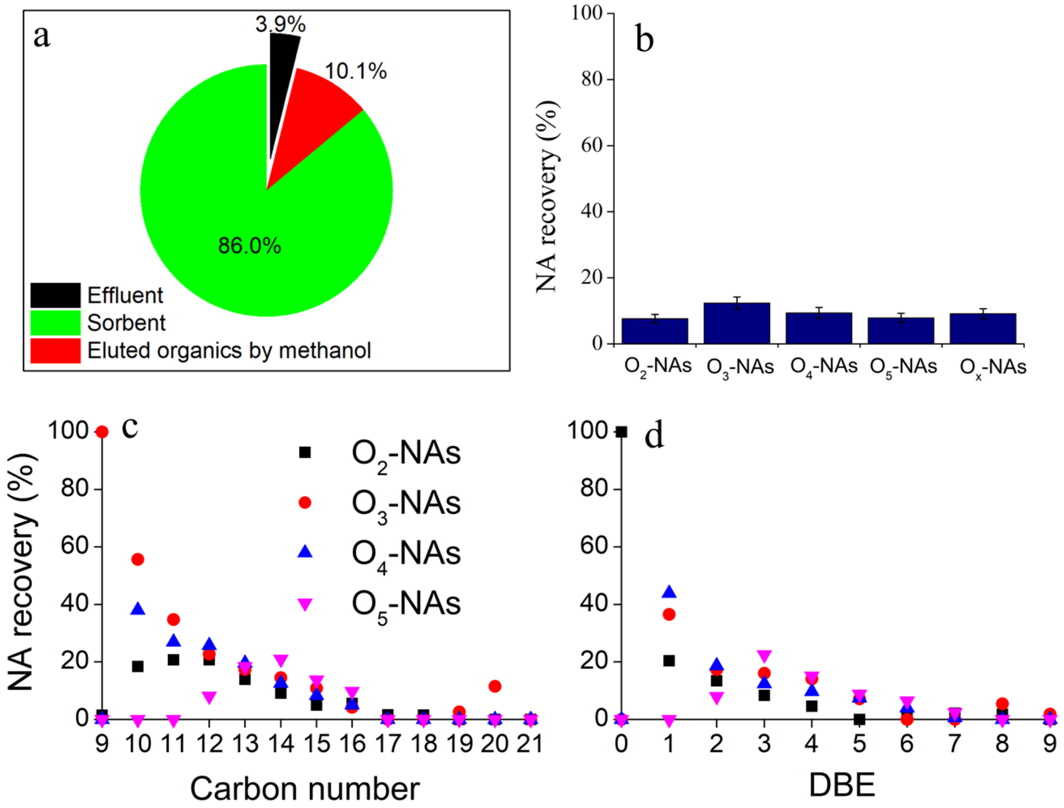

Figure 3.7 Proportion of organic carbon in effluent, eluted organics by methanol and organics retained in GAC after the organic matter adsorbed by GAC followed with the methanol elution (a), NA recovery from GAC after methanol elution (b), NA recovery for O_2, O_3, O_4 and O_5 species according to the carbon number (c), and DBE (d). (Note: O_6-NAs was not observed to be recovered. O_x-NAs is the sum of O_2-O_5 NAs).

3.4 Conclusion

HLB SPE process achieved the highest DOC and NA recovery (95.4% DOC, 90.0% O_x-NAs) as compared to other SPE cartridges and DCM LLE (48.8% DOC, 81.1% O_x-NAs), which indicated that the HLB SPE extraction method was validated to be not only suitable for the extraction of NA from OSPW but also other organic species from OSPW. This would allow the further characterization and study of other organic species in OSPW that would assist in the advancement in OSPW treatment process and on the toxicity study of OSPW.

After GAC adsorption, DOC of the effluent was 2.0 ± 0.1mg/L, with 96.1% of DOC removed. Insignificant difference in the properties between original OSPW and the GAC effluent was observed. The adsorption and leaching of ions after the GAC adsorption were negligible. Thus, GAC adsorption was able to isolate OSPW inorganic fraction that are representable to real OSPW and thus be able to be used for the study of OSPW inorganic fraction toxicity and the influence of the degradation of OSPW organics during treatment.

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Chapter 4 Assessment of Ozonation Reactivity of Aromatic and Oxidized Naphthenic Acids Species Separated Using a Silver-ion Solid Phase Extraction Method

4.1 Introduction

Increasing global energy demand has greatly encouraged the exploration and exploitation of unconventional oil reserves, such as oil sands in the northern Alberta of Canada (Kelly et al., 2009; Headley et al., 2016). However, large amounts of oil sands process water (OSPW) have been generated during the extraction process of bitumen deposits, raising public concerns due to the presence of persistent recalcitrant compounds in OSPW, such as naphthenic acids (NAs), which may adversely affect the environmental and public health (Kim et al., 2012; Kurek et al., 2013; Swigert et al., 2015; Headley et al., 2016). NAs are a complicated mixture of compounds with empirical formulae as $C_nH_{(2n+Z)}O_x$ and $C_nH_{(2n+Z)}O_yS$, where "n" is the carbon number ($7 \leq n \leq 26$), "Z" is zero or a negative even integer ($0 \leq |Z| \leq 18$) that specifies the hydrogen deficiency, and "x" and "y" represent the number of oxygen atoms ($2 \leq x \leq 5$, $2 \leq y \leq 4$) (Huang et al., 2016a). Compared to classical NAs ($x = 2$), oxidized NAs ($x > 2$) contain additional oxygen atom(s). NA species have been reported to induce acute and subchronic toxic effects to aquatic organisms through multiple modes of action, including narcosis, endocrine disruption, immunotoxicity, and carcinogenicity (Hagen et al., 2012; He et al., 2012; Tollefsen et al., 2012; Scarlett et al., 2013). Recent effects-directed analysis studies confirmed that classical NAs (O_2 species) are the toxic acid-extractable organics (AEO) in OSPW and some O_x−NAs ($x=2-4$, $n=17-20$, and $|Z|=6-10$) are estrone- and estradiol-like compounds with estrogenicity effects (Morandi et al., 2015; Yue et al., 2015), bringing attention to the investigation of stringent treatment measures to remove NAs from OSPW.

Ozonation is a common treatment method used to degrade most of organic pollutants in OSPW, although some recalcitrant organics may still be present after ozonation (Pereira et al., 2013). It has been reported that ozonation ameliorates the OSPW toxicity to the mammalian immune system (Garcia-Garcia et al., 2011). Also, ozonation can partially mitigate the OSPW anti-androgenicity as well as androgen potentiating effect, without increasing estrogen potency (He et al., 2011). Ozonation could be used as a pre-treatment step prior to other treatments (e.g., wetland biodegradation). For instance, studies have showed that ozonation of OSPW could selectively oxidize the most biopersistent NA fraction, thereby accelerating the NA biodegradation by microbial bioremediation (Martin et al., 2010; Zhang et al., 2016).

To investigate the oxidation mechanisms, model carboxylic acids such as cyclohexanoic acid were previously selected to study the ozonation process (Kumar et al., 2014; Afzal et al., 2015). However, there is no substantial evidence to confirm that these model compounds are actually present in OSPW. Commercial NA mixtures have also been used to study ozonation. It has been reported that the degradation of commercial NAs was found via hydrogen abstraction reactions of the hydroxyl (•OH) radical with NA molecules, and that reactivity was observed to increase along with the carbon and |Z| numbers of NAs (Perez-Estrada et al., 2011). It is worth noting that commercial NAs were comprised of only classical NAs without oxidized NAs and aromatic NAs, all of which are present in natural occurring NAs (Huang et al., 2016a). To date, studies regarding ozonation of OSPW reported that molecular ozone and free •OH radicals play important roles in the degradation of NAs. However, the possible oxidation mechanisms for distinct NA species have not been reported because the complexity of dissolved organics and the saline matrix in OSPW prevent further investigation (Wang et al., 2013; Klamerth et al., 2015; Meshref et al., 2017a). Klamerth et al. (2015) studied the ozonation of OSPW fractions from pH-dependent fractionation extractions; however, because the dissociation constants of individual NA species were close, distinct NA species could not be well separated via pH-dependent sequential liquid-liquid extractions (Perez-Estrada et al., 2011; Klamerth et al., 2015). The investigation of ozonation processes for different NA species remains a challenge, due to the difficulties to separate the distinct NA species before ozonation treatment.

Silver-ion solid phase extraction (Ag-ion SPE) was able to separate different NA species into SPE fractions without the requirement of pre-methylation for NAs, thus these SPE fractions could be applied for subsequent ozonation directly without conducting de-methylation process (Huang et al., 2016a). The Ag-ion SPE process simplified the composition of OSPW NAs and removed the matrix salinity, facilitating further investigation of ozonation process for individual NA species. In short, this work aims to study the ozonation process for individual NA species that were separated from OSPW via Ag-ion SPE as classical, aromatic, oxidized, and sulfur-containing NAs, to enhance the understanding of ozonation mechanism in order to facilitate future related treatment and toxicological studies (Huang et al., 2016a; Meshref et al., 2017a). Ultra-performance liquid chromatography ion mobility time-of-flight mass spectrometry (UPLC-IM-TOF-MS) was used to characterize NA species in untreated and ozonated SPE fractions to provide qualitative comparison with relative abundances, despite the quantification capacity is currently not available for UPLC-IM-TOF-MS analysis (Huang et al., 2015a; Huang et al., 2016a; Paglia and Astarita, 2017). This work studied the ozonation reactivity of aromatic and oxidized NA species for the first time and the impacts of carbon and Z numbers on their reactivity. Understanding the reactivity of different NA species is beneficial for the design of treatment approaches for OSPW. In particular, the results of the present study can be used to evaluate degradation rates, pathways and persistence. This will help to design possible discharge and/or reclamation scenarios and to develop targeted treatment strategies.

4.2 Experimental Methods

4.2.1 Reagents and Materials

OSPW was collected in December 2014 from a tailings pond located in Fort McMurray, Alberta, Canada, and stored at 4 °C prior to use. OSPW was stable under this storage condition given the natural degradation half-lives for OSPW NAs were reported as 13 years in the field (Han et al., 2009). Sulfuric acid (H_2SO_4) and sodium bicarbonate ($NaHCO_3$) (Sigma-Aldrich, Canada) were used to adjust the solution pH and alkalinity for the ozonation experiments, respectively. Dichloromethane, hexane, and acetone (Fisher Scientific, Canada) were used in the liquid−liquid extraction and/or solid phase extraction processes. A Discovery Ag-ion SPE cartridge (Sigma-Aldrich, Canada) was used for SPE separation of NA species from OSPW. Optima-grade water, methanol, and acetonitrile (Fisher Scientific, Canada) were used in the instrumental analysis.

4.2.2 Ag-Ion Solid Phase Extraction

Raw OSPW was fractionated using an Ag-ion SPE cartridge to provide fractions for subsequent ozonation experiments. Prior to the Ag-ion SPE process, the samples were extracted and dissolved in hexane. However, liquid−liquid extraction directly using hexane could change the composition of NA species from OSPW (Huang et al., 2016b). Therefore, the raw OSPW was firstly extracted using dichloromethane (DCM). OSPW was centrifuged at 10,000 rpm for 10 min to remove the suspended particles. The H_2SO_4 solution (1.8 M) was added dropwise to adjust the pH of the OSPW supernatant (natural pH 9.4) to 1.0 prior to extraction. A 500 mL sample was extracted with 250 mL of DCM (90, 80, and 80 mL sequentially with a sample to total solvent ratio of 2:1). The organic layers were separated, combined (~250 mL), and air-dried completely in a fume hood at room temperature. The dried fraction was re-dissolved into 10 mL hexane and stored at 4 °C prior to use.

For Ag-ion solid phase extraction, the Ag-ion SPE cartridge was preconditioned using 5 mL acetone for three times and then pre-equilibrated using 5 mL hexane for three times. The OSPW extract (5 mL) was loaded onto the cartridge and then rinsed using 5 mL hexane for three times. SPE fractions were achieved by varying the composition and polarity of the eluent solvent mixture. The elution process was optimized as follows: fractions 1−7 (F1−F7) using 5 mL of a 97:3 (v/v) hexane/acetone mixture for eluting each fraction, F8−F12 using 5 mL of a 93:7 (v/v) hexane/acetone mixture for each fraction, F13−F16 using 5 mL of an 85:15 (v/v) hexane/acetone mixture for each fraction, F17−F19 using 5 mL of a 75:25 (v/v) hexane/acetone mixture for each fraction, and F20 using 5 mL of acetone. The 100% acetone for F20 was applied to elute the remaining NAs from the SPE cartridge (Huang et al., 2016a). The SPE fractions were collected in test tubes, which were weighed precisely before use, and air-dried completely in the fume hood at room temperature. The test tubes with dried fractions were weighed again to give the mass of each fraction (Table 4.1). Each dried fraction was re-dissolved using 1 mL water and stored at 4 °C prior to analysis.

4.2.3 Ozonation Treatment

The ozonation of SPE fractions was performed by adding the ozone stock solution to the re-dissolved fractions. The ozone stock solution was prepared by sparging ozone with an ozone generator (Model GLS-7, PCI-WEDECO, Herford, Germany) into 1 L optima-grade water continuously for 2 hours in an ice bath. The concentration of the ozone stock solution was calibrated by determining the UV absorbance at 260 nm using a UV-vis spectrophotometer (Varian Inc., Santa Clara, CA, USA). An absorption coefficient ε (260 nm) of 3200 $M^{-1}\cdot cm^{-1}$ was adopted to calculate the ozone concentration as 42.0 ± 0.3 mg/L (Ramseier et al., 2011; Sonntag and von Gunten, 2012). Given the small volume of Ag-ion SPE fraction, the ozonation was performed via the addition of ozone stock solution to the SPE fractions in capped vials with no head space. Immediately after the preparation of ozone stock solution, the ozonation tests were performed in 2 mL capped vials with two applied ozone dosages. The first dosage used 300 µL re-dissolved fraction with addition of 100 µL 200 mM $NaHCO_3$, 800 µL ozone stock solution, and 800 µL water, resulting in a final ozone dosage of 16.8 mg/L and alkalinity of 10 mM $NaHCO_3$. The second dosage used 300 µL re-dissolved fraction with addition of 100 µL 200 mM $NaHCO_3$, 1600 µL ozone stock solution, resulting in a final ozone dosage of 33.6 mg/L and alkalinity of 10 mM $NaHCO_3$. The addition of $NaHCO_3$ provided similar alkalinity (10 mM $NaHCO_3$) to that in OSPW (Pourrezaei et al., 2011; Wang et al., 2015), and a pH between 8 and 9, typical values in real OSPW (Marti et al., 2010; Meshref et al., 2017b). The 2 mL capped vials were sealed with no air remaining inside, placed at room temperature overnight to allow complete consumption of ozone, and then stored at 4 ºC before analysis.

4.2.4 Instrumental Analysis

The UPLC-IM-TOF-MS method was applied to achieve two-dimensional (2D) separation (drift time vs retention time) with integrated travel wave ion mobility mass spectrometry (TWIMS) (Synapt G2, Waters Canada). The drift time of TWIMS provided an extra dimension for the separation of molecules based on relative molecule sizes. The chromatographic separations were performed using a Waters UPLC Phenyl-BEH column (1.7 µm, 150 mm × 1 mm) with a prefilter (0.2 µm). The mobile phases consisted of 10 mM ammonium acetate in water (A) and 10 mM ammonium acetate in a 50:50 methanol/acetonitrile mixture (B). The elution gradient was as follows: 0 to 2 min, 1% B; 3 min, 60% B; 7 min, 70% B; 13 min, 95% B; 14 min, back to 1% B until 20 min to equilibrate the column at a flow rate of 100 µL/min. The column temperature was 50 °C, while the sample temperature was 10 °C. The UPLC method was developed and verified previously (Huang et al., 2015b, 2016b, 2017). The samples were analyzed with the electrospray ionization (ESI) source, operated in negative-ion mode, TWIMS in mobility TOF mode, and the TOF analyzer in high-resolution mode (mass resolution of ∼40,000 at m/z 1431). The gas control was set as 0 mL/min source, 2.0 mL min^{-1} trap, 180 mL/min helium cell, and 90 mL min^{-1} for IMS. The data acquisition process was controlled using MassLynx (Waters Canada), and the peak detection from 2D separation spectra was performed using DriftScope (Waters Canada). The "peak detection" algorithm parameters were as follows: chromatographic mode; minimal chromatographic peak width, 2.0 min; drift peak width range, 8−42 bins (bin is the drift time unit); and minimal intensity threshold (MIT) set as 100 counts for untreated fractions and 50 counts for ozonated fractions.

4.3 Results and Discussion

4.3.1 UPLC-IM-TOF-MS Analysis of Untreated and Ozonated SPE Fractions

The Ag-ion SPE has been utilized to separate classical, aromatic, oxidized, and sulfur-containing NAs from OSPW using a mixture of hexane and acetone as the eluent solvent (Huang et al., 2016a). The Ag-ion SPE method was able to separate the different NA species based on the degree of saturation without the requirement of pre-methylation (Huang et al., 2016a). The polarity indexes for hexane and acetone are 0.1 and 5.1, respectively (Snyder et al., 2010). In this study, the separation method was optimized based on previous study by gradually increasing the percentage of acetone in the eluent solvent (3% for fraction 1- fraction 7 (F1-F7), 7% for F8-F12, 15% for F13-F16, 25% for F17-F19, and 100% for F20) (Figure 4.1). Compared to previous elution curve (Huang et al., 2016a), current elution curve increased the percentage of acetone for the elution of SPE fractions 13-19, to flush out earlier the compounds (e.g., O_4− and O_5−NAs) with high affinity to the solid phase, facilitating subsequent investigation of chemical reactions of those species in the ozonation experiments.

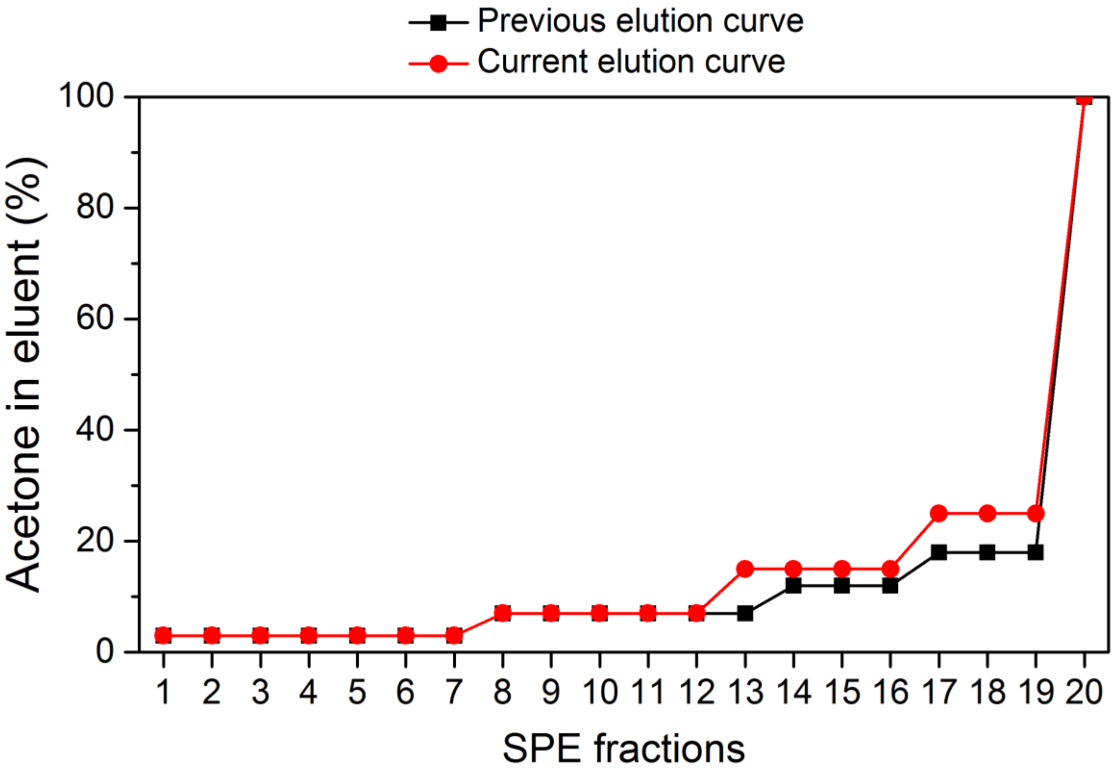

Figure 4.1 Percentage of acetone in the eluent in the current elution curve compared with the previous elution curve (Huang et al., 2016a).

The Ag-ion SPE fractions before and after ozonation were characterized by two-dimensional (2D) drift time versus retention time separation using UPLC-IM-TOF-MS, and O_x–NAs ($2 \leq x \leq 5$) and O_yS–NAs ($2 \leq y \leq 4$) species were identified using accurate mass matching (Appendix A Figure A1-A3). The results shown in Figures A1-A3 indicated that, in general, the polarity of NA compounds followed the order as classical O_2–NAs < aromatic O_2–NAs < O_2S–NAs < O_3–NAs < O_3S–NAs ~ O_4S–NAs < O_4–NAs < O_5–NAs, based on the fact that high polarity of compounds reduces the retention time on a reversed phase column (Snyder et al., 2010). This is consistent with previous results of UPLC-IM-TOF-MS analysis of raw and ozonated OSPWs (Huang et al., 2016a). The comparison of intensity for individual NA species is shown in Figure 4.2 for O_x species and Figure 4.3 for O_yS species that were detected with low intensity. This work mainly focused on the investigation of ozonation transformation of O_x–NA species rather than O_yS–NA species because the removal of O_yS–NA based on low detected intensities could not reliably reveal the chemical processes involved during the ozonation of those species (Figure 4.6).

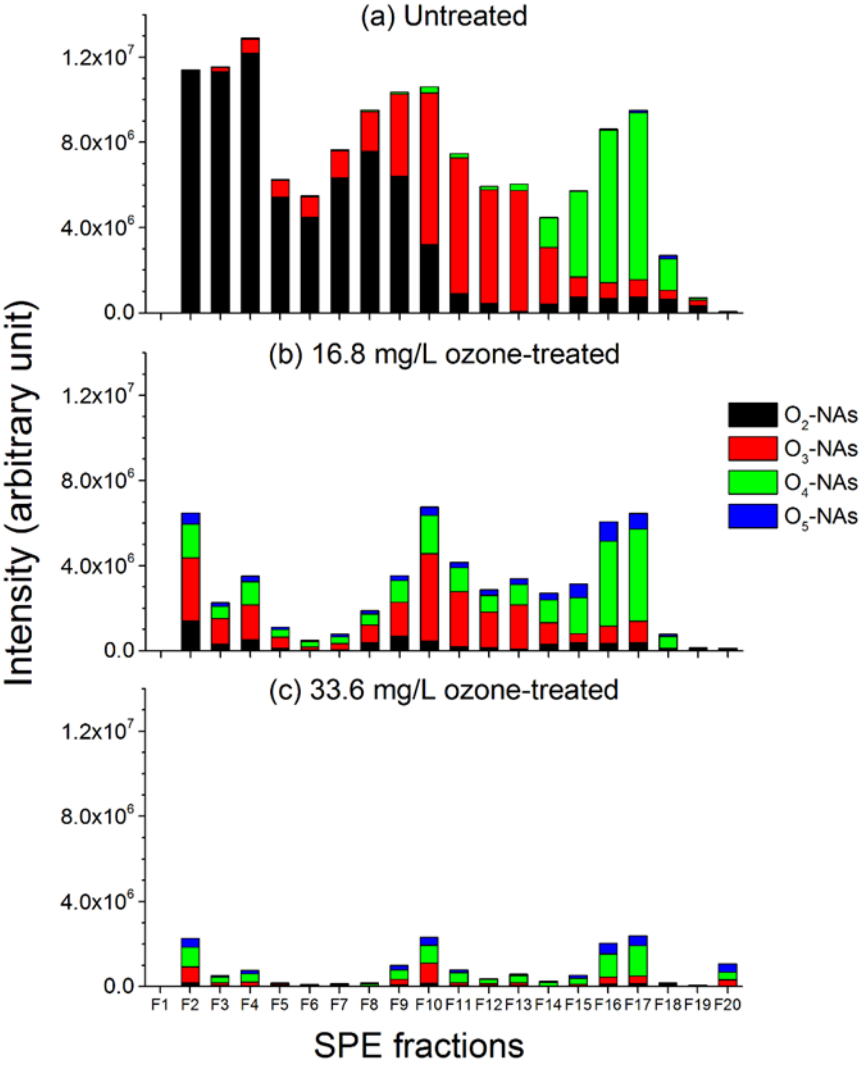

Figure 4.2 Intensities (peak areas) of O2-, O3-, O4-, and O5- NAs in the untreated Ag-ion SPE fractions (a) and ozonated SPE fractions with applied ozone dosage of 16.8 mg/L (b) and 33.6 mg/L (c), obtained from UPLC-IM-TOF-MS measurements.

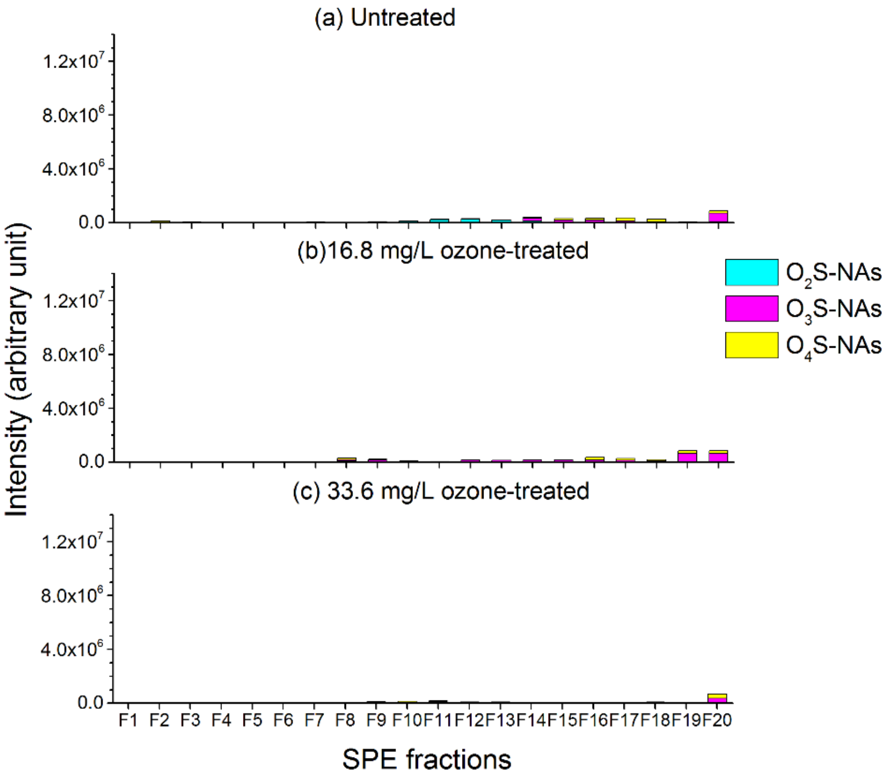

Figure 4.3 Intensities (peak areas) of O_2S-, O_3S-, and O_4S-NAs in untreated Ag-ion SPE fractions (a) and ozonated SPE fractions with applied ozone dosages of 16.8 mg L^{-1} (b) and 33.6 mg/L obtained from UPLC-IM-TOF-MS measurements (c).

Figure 4.2a shows that, in untreated fractions, O_2-NAs were mainly separated into fractions F2-F9. Given the aliphatic and aromatic O_2-NAs were clearly separated as different clusters in 2D separation maps (Figures A1-A3), the results showed that F2-F5 comprised of mainly aliphatic O_2-NAs, F7-F9 comprised of mainly aromatic O_2-NAs, and F6 comprised of both species. O_3-NAs and O_4-NAs were mainly fractionated into fractions F10-F14 and F15-F18, respectively. O_5-NAs were found in F17-F19 with low intensity. Compared to previous work (Huang et al., 2016a), O_4-NAs were better separated due to the improved elution curve in Figure 4.1, though O_5-NAs were still not well separated. After ozonation, dosage responses were clearly observed for the two applied ozone dosages (Figure 4.5b & 4.5c), indicated by the decrease of intensity of O_x−NAs. The intensity of O_5−NAs, as ozonation products, increased after ozonation in all fractions.

4.3.2 Ozonation Patterns for Aliphatic and Aromatic O_2−NAs and Oxidized NAs in Terms of Carbon and Z Numbers

Figure 4.7 shows that the fraction F3 comprised of 97.6% O_2−NAs (mainly aliphatic O_2−NAs), F8 comprised of 79.5% O_2−NAs (mainly aromatic O_2−NAs), F11 comprised of 82.5% O_3−NAs, and F17 comprised of 79.2 % O_4−NAs, based on the measured abundances. Given the predominant species in respective fractions were higher than 79.2%, these four fractions were used to further investigate the ozonation processes of individual NA species. After ozonation, aliphatic O_2–NAs in F3 were removed by 97.2% (16.8 mg/L ozone) and 99.5% (33.6 mg/L ozone), respectively (Figure 4.5). Abundances of O_3–NAs, O_4–NAs, and O_5–NAs increased because they were ozonation products from aliphatic O_2−NAs (Sun et al., 2014; Huang et al., 2015a). The degradation of organic contaminants typically occurs through reactions with molecular ozone or free •OH radicals in the solution. Although direct reaction between ozone and aliphatic carbon is a slow process, it is still kinetically competitive to the radical reaction due to the high concentration of molecular ozone in the solution. Therefore, both pathways are kinetically active in the oxidization of aliphatic NAs (Wang et al., 2016b). Previous study with utilization of an •OH scavenger reported that the molecular ozone pathway was responsible for 40-50% of the degradation of O_2−NAs (Meshref et al., 2017b), which included both aliphatic and aromatic O_2−NAs without pre-separation.

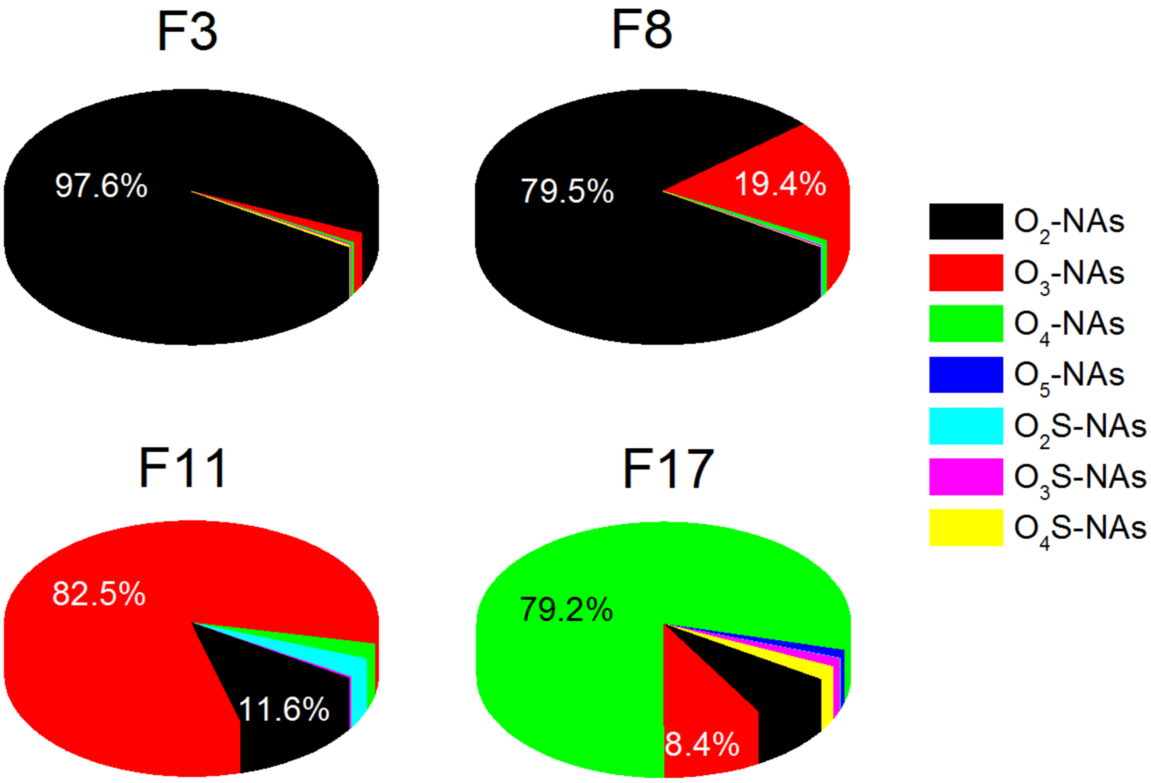

Figure 4.4 Composition of NA species in the SPE fractions F3, F8, F11 and F17, which were selected to further study the aliphatic O_2−NAs, aromatic O_2−NAs, O_3−NAs, and O_4−NAs, respectively, due to their dominant abundances. The aliphatic O_2−NAs (F3) and aromatic O_2−NAs (F8) were present as separate clusters on 2D maps based upon retention time versus drift time.

Aromatic O_2–NAs in F8 were degraded by 94.7% and 99.5% after ozonation with 16.8 and 33.6 mg/L ozone, respectively (Figure 4.5). Molecular ozone selectively reacts with electron-rich compounds such as unsaturated hydrocarbon and aromatic compounds via electrophilic addition, during which process, oxy-compounds such as carboxylic acids, aldehydes, ketones and alcohols are produced (von Gunten, 2003; Lee and von Gunten, 2010; Phungsai et al., 2016). Compared to ozonated F2 in Figure 4.2c, much less oxidized NAs were produced in ozonated F8, because after reaction with molecular ozone, aromatic groups were broken down into smaller molecules that may not be measured using negative ESI (Beltran, 2004). Given the high reactivity of molecular ozone towards aromatics and the much higher concentration of molecular ozone than •OH radical in the solution (Beltran, 2004; Wang et al., 2016b), the molecular ozone pathway may play critical role in the ozonation of aromatic O_2–NAs.

Previous studies showed that the abundance of oxidized NA species increased after ozonation of raw OSPW (Huang et al., 2016a; Wang et al., 2016a). However, the reactivity of oxidized species towards ozone could not be revealed, because without separation of oxidized NAs from classical NAs, both production and degradation of oxidized NAs occurred during the ozonation process. In this study, oxidized NAs were largely separated from other NA species before ozonation, thus the interference from new production during treatment process was minimized to provide accurate estimation of their degradation. After treatment with 16.8 and 33.6 mg/L ozone, the removals of O_3–NA (F11) were 59.4% and 97.9%, while the O_4–NA removals (F17) were 44.7% and 81.9%, respectively. The percentage removals of O_3– and O_4–NA species were lower than those of aliphatic and aromatic O_2–NAs, because O_3– and O_4–NAs were recalcitrant at low ozone dosages (Klamerth et al., 2015).

Figure 4.8 shows that aliphatic and aromatic O_2–NAs, O_3–NAs, and O_4–NAs with higher carbon number were preferably degraded with either applied ozone dosage. The trend of O_2–NAs is consistent with previous results about ozonation of raw OSPW (Wang et al., 2013; Wang et al., 2016b), and furthermore in this work, oxidized NAs were observed with the same trends. The main process of reaction between •OH and organic compounds is H-abstraction (Glaze, 1987; Perez-Estrada et al., 2011). Organic compounds with larger carbon number could provide more available hydrogen, which contributes to the H-abstraction process to happen (Wang et al., 2013). The increasing removal of O_2–NAs with higher |Z| in F2-F4 and F7-F9 was observed (Figure 4.9), which is consistent with previous results about ozonation of raw OSPW (Gamal El-Din et al., 2011;

Wang et al., 2013; Wang et al., 2016b). Higher NA removal at higher |Z| attributes to the increasing numbers of tertiary carbons and/or increasing hydrogen deficiency. H abstraction is easier to happen with H atoms on the tertiary carbon than those on the secondary or primary carbon as the carbon centered radical production after the H abstraction on the tertiary carbon is more stable (Perez-Estrada et al., 2011).

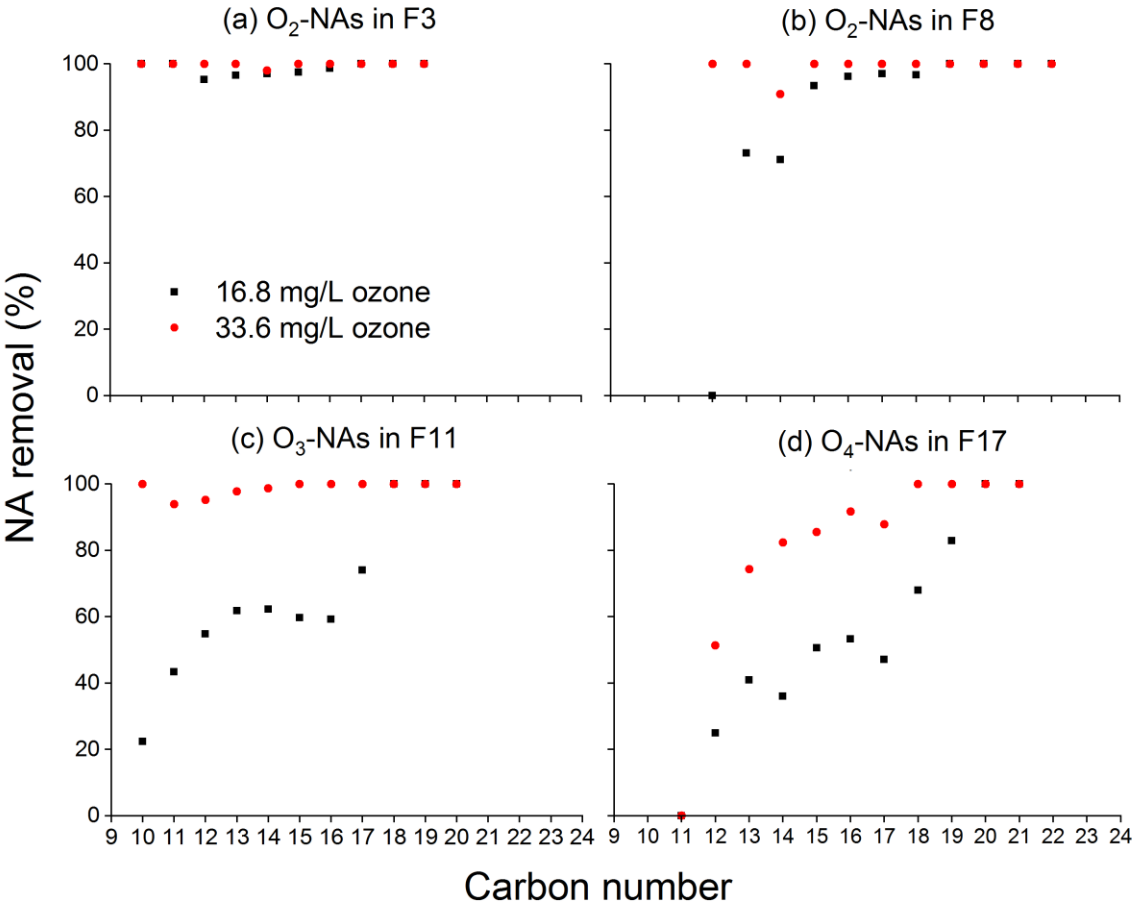

Figure 4.5 Removal of dominant NA species in the SPE fractions F3 (a), F8 (b), F11 (c) and F17 (d) in terms of carbon number, with applied ozone dosages of 16.8 and 33.6 mg/L. The O_2-NAs were mainly aliphatic in fraction F3 and aromatic NAs in fraction F8, The NA removal was calculated based on the reduced intensity of O_2-, O_3- or O_4-NA from ozone treated fractions compared to the intensity of that from untreated fractions.

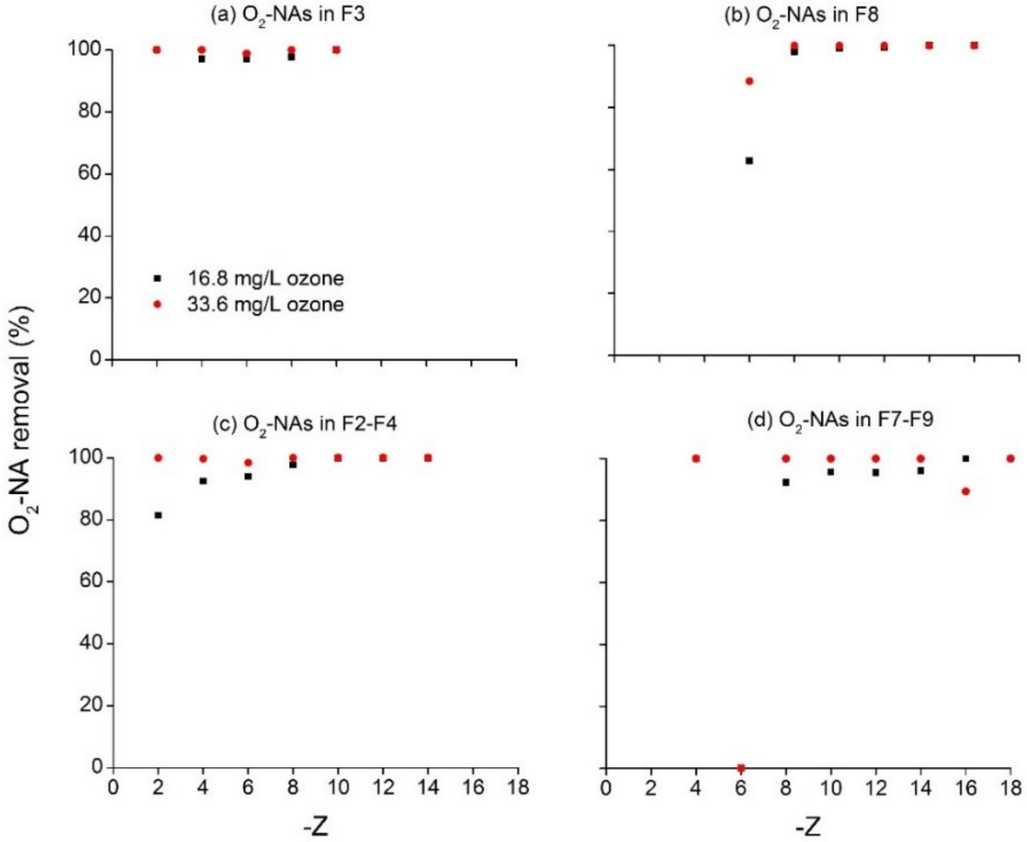

Figure 4.6 Removal of O_2−NA species in the SPE fractions F3 (a), F8 (b), F2-F4 (c), and F7-F9 (d), in terms of Z number, with applied ozone dosages of 16.8 and 33.6 mg/L.

The ozonation reactivity of aliphatic O_2−NAs specie increased along with carbon number due to the number of H atoms available for •OH attack on the NA structure increased along with the carbon number. Similarly, the NA reactivity increased along with the number of rings due to increasing numbers of tertiary carbon atoms that are introduced to a structure by the presence of each ring. No obvious change of the carbon number distribution of the oxidized species was observed. However, ozonation shifted the hydrogen deficiency distribution towards higher |Z| number due to the generation of carbonyl groups such as ketone, aldehyde, and carboxyl groups as reported previously (Wang et al., 2016a).

In order to verify the reactivity of NAs with high carbon number, NA species in the dominant fractions were combined to observe the removal of the sum of O_2–NAs and O_x–NAs (i.e., oxidized NAs). Figures 4.7 a,c,e,g show the removal of aliphatic O_2–, aromatic O_2–, O_3–, and O_4–NAs with different carbon number in the combined fractions. The results confirmed the positive correlation between higher carbon number and higher removal of NAs. In addition, as showed in Figure 4.5 and discussed above, O_3–, O_4–, and O_5–NAs (oxidized NAs) were produced after ozonation treatment. Their production and degradation happened simultaneously during the ozonation process. The removal of O_x–NAs (sum of O_x–NAs) considered the transformation of NA species and provided an overall ozonation reactivity of OSPW NAs (Figures 4.7 b,d,f,h). The results showed that O_x–NAs with larger carbon number achieved high ozonation reactivity, which demonstrated that the production of oxidized NAs did not influence the high reactivity of NAs with large carbon number given their reactivity was sustained by the relatively abundant reactive sites in their molecular structure.

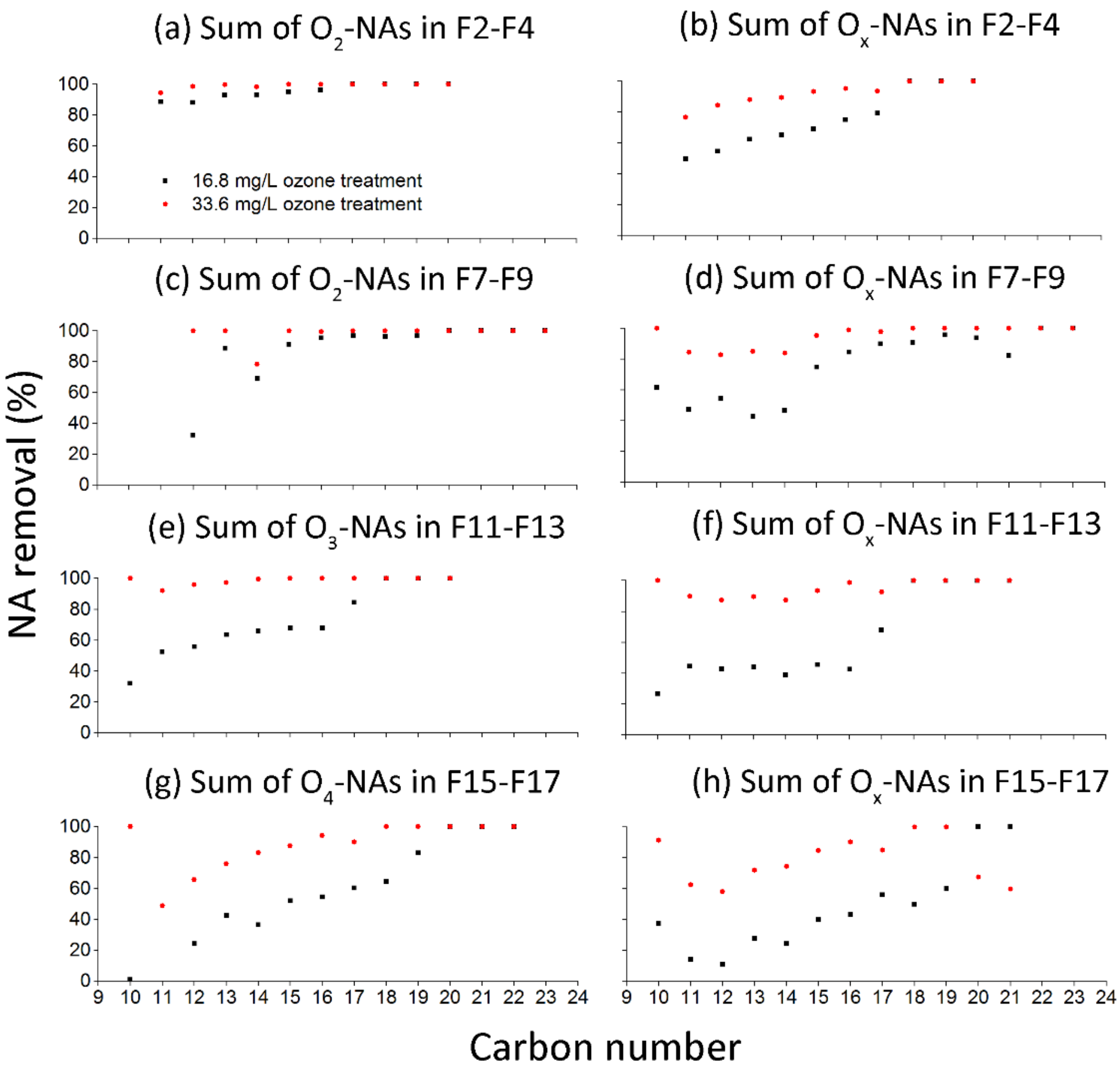

Figure 4.7 Removal of O_2−NAs, O_3−NAs, O_4−NAs (a,c,e,g) and O_x−NAs (b,d,f,h) in combined fractions, in terms of the carbon number, after ozonation with applied dosages of 16.8 and 33.6 mg/L. The NA removal was calculated based on the reduced intensity of O_2−, O_3−, O_4−, or O_x−NAs from ozone-treated fractions compared to the intensity of that from untreated fractions.

The NAs in this work were fractionated into different NA species prior to ozonation experiments. The high reactivity of aromatic NAs as well as NAs with large carbon number and hydrogen deficiency in this research is in accordance with the previous study about the ozonation of commercial NAs and raw OSPW (Perez-Estrada et al., 2011; Wang et al., 2013; Wang et al., 2016b).

4.3.3 Reactivity of Individual NA Species Towards Ozone

Figure 4.8 presents the percentage removal of O_x−NAs and the ozone utilization for O_x−NAs removal in each fraction with applied ozone dosages of 16.8 and 33.6 mg/L. Figure 4.8a shows that after 16.8 mg/L ozone treatment, the removal of oxidized NAs (F10-F17) was lower than that of aliphatic and aromatic O_2−NAs (F3-F9); while after 33.6 mg/L ozone treatment, the removal of oxidized NAs (F10-F17) was dramatically improved and was comparable to O_2−NA removal (F3-F9). The low removal of oxidized NAs at low ozone dosage may be caused by their high resistance to ozonation compared to aliphatic and aromatic O_2−NAs. It is worth noting that the calculated percentage removal and ozone utilization for O_x−NAs in F2 may be influenced by the sample matrix compounds, because F2 contained unknown organics that may interfere the ozonation of NAs (Table 4.1 shows the extraction mass for F2 was much higher than that for the other fractions).

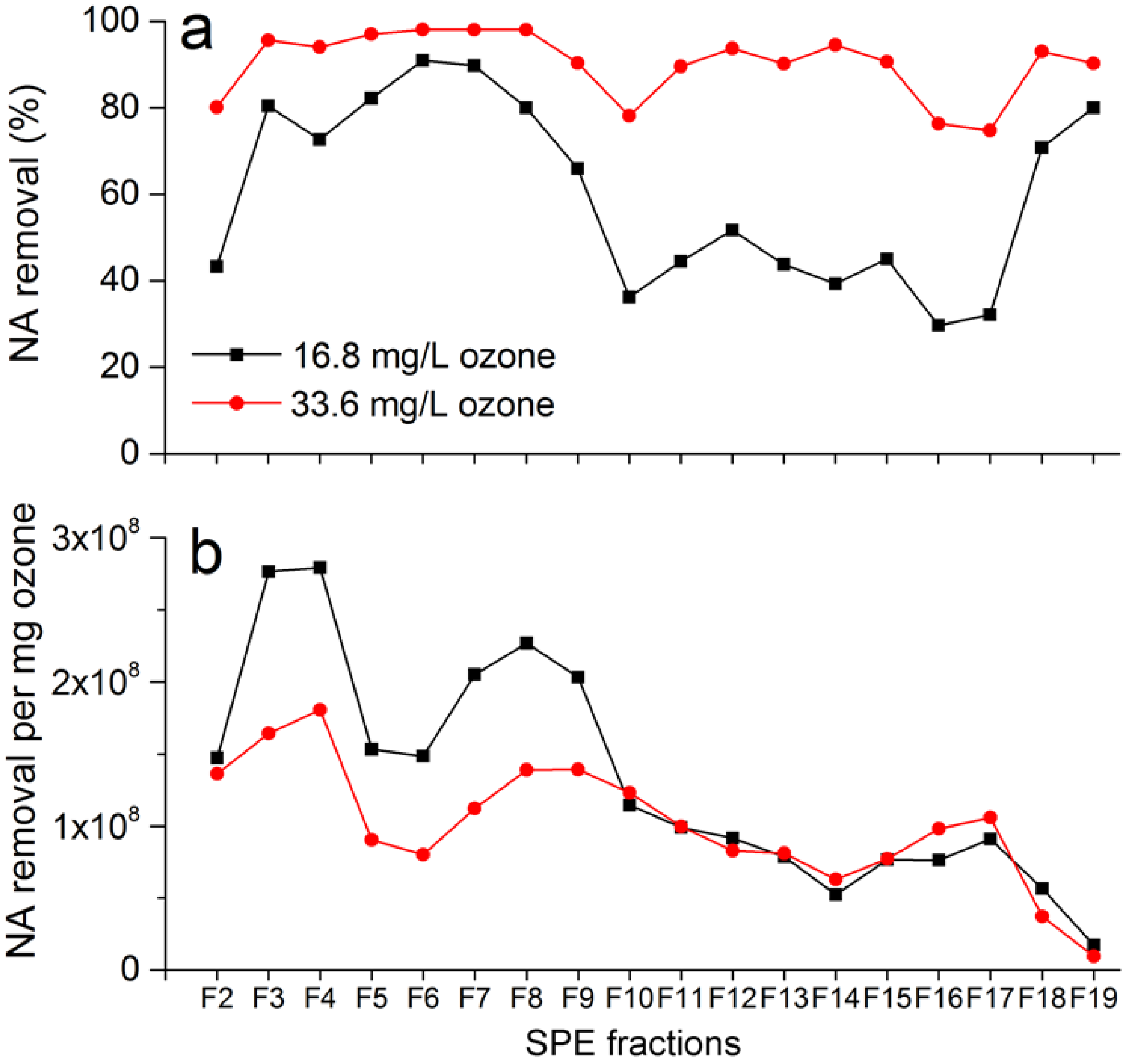

Figure 4.8 The percentage of O_x−NA removal (a), and ozone utilization efficiency for O_x−NA removal (b) of different fractions with applied ozone dosages of 16.8 and 33.6 mg/L. The NA removal was calculated based on the reduced intensity of O_x−NAs from ozone-treated fractions compared to the intensity of those in untreated fractions. The NA removal per mg ozone was calculated based on the reduced intensity of O_x−NA from ozone-treated fractions divided by the ozone dosage in mg, which could be calculated as 0.0336 mg and 0.0672 mg, respectively.

Table 4.1 Accurate weights of dried Ag-ion SPE fractions from OSPW.

SPE Fractions	Fraction mass (mg)
F1	0.77
F2	4.17
F3	1.51
F4	0.52
F5	0.29
F6	0.21
F7	0.40
F8	0.79
F9	1.18
F10	0.79
F11	0.46
F12	0.45
F13	0.29
F14	1.18
F15	1.28
F16	0.78
F17	0.32
F18	0.23
F19	0.14
F20	0.38

Figure 4.8b shows that the ozone utilization efficiency for oxidized NAs (F10-19) was almost the same for the two applied ozone dosages; while for O_2−NAs (F3-F9), degradation with 16.8 mg/L ozone treatment was more efficient than that with 33.6 mg/L dosage. This is likely because after ozone treatment with low ozone dosage, O_2−NAs were degraded into oxidized NAs that could require more ozone in the molar ratio to complete oxidation. Although the removal of oxidized NAs (F10-17 in Figure 4.8a) increased with higher ozone dosage, the ozone utilization efficiency

for their removal remained similar, indicating that the removal of NAs in F10-F17 was proportional to the ozone dosage in the molar ratio. Overall, ozone utilization efficiency for O_2−NA removal was higher than that of oxidized NAs. This result can be explained by the different oxidation pathways for O_2−NAs and oxidized NAs. To validate potential pathways in future study, model compounds of O_2−NA, O_3−NA, and O_4−NA with similar structure could be characterized after ozonation with and without application of a hydroxyl radical scavenger.

Previous study about the ozonation of raw OSPW (the same OSPW as in this work) showed that with the ozone dosage of 24 mg/L, the removal of O_2−, O_3−, and O_4−NAs were 56.9%, 1.5% and 25.5%, respectively (Wang et al., 2016b). As comparison, in this study, after the NA species were isolated physically, the removals of aliphatic O_2−NAs (F3), aromatic O_2−NAs (F8), O_3−NAs (F11) and O_4−NAs (F17) with the ozone dosage of 16.8 mg/L were 97.2%, 94.7%, 59.4% and 44.7%, respectively. The NA removals obtained in this work were all higher than those from previous study about ozonation of raw OSPW. This is partially because the SPE process separated individual NA species into different fractions, altering their concentration and profile, and partially because raw OSPW contained other unknown components that may also consume ozone and were removed during the SPE process.

4.4 Conclusions

This work utilized an Ag-ion SPE method to separate individual NA species into fractions prior to ozone treatment, to study the reactivity of individual NA species. The untreated and treated OSPW fractions were characterized using UPLC-IM-TOF-MS analysis. After the NA species were physically isolated, the removals of aliphatic O_2−NAs (F3), aromatic O_2−NAs (F8), O_3−NAs (F11), and O_4−NAs (F17) with an applied ozone dosage of 16.8 mg/L were 97.2%, 94.7%, 59.4% and 44.7%, respectively. The ozone dosage response for different fractions and the ozone utilization efficiency for different NA species degradation were also investigated. The results indicated that the degradation of oxidized NAs consumed more ozone in the molar ratio than the degradation of aliphatic and aromatic O_2−NAs. The reactivity of oxidized NAs was lower than that of classical NAs because they consumed more ozone in molar ratio during reactions. These results are important for the design of future ozonation systems. Moreover, the utilization of silver-ion SPE in this work was proved to be a suitable method to study the reactivity of individual NA species under other treatment conditions.

4.5 Reference

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Chapter 5 The Impact of Oil Sands Process Water Matrix on The Ozonation of Naphthenic Acids: From a Model Compound to a Natural Mixture

5.1 Introduction

Oil sands process water (OSPW) is generated during the bitumen extraction from oil sands. Although almost ¾ of the OSPW in Alberta, Canada is recycled for bitumen extraction, large volumes of OSPW are retained in tailings ponds and need to be reclaimed because of the zero discharge approach in place (NRC, 2018). OSPW is a complex alkaline mixture containing organics, inorganics as well as sand, silt and clay particles (Gamal El-Din et al., 2011; Wang, 2016). OSPW organics include naphthenic acids (NAs), aliphatic hydrocarbons, phenolic compounds, polycyclic aromatic hydrocarbons (PAHs), and BTEX compounds (benzene, toluene, ethylbenzene, and xylene) (Frank et al., 2016; Huang et al., 2018). NAs, is a mixture of aliphatic and (poly-) alicyclic carboxylic acids (Grewer et al., 2010) and are responsible for the acute toxicity of OSPW towards microorganisms (Zhao et al., 2012; Klamerth et al., 2015), aquatic organisms (Marentette et al., 2015; Morandi et al., 2015) and mammals (Fu et al., 2017; Li et al., 2017).

To remove the NAs from OSPW, several treatment processes, such as coagulation/flocculation followed by sedimentation (Pourrezaei et al., 2011; Wang et al., 2015), biological processes (Xue et al., 2018; Zhang et al., 2018), adsorption (Zubot et al., 2012; Islam et al., 2015; Benally et al., 2019), forward osmosis (Zhu et al., 2017), membrane filtration (Alpatova et al., 2014) and advanced oxidation processes using ozonation (Gamal El-Din et al., 2011), O_3/H_2O_2 (Meshref et al., 2017), UV/chlorine (Shu et al., 2014), UV/Fenton (Zhang et al., 2016), and UV/H_2O_2 (Afzal et al., 2012) have been studied.

Ozonation could not only efficiently degrade OSPW organic contaminants but also accelerate OSPW biodegradation and reduce OSPW toxicity (Gamal El-Din et al., 2011; Hwang et al., 2013; Xue et al., 2018; Zhang et al., 2018). Moreover, ozonation can exert higher organic pollutants degradation activities in alkaline condition, which means that pH adjustment will not be required for the ozonation of alkaline OSPW (Perez-Estrada et al., 2011; Bourgin et al., 2017).

Ozonation of OSPW organics occurs via two pathways: direct ozonation with molecular ozone or indirect reaction with radicals (Wang et al., 2016; Meshref et al., 2017). Hydroxyl radical (•OH), the main oxidant during the indirect radical pathway, can oxidize organic compounds non-selectively, while molecular ozone selectively reacts with compounds containing electron-rich groups such as unsaturated, aromatic compounds and deprotonated amines (Von Sonntag and Von Gunten, 2012). In general, the production of •OH during ozonation process attributes to a chain reaction, including three key steps: initiation, propagation, and termination. Some water matrix works as initiators (e.g. OH^-, Fe^{2+}) or scavengers (e.g. HCO_3^- and CO_3^-) in the chain reaction, which affects the production of •OH (Staehelin and Hoigne, 1985; Lado Ribeiro et al., 2019). Moreover, some transition metal ions (e.g. Mn^{2+}, Fe^{2+}, Fe^{3+}, and Co^{2+}) may react with molecular ozone to produce •OH, which contributes to homogeneous catalytic ozonation process (Nawrocki and Kasprzyk-Hordern, 2010). Thus, water parameters may affect the generation of •OH, which eventually influence the abatement of organic contaminants (Buffle et al., 2006; Von Sonntag and Von Gunten, 2012). In addition, as showed in Table 5.1, some inorganic ions could react with ozone and •OH, which may reduce the available ozone and •OH for organic compounds degradation. Saline OSPW contains varieties of inorganic ions including relatively high concentration of Na^+, Cl^-, SO_4^{2-}, HCO_3^- and other metal ions such as K^+, Mg^{2+}, Mn^{2+}, and Ca^{2+} (Wang et al., 2015). The inorganic ions in OSPW may affect the degradation of organic compounds during the OSPW ozonation process. Besides inorganics and organics, there are particles existing in OSPW, with the turbidity of OSPW to be 130-200 NTU (Gamal El-Din et al., 2011; Afzal et al., 2015; Wang et al., 2015), which may also affect the ozonation of organic compounds. Nawrocki and Kasprzyk-Hordern (2010) pointed out that suspended particles affect the decomposition of ozone. Zucker et al. (2015) reported that the ozone degradation of trace organic contaminants was suppressed in the presence of particles due to their consumption of ozone and •OH. Therefore, the effect of particles existing in OSPW on the ozonation process should also be clarified.

Table 5.1 Reaction rate constants of selected inorganic ions with ozone (O_3) and hydroxyl radical (·OH) at ambient temperature.

Ions	**Reaction rate constant k ($M^{-1}s^{-1}$)**	**Water matrix**	**Reference**
Nitrite (NO_2^-)	k_{O_3} : $3.7 \pm 0.5 \times 10^5$	NaOH /H_3PO_4 buffer, total phosphate concentration 0.05 M, pH 4	Hoigné and Bader, 1983; Hoigné et al., 1985
	$k_{\cdot OH}$: $6.0 \pm 1.0 \times 10^9$	$NaNO_2$ solution buffered with 1 mM borax, pH 9.5	Logager and Sehested, 1993
Ammonia (NH_3/NH_4^+)	k_{O_3} : 1.0	NaOH /H_3PO_4 buffer, total phosphate concentration 0.05 M, pH 8	Hoigné and Bader, 1983; Hoigné et al., 1985
	$k_{\cdot OH}$: $9.7 \pm 1.0 \times 10^7$	Ammonia solution, pH range 10.1-10.6	Hickel and Sehested, 1992
Bromide (Br^-)	k_{O_3} : 160 ± 20	HOBr solution containing 0.5 M H_3PO_4, pH 3-7	Haag and Hoigne, 1983
	$k_{\cdot OH}$: $1.06 \pm 0.08 \times 10^{10}$	NaBr solution, pH 7	Zehavi and Rabani, 1972
Carbonate (CO_3^{2-})	k_{O_3} :<0.01	NaOH /H_3PO_4 buffer with total phosphate concentration of 0.05 M, pH 8-10	Hoigné et al., 1985
	$k_{\cdot OH}$: 4.2×10^8	Bicarbonate solutions over the pH range 7.0-9.4	Buxton and Elliot, 1986
Bicarbonate (HCO_3^-)	k_{O_3} : <0.01	NaOH /H_3PO_4 buffer, total phosphate concentration 0.05 M, pH 8-10	Hoigné et al., 1985
	$k_{\cdot OH}$: 8.5×10^6	Bicarbonate solution, pH range 7.0-9.4	Buxton and Elliot, 1986
Manganese ($Mn^{2+)}$	k_{O_3}: :$1.8 \pm 0.2 \times 10^3$	$MnSO_4$ solution, pH adjusted to 0-2 by H_2SO_4	Jacobsen et al., 1998

	$k_{\cdot OH}$: 2.6±0.1×10^7	$Mn(ClO_4)_2$ solution, pH 9	Jacobsen et al., 1998
Iron (Fe^{2+})	k_{O_3} : 8.2±0.3×10^5	0.02-0.1 mM $NH_4Fe(SO_4)_2$ solution with 1 M $HClO_4$ and 0.4 M H_2SO_4, pH 0-2	Loegager et al., 1992
	$k_{\cdot OH}$: 3.2±0.4×10^8	0.1-100 mM $FeSO_4$ solution, pH 7	Loegager et al., 1992

Ozonation is a promising technique for OSPW reclamation, which can be influence by the varieties of inorganic ions and particles existing in OSPW. Therefore, it is vital, to clarify how the inorganic fraction and particles in OSPW affect the ozonation performance. This information will provide fundamental knowledge for the better understanding of the OSPW ozonation process which would allow the suggestion of best approach to integrate ozonation into the OSPW reclamation treatment procedures.

5.2 Materials and Methods

5.2.1 Reagent and Materials

Sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium nitrate ($NaNO_3$), calcium nitrate (Ca(NO3)2), magnesium nitrate ($Mg(NO_3)_2$), ammonium nitrate (NH_4NO_3), sodium chloride (NaCl), sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), manganese sulfate ($MnSO_4$), sodium thiosulfate ($Na_2S_2O_3$), *tert*-butylalcohol (TBA) and optima-grade methanol were purchased from Fisher Scientific Co. Canada. Potassium indigo trisulfate and model compound cyclohexanecarboxylic acid (CHA) were obtained from Sigma-Aldrich Co. Canada. Granular activated carbon (GAC) was purchased from Calgon Carbon Corporation, PA, USA. Oasis HLB cartridge (6 mL, 500 mg) was obtained from Waters Co., ON., Canada. 8-µm filter paper (Whatman), 0.45-µm nylon membrane (Whatman), and 0.2-µm nylon membrane (Whatman) were purchased from Fisher Scientific Co. Canada.

5.2.2 Sample Preparation

OSPW was collected from a tailing pond located in Fort McMurray, Alberta and stored in polyvinyl chloride barrels at 4 °C. The OSPW was allowed to reach room temperature (20 ± 2 °C) before it was used for any experiment. All the solutions were prepared using ozone-demand-free (ODF) water and the glassware used in the experiments were pre-ozonated and rinsed with ODF water.

5.2.2.1 Extraction of OSPW inorganics and organics

OSPW containing only inorganic fraction (OSPW-IF) and extraction of OSPW organic fraction (OSPW-OF) was obtained using the procedures outline in Chapter 3 section 3.3.2. In summary the OSPW-IF was obtained after the organics were adsorbed onto GAC, while the OSPW-OF was extracted by SPE using HLB cartridge.

5.2.2.2 Preparation of CHA-Buffer, CHA-OSPW-IF and CHA-Buffer with individual ions

A model NA compound, cyclohexanecarboxylic acid (CHA), was spiked into either OSPW-IF to prepare the solution of 50 mg/L CHA in OSPW-IF (CHA-OSPW-IF) (pH=8.7) or in buffer (5 mM $NaHCO_3$ solution) with pH adjusted to 8.7 to obtain 50 mg/L CHA in buffer (CHA-Buffer). OSPW has high alkalinity of around 600 mg/L $CaCO_3$ due to the presence of bicarbonate salts (775-950 mg/L HCO_3^-), which stabilizes the pH of OSPW (Gamal El-Din et al., 2011; Wang, 2016). Thus, the $NaHCO_3$ buffer solution was used in the experiments to mimic the real OSPW to keep the stability of solution pH.

Three concentrations (low, medium and high) were prepared for $NaNO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, NH_4NO_3, $MnSO_4$, NaCl, $NaHCO_3$ and Na_2SO_4 by adding pre-determined volume of individual stock solution into 50 mg/L CHA-Buffer to obtain CHA-Buffer in the presence of individual ion. The concentration of each ion was determined based on their concentration in real OSPW obtain from this study (Table 5.2) and from previous studies (Allen, 2008; Afzal et al., 2015; Wang et al., 2015) with the exception of $MnSO_4$ which added due to previous studies (Ma and Graham, 2000) suggesting that Mn would catalyze ozonation process. The three specific concentrations of each ion used in the experiments are listed in Table 5.3.

Table 5.2 Main properties of raw OSPW and OSPW-IF [a]

Properties	OSPW	OSPW-IF
pH	8.74±0.03	8.86±0.05
Alkalinity (mg/L)	468±12	483±19
Conductivity (µS/cm)	2.631±0.020	2.767±0.036
DOC (mg/L)	52.95±0.91	1.62±0.03
Analytes / Ions (mg/L)		
Lithium (Li)	0.211±0.001	0.229±0.018
Boron (B)	2.025±0.045	1.71±0.115
Sodium (Na)	633.942±0.988	630.531±6.102
Magnesium (Mg)	24.234±0.139	22.983±0.705
Aluminum (Al)	0.012±0.000	0.073±0.021
Silicon (Si)	3.121±0.011	3.664±0.131
Potassium (K)	29.095±0.38	29.376±0.052
Calcium (Ca)	11.784±0.062	16.229±0.467
Titanium (Ti)	0.009±0.001	0.009±0.001
Vanadium(V)	0.012±0.000	0.016±0.000
Chromium (Cr)	0.018±0.002	0.018±0.000
Manganese (Mn)	0.001±0.000	0.001±0.000
Nickel (Ni)	0.008±0.000	0.004±0.001
Copper (Cu)	0.011±0.000	0.010±0.000
Arsenic (As)	0.005±0.000	0.007±0.000
Selenium (Se)	0.006±0.001	0.007±0.001
Rubidium (Rb)	0.038±0.000	0.037±0.001
Strontium (Sr)	0.904±0.002	0.902±0.024
Zirconium (Zr)	0.001±0.000	0.002±0.000
Molybdenum (Mo)	0.092±0.000	0.093±0.001
Antimony (Sb)	0.003±0.000	0.003±0.000
Barium (Ba)	0.057±0.000	0.065±0.001
Uranium (U)	0.011±0.000	0.012±0.000
Ammonium (NH_4^+)	1.714±0.347	2.003±0.025
Fluoride (F^-)	3.242±0.026	2.886±0.125
Chloride (Cl^-)	391.512±3.264	439.985±4.496
Sulfate (SO_4^{2-})	434.120±5.174	394.46±5.234
Nitrate (NO_3^-)	17.959±0.142	14.46±0.304

[a] OSPW-IF is defined as OSPW containing only inorganic fraction. OSPW-IF was obtained after the organic compounds in OSPW was adsorbed onto activated carbon with a final DOC of 1.62±0.03 mg/L.

Table 5.3 Concentration of inorganic salts conducted in the experiments to investigate the influence of individual ions.

Salts	Low concentration (mM)	Medium concentration (mM)	High concentration (mM)
$NaNO_3$	4	12	28
$Ca(NO_3)_2$	0.5	1	2
$Mg(NO_3)_2$	0.5	1	2
NH_4NO_3	0.1	0.5	1
$MnSO_4$	0.005	0.05	0.5
$NaHCO_3$	4	8	12
Na_2SO_4	0.5	2	6
NaCl	4	8	16

5.2.2.3 OSPW with Different Particles

OSPW was filtered through 8-µm filter paper, 0.45-µm and 0.2-µm nylon membrane to obtain OSPW samples with different particles. The particle size distribution of OSPW samples before and after ozonation was analyzed by a Malvern Zetasizer Nano instrument (Malvern Instruments, Worcestershire, UK).

5.2.3 Ozonation

5.2.3.1 Batch Ozonation Experiments

Ozonation experiments of OC-Buffer, OSPW, and CHA-Buffer with individual ions were conducted in 30 mL glass reactors with caps to avoid headspace. Ozone stock solution with a concentration of 41.0 ± 0.5 mg/L was produced as described previously (Afzal et al., 2015). 15 mL of ozone stock solution was spiked into 15 mL of water samples to achieve an initial ozone concentration of 20 mg/L. The reaction solution was stirred for 24 h at room temperature (20 ± 2 °C) to allow of the ozone to be consumed (residual ozone concentration after ozonation was measured to be around zero). The concentrations of NA mixture and CHA before and after ozonation were measured

Kinetic study for the ozonation of CHA-buffer and CHA-OSPW-IF was conducted in a 1 L beaker with a lid which would drop down automatically after the samples were withdrawn, to avoid headspace. 250 mL of ozone stock solution was mixed with 250 mL CHA solution and stirred. Samples were withdrawn for ozone concentration measurement and quenched by $Na_2S_2O_3$ solution for CHA concentration measurement at designed time from 1 min to 60 mins.

5.2.3.2 Semi-batch Ozonation

Ozonation of CHA-Buffer and CHA-OSPW-IF were carried out in semi-batch conditions in a 2 L filter flask. Ozone gas generated by an ozone generator (Model GLS-7, PCI-WEDECO) was continuously fed into 1.9 L samples at the flow rate of 0.6 L/min through a gas diffuser placed on the bottom of the reactor. The input and output ozone concentrations were monitored by two ozone monitors (Model HC-500, PCI-WEDECO). The utilized ozone dose was calculated by the accumulated difference of input and output ozone concentrations subtracting the residual ozone dosage in the sample after the reaction. The detailed calculation process was reported in previous study (Wang et al., 2013). In our work, three ozone doses were applied for each treatment, which are 20 mg/L of ozone applied for 10 min (low ozone dose), 24 mg/L of ozone applied for 15 minutes (medium ozone dose) and the 33 mg/L of ozone applied for 23 minutes (high ozone dose). Afterwards, samples were taken for residual ozone concentration measurement. Meanwhile, 4 mL samples were quenched by $Na_2S_2O_3$ for CHA concentration measurements.

5.2.4 Analytical Methods

The ozone concentration during the experiments was measured by indigo method. The concentration of CHA was measured by liquid chromatograph-mass spectrometry (SQ Detector 2, Waters, Canada). The concentration of NAs was measured by ultra-performance liquid chromatograph time-of-flight mass spectrometry (UPLC-TOF-MS) (Synapt G2, Waters, Canada) as described in the work by Sun et al. (2014). The analysis of anion concentrations was conducted by ion chromatography (ICS-2000 and 2500, Dionex, Sunnyvale, CA, USA). The concentrations of trace elements were quantified by inductively coupled plasma mass spectrometry (ICP-MS, Elan 6000 ICP mass spectrometer, PerkinElmer, Waltham, MA, USA). Dissolved organic carbon (DOC) was measured using a total organic carbon analyzer (Shimadzu, TOC-V CHS/CSN).

5.3 Results and Discussion

5.3.1 Influence of The Inorganic Fraction of OSPW on The Ozonation of CHA

The DOC of OSPW-IF was 1.62 ± 0.03 mg/L after around 97% DOC was removed by GAC. There was no obvious difference for the main anions and cations concentration, pH and alkalinity between OSPW and OSPW-IF (Table 5.2), which indicated that the obtained OSPW-IF was representative of real OSPW for the experiments in this paper.

CHA removal in CHA-Buffer and CHA-OSPW-IF after three doses (20 mg/L ozone for 10 min, 24 mg/L ozone applied for 15 minutes, and 33 mg/L ozone for 23 minutes) of ozone treatment is shown in Figure 5.1a. CHA removal was 14.03%, 18.25% and 30.99% in CHA-Buffer and 9.49%, 12.85% and 20.78% in CHA-OSPW-IF after 20, 24 and 33 mg/L of ozone treatment, respectively. The lower CHA removal in CHA-OSPW-IF indicates that inorganic fraction of OSPW negatively affected the ozonation of CHA. Lower utilized ozone doses in CHA-Buffer (16.91, 23.44 and 45.06 mg/L) than those in CHA-OSPW-IF (20.28, 28.72 and 55.16 mg/L) were observed (Figure 5.1b) which indicated the consumption of ozone by OSPW-IF. The higher consumed ozone in CHA-OSPW-IF during the ozonation process also confirmed the ozone consumption by some inorganic ions. Similarly, Figure 5.2 illustrates that the amount of the consumed ozone in CHA-

OSPW-IF was also higher than that in CHA-Buffer during both the medium and high dosages of ozone treatment. Figure 5.1c presents the ozone utilization efficiency in CHA-Buffer and CHA-OSPW-IF. The ozone utilization efficiency was described as mg of CHA degraded by per mg of utilized ozone. CHA removal by per mg of utilized ozone was higher in CHA-Buffer (0.47, 0.40 and 0.36 mg) than that in CHA-OSPW-IF (0.26, 0.23 and 0.19 mg), which again demonstrated the consumption of ozone by OSPW-IF. Moreover, in both CHA-Buffer and CHA-OSPW-IF, ozone utilization efficiency decreased with higher applied ozone dose. Thus, for the ozonation of CHA, lower ozone dosage was more efficient than that at higher dosage, which was consistent with previous study by Huang et al. (2019) that ozone utilization efficiency for O_2-NA was higher at lower ozone dosage (16.8 mg/L) than that at higher dosage (33.6 mg/L). Considering the above observation and possible reaction between inorganic ions with ozone and •OH (von Gunten, 2003), the inhibitory effect of OSPW-IF on the ozonation of CHA may partly due to the competition of inorganic fraction with CHA on •OH, reducing the available ozone and •OH for CHA degradation.

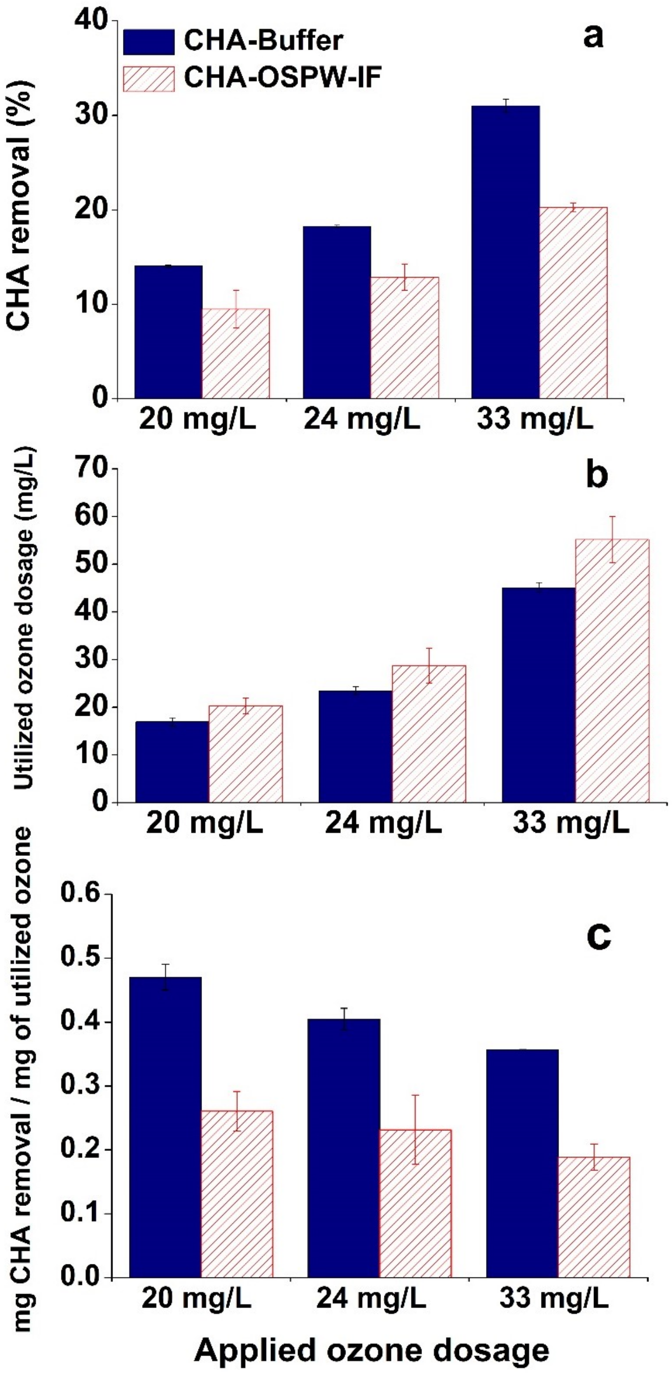

Figure 5.1 CHA removal (a), utilized ozone dosage (b), and mg of CHA removal per mg of utilized ozone (c) in CHA-Buffer and CHA-OSPW-IF after the semi-batch ozonation processes with applied ozone dosage of 20 mg/L (10 min), 24 mg/L (15 min) and 33 mg/L (23 min). Experimental condition: $[CHA]_0$=50 mg/L, pH=8.7.

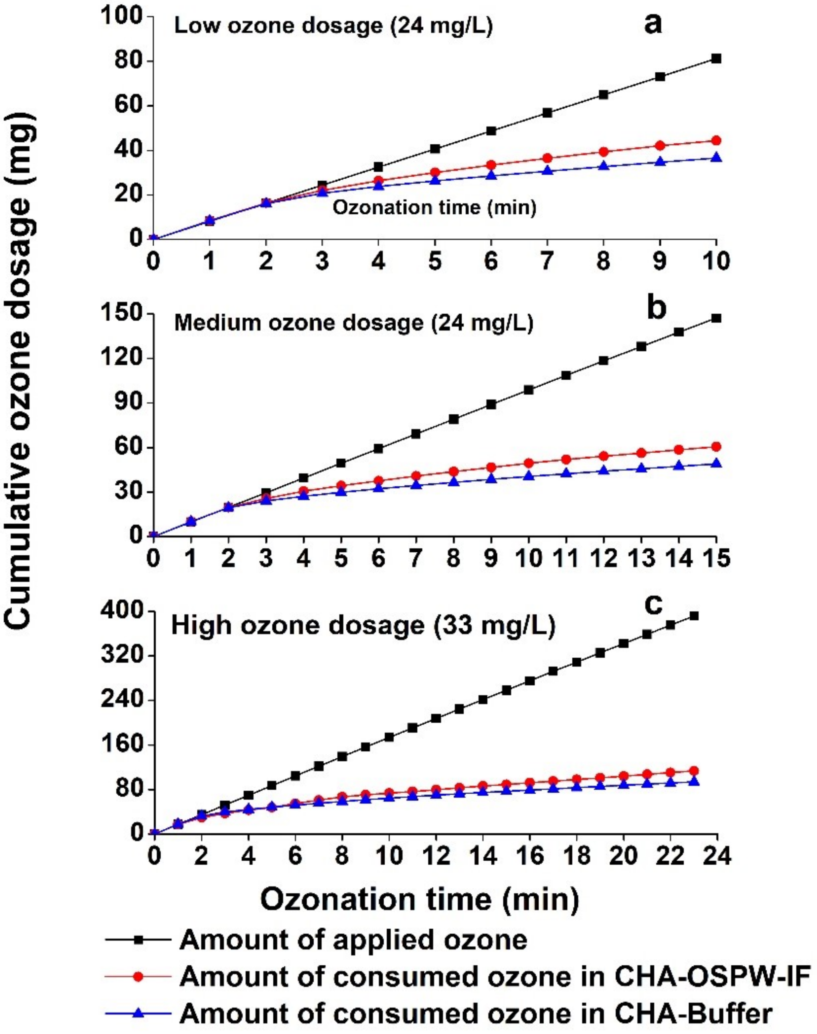

Figure 5.2 Cumulative applied (inlet gas) and consumed ozone dosage (sum of residual and utilized ozone dosage (mg) in the liquid sample) in CHA-Buffer and CHA-OSPW-IF during the semi-batch ozonation process with (a) low, (b) medium, and (c) high ozone dosages at pH 8.7.

Ozonation of CHA-Buffer with the introduction of *tert*-butylalcohol (TBA) was performed to determine whether the CHA degradation was achieved by direct molecular ozone or indirect radical pathway. TBA was chosen as the radical scavenger as it reacts rapidly with •OH (k = 6.0×10^{8} M^{-1} s^{-1}) (Buxton et al., 1988), but slowly with molecular ozone (k =10^{-3} M^{-1} s^{-1}) (Hoigné and Bader, 1983). The degradation of CHA was largely inhibited in the presence of 50 mM of

TBA as shown in Figure 5.3, indicating that the ozonation of CHA at pH 8.7 was dominated by •OH pathway. Thus, the negative effect of OSPW inorganic fraction on the ozonation of CHA was probably due to the consumption of •OH or the scavenging effect of some inorganic species on •OH production (Ma and Graham, 2000; von Gunten, 2003; Petre et al., 2013; Afzal et al., 2015).

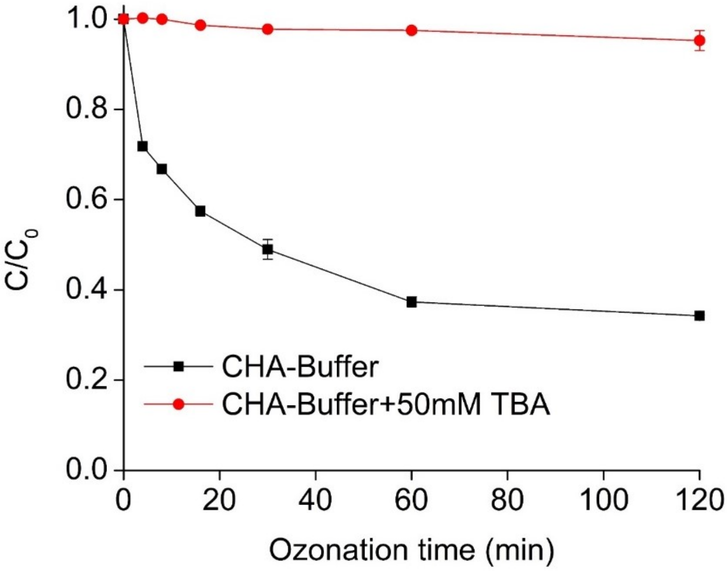

Figure 5.3 Ozonation of CHA in the presence of 50 mM TBA. Experimental condition: applied ozone dosage=20 mg/L, $[CHA]_0$=50 mg/L, [TBA]=50 mM, pH=8.7.

CHA degradation kinetics (Figure 5.4a) showed that CHA degradation in CHA-OSPW-IF (k=0.0028 min^{-1}) was more retarded compared with that in CHA-Buffer (k=0.0063 min^{-1}), which demonstrated the adverse effect of OSPW-IF on the degradation of CHA. However, a slightly faster ozone decomposition in CHA-OSPW-IF (k=0.0217 min^{-1}) was observed compared with that in buffer (k= 0.0196 min^{-1}), indicating that ozone decomposition was accelerated in the presence inorganic fraction (Figure 5.4b). In addition, the initial ozone demand (t=0-1 min) in CHA-OSPW-IF (1.483 mg/L) was almost doubled than that in CHA-Buffer (0.735 mg/L). The faster ozone decomposition but slower CHA degradation in CHA-OSPW-IF than those in CHA-Buffer indicated that OSPW-IF could enhanced ozone decomposition, while the generated •OH was scavenged or consumed by some inorganic which agreed with previous studies (Petre et al., 2013; Afzal et al., 2015) that inorganic in OSPW-IF could accelerate ozone decomposition and scavenge the generated •OH.

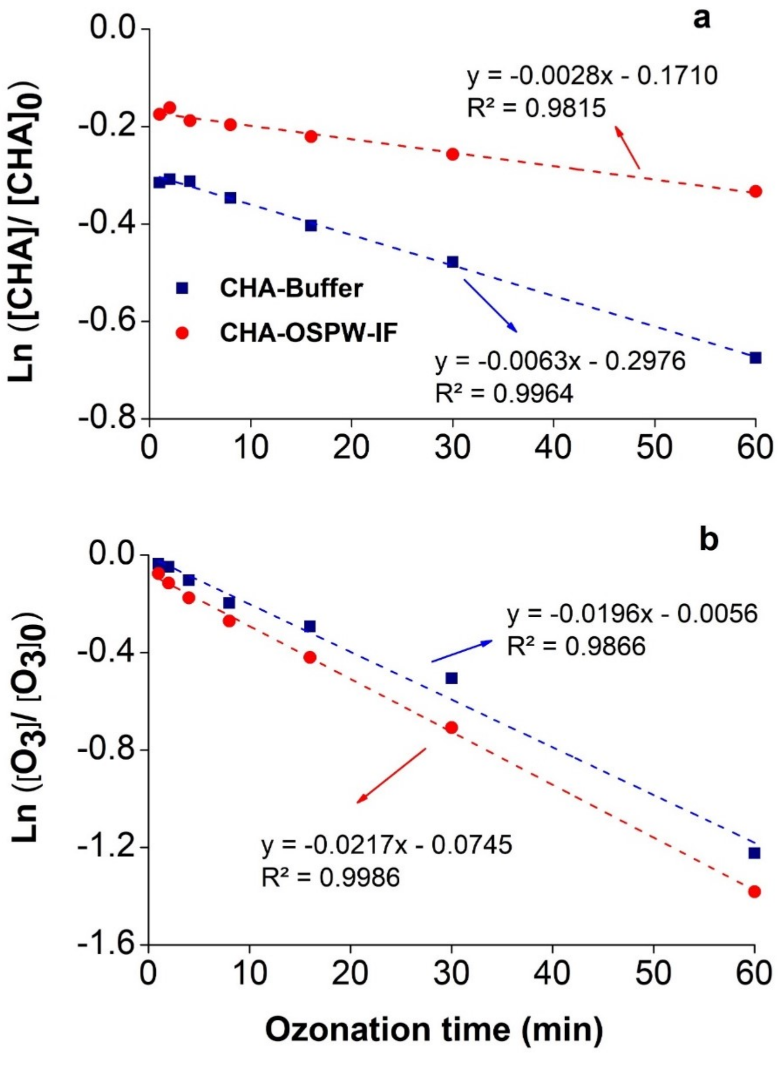

Figure 5.4 CHA degradation (a) and ozone decomposition (b) in CHA-Buffer and CHA-OSPW-IF. Experimental condition: $[CHA]_0$=50 mg/L, pH=8.7, applied ozone dosage=20 mg/L.

5.3.2 Influence of Individual Ions on The Ozonation of CHA

As it was clear from the previous section (Section 5.3.1) that OSPW-IF inhibited the degradation of CHA by ozonation, seven main inorganic ions identified in OSPW (Na^+, Mg^{2+}, Ca^{2+}, NH_4^+, HCO_3^-, Cl^- and SO_4^{2-}) and Mn^{2+}, were selected to clarify their individual influence on the degradation of CHA. Figure 5.5 shows the CHA degradation in the presence of different concentrations of inorganic ions. The degradation of CHA was nearly the same with different concentration of NO_3^-, Mg^{2+} and SO_4^{2-}. However, the CHA degradation decreased with increasing concentration of Ca^{2+}, NH_4^+, Mn^{2+}, HCO_3^- and Cl^-. Before ozonation, a white precipitate was generated after medium and high concentration of $Ca(NO_3)_2$ was added into CHA-Buffer, which resulted in a decrease of pH from 8.73 (no $Ca(NO_3)_2$) to 8.32 (medium concentration of $Ca(NO_3)_2$) and 7.95 (high concentration of $Ca(NO_3)_2$). Thus, less CHA removal in the presence of medium and high concentration of Ca^{2+} was observed because the generation of $CaCO_3$ or $Ca(OH)_2$ precipitate which decreased the solution pH and thus reduced the generation of •OH. As the reaction of NH_4^+/NH_3 with ozone and •OH was reported previously (Singer and Zilli, 1975; Hoigné et al., 1985; Ichikawa et al., 2014), the CHA degradation in the presence of NH_4^+ decreased because of the consumption ozone and •OH by NH_4^+ thus reduced the available ozone and •OH for CHA degradation. The inhibition of ozonation of CHA by Mn^{2+} contradicted with the observation by Ma and Graham (2000), who reported that that Mn^{2+} initiated the generation of •OH and enhanced the ozonation of atrazine at pH of 7.0 (Ma and Graham, 2000). Moreover, Andreozzi et al. (1992) also reported that Mn^{2+} accelerated the ozonation of oxalic acid at pH of 4.7 due to the formation of easier oxidized Mn-oxalic acid complex. In this work, the negative effect of Mn^{2+} on the ozonation of CHA might be due to the formation of MnO_2 (oxidized form of Mn, reddish brown sedimentation was observed after ozonation of CHA-Buffer with medium and high concentration of $MnSO_4$). The formation of MnO_2 indicating that Mn^{2+} competed with CHA to consume ozone and •OH. Thus, it was possible that at pH of 8.7, the initiated production of •OH by Mn^{2+} or the production of any easier oxidized complex did not overcome the competitive consumption of ozone and •OH by the reductant Mn^{2+}. The decreasing CHA degradation with the increasing concentration of $NaHCO_3$ and NaCl was expected as HCO_3^- and Cl^- are known •OH scavengers (Ma and Graham, 2000; Petre et al., 2013) and thus, HCO_3^- and Cl^- prevented the chain reaction for •OH production and eventually reduced CHA degradation.

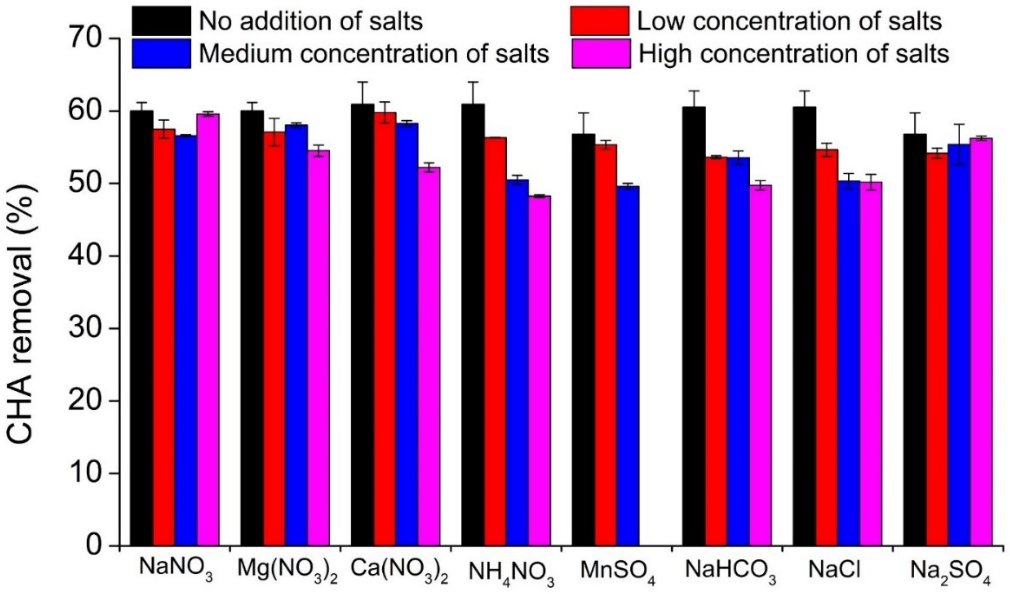

Figure 5.5 CHA degradation with three concentrations of individual ions after ozonation treatment with the utilized ozone dosage of 20 mg/L. Experimental condition: $[CHA]_0$=50 mg/L, pH=8.7, ozonation time=24h (Note: Concentration of each salt is listed in Table 5.3).

In general, the results of the influence of individual ions clarify that the presence of NH_4^+, Mn^{2+}, HCO_3^- and Cl^- in OSPW suppressed the CHA degradation. The inhibition effect was probably due to their competition consumption of ozone and •OH, and their scavenging effect on •OH during the ozonation process.

5.3.3 Influence of Inorganic Fraction on The Ozonation of NA Mixture in OSPW

In order to understand the influence of OSPW-IF on the ozonation of natural NA mixture in OSPW. OSPW-OF (without inorganic fraction) dissolved in 5 mM of $NaHCO_3$ (OSPW-OF) and OSPW (with organic fraction) were ozonated for 24h with utilized ozone dosage of 20 mg/L. The concentrations of NA species in OSPW and OSPW-OF were measured by UPLC-TOF-MS and presented as NA species of two (O_2-NAs) to six oxygen (O_6-NAs) numbers. O_x-NAs is the sum of O_2-O_6 NAs. NAs concentration of OSPW and OSPW-OF is listed in Table 5.4.

Table 5.4 Concentration of NA species in OSPW and OSPW-OF[a]

NA species	OSPW (mg/L)	OSPW-OF (mg/L)
O_2-NAs	20.11	17.44
O_3-NAs	11.94	11.90
O_4-NAs	10.02	9.85
O_5-NAs	2.09	1.47
O_6-NAs	0.81	0.38
O_x-NAs[b]	44.96	41.04

[a] Extracted organic fraction in OSPW was re-dissolved into 5 mM of $NaHCO_3$ solution with pH adjusted 8.7 to obtain OSPW-OF.

[b] O_x-NAs was the sum of O_2-, O_3-, O_4-, O_5- and O_6-NAs.

Figure 5.6a shows the removal of O_2-NAs, O_3-NAs, O_4-NAs and O_x-NAs in OC-Buffer and OSPW after ozonation for 24h with utilized ozone dosage of 20 mg/L. As O_5-NAs and O_6-NAs concentration would increase after ozonation due to the production of higher oxidized NAs from less oxidized NAs (Sun et al., 2014; Huang et al., 2015), their removal was not presented. O_2-NAs, O_3-NAs, O_4-NAs and O_x-NAs removal were 86.62%, 66.70%, 55.99% and 68.70% in OC-Buffer, while they were 82.72%, 51.76%, 43.26% and 60.39% in OSPW, respectively. Lower NA removal in OSPW in the presence of inorganic fractions demonstrates the negative influence of inorganic fraction on the ozonation of NAs. While the lower removal of oxidized NAs (O_3-NAs and O_4-NAs) as compared to O_2-NAs agreed with previous study (Huang et al., 2019) that the ozonation reactivity of oxidized NAs was lower than that of O_2-NAs as the degradation of oxidized NAs required more ozone in the molar ratio than that of O_2-NAs. This may explain why the inhibitory effect of inorganic fraction on oxidized NAs is more severe than that on O_2-NAs.

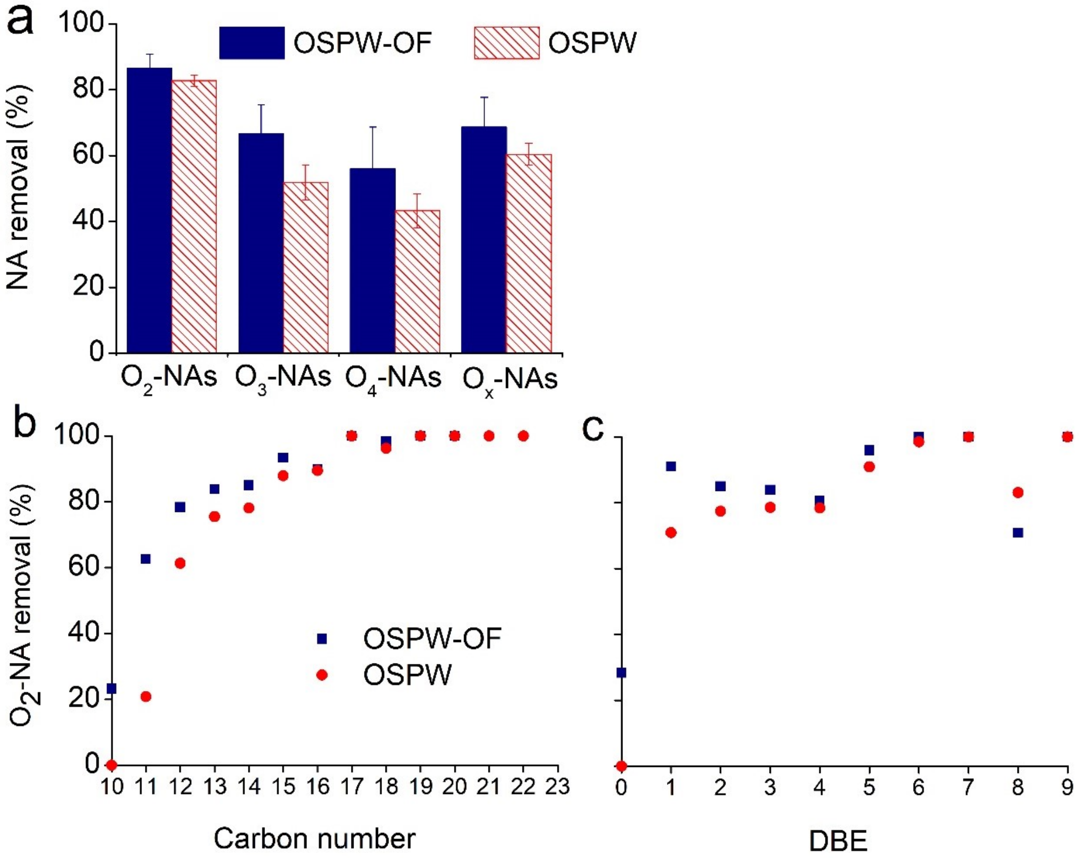

Figure 5.6 NA removal (a), O_2-NA removal with respect to (b) carbon number and (c) DBE in OSPW-OF (without inorganic fraction) and OSPW (with inorganic fraction) after ozonation. Experimental conditions: utilized ozone dosage = 20 mg/L, pH=8.7, ozonation time=24h. (Note: initial concentration of NA species is listed in Table 5.3).

Figure 5.6b shows that O_2-NAs with more carbon numbers were favored to be degraded in OSPW-OF and OSPW, which was consistent with previous studies about the ozonation of O_2-NAs in whole OSPW and fractionated O_2-NAs (Wang et al., 2016; Huang et al., 2019). For the indirect ozonation, •OH attacks organic compounds mainly by hydrogen abstraction. NAs with more carbon numbers provide more available hydrogen for the hydrogen abstraction, which ultimately enhances the hydrogen abstraction process and results in higher NA removal (Perez-Estrada et al., 2011; Wang et al., 2013). Increasing removal of O_2-NAs with higher DBE was also observed in OC-Buffer and OSPW after ozonation (Figure 5.6c). The same trend was observed for the ozonation of whole OSPW and fractionated O_2-NAs in previous research (Wang et al., 2016; Huang et al., 2019). As hydrogen abstraction preferably occurs with hydrogen atom on the tertiary carbon due to the production of more stable carbon centered radial, NAs with higher DBE tend to have more tertiary carbons and are, therefore, more favored to be degraded (Perez-Estrada et al., 2011).

5.3.4 Influence of Particles on The Ozonation of NAs

OSPW was filtered with 8-µm filter paper, 0.45-µm nylon membrane, and 0.2-µm nylon membrane. Non-filtered OSPW and the above filtered samples were ozonated with the utilized ozone dosage of 20 mg/L. The degradation of O_2-NAs, O_3-NAs, O_4-NAs and O_x-NAs in different pore-size-filtered OSPW samples is illustrated in Figure 5.7. As discussed in Section 5.3.3, the removals of O_5-NAs and O_6-NAs are not presented, as their concentration increased after ozonation due to the production of oxidized NAs (Sun et al., 2014; Huang et al., 2015). The results indicated that there was insignificant difference for the degradation of O_2, O_3, O_4 and O_x-NAs in non-filtered, 8-µm filter paper, 0.45 and 0.2-µm membrane filtered OSPW. Similar results were observed in the previous research (Gamal El-Din et al., 2011) that suspended particles did not affect the degradation of acid-extracted organics from OSPW during the semi-batch ozonation process with a utilized ozone dosage of higher than 100 mg/L. This result indicated that the presence of particles in OSPW may not be a concern for the application of ozonation treatment for NA removal.

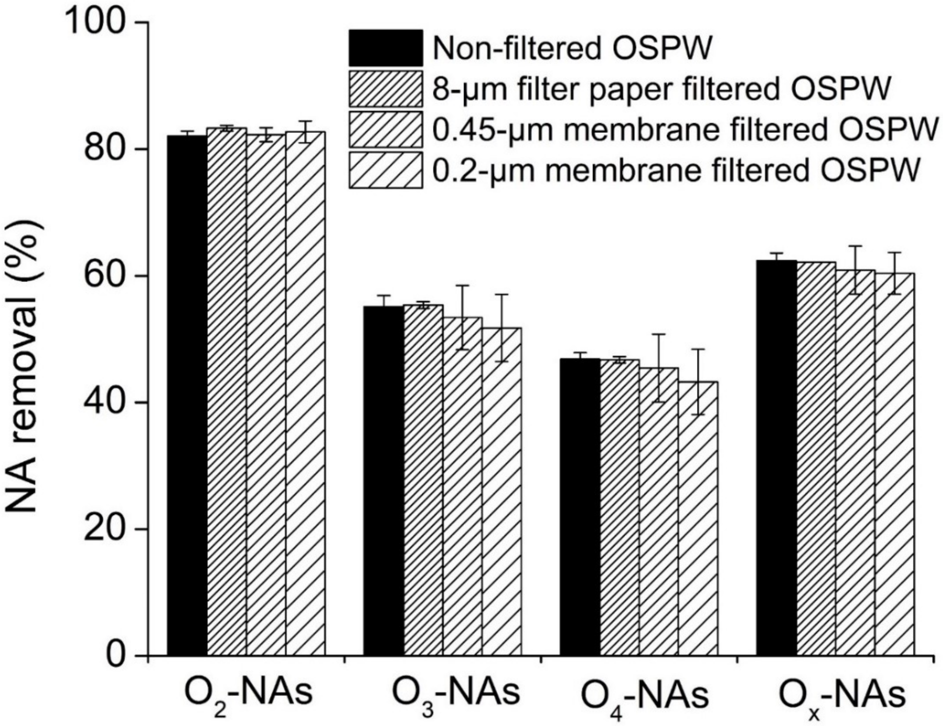

Figure 5.7 NA removal in filtered and non-filtered OSPW after 20 mg/L utilized ozone treatment at pH 8.7 for 24h.

Particle size distribution in non-filtered OSPW before and after 20 mg/L of ozone treatment was analyzed. Figure 5.8 showed that most of the particles in OSPW were in the size range from 0.2 µm to 0.4 µm. Particle size was dispersed, especially for shifting to larger size, after ozonation treatment, suggesting that particle aggregation happened. A plausible explanation for the particle aggregation was because ozone transformed the organic matter adsorbed on particles surface to higher polarity molecules and resulted in their desorption from the particles surface, which reduces the surface charge and stability (Paode et al., 1995), and caused the particles to aggregate together. Moreover, a slight intensity increase of smaller particles was observed after ozonation, which demonstrated the breakdown of large particles. The observation agreed with Zucker et al. (2015), who reported that both particle aggregation and breakage occurred concurrently during the ozonation of secondary wastewater effluent. Zucker et al. (2015) pointed out that at low ozone dosage of 0.17 mg O_3/mg DOC, the dominant process was the growth of particles. However, when a high ozone dosage (up to 0.93 mg O_3/mg DOC) was applied, the dominant process shifted to particles breakage. In this research, the ozone dosage was 0.37 ± 0.02 mg O_3/mg DOC, which was a relative low dosage as compare to the previous study. Thus, the particles breakage in this study would be insignificant.

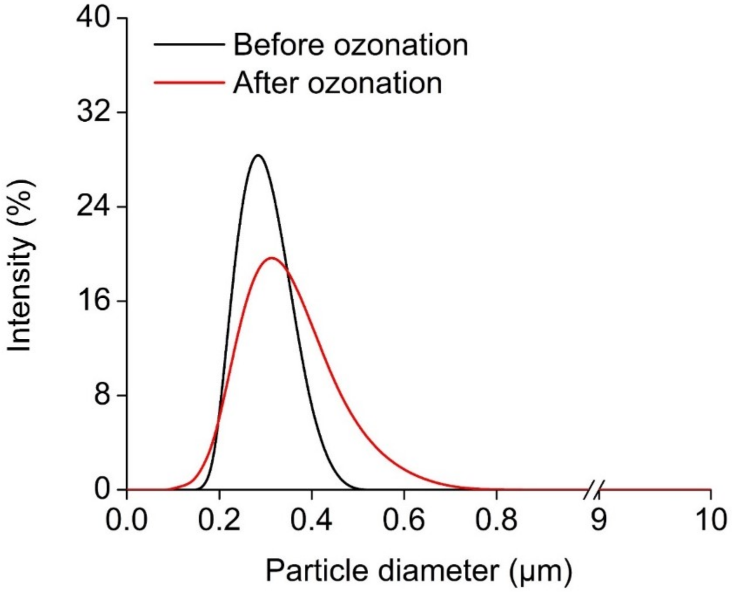

Figure 5.8 Particle size distribution in OSPW before and after ozonation treatment with the utilized ozone dosage of 20 mg/L of ozone treatment at pH 8.7 for 24 h.

5.3.5 Significance of The Results on The Application of Ozonation for OSPW Treatment

As OSPW is a saline water containing a variety of inorganics, organics and particles, this fundamental research on the effect of OSPW-IF and particles on the ozonation of NAs is significant for process optimization and control in actual full-scale ozonation applications for OSPW remediation. The experimental results obtained in this work showed limited effect of particles but negative effect from the inorganic fraction on the treatment performance in terms of NA removal. Accordingly, when ozonation would be implemented for full-scaled OSPW remediation, the impact of inorganic fraction rather than particles in OSPW will be noticeable. Although pretreatment processes such as coagulation, flocculation, precipitation, and ion exchange could be used to remove the inorganics, thus improving the ozonation performance in terms of organic contaminants removal, the implementation of pretreatment processes for the sole purpose of improving organic removal (for around 10% improvement) is impractical considering the high cost of building and maintaining these processes. However, in a treatment train, ozonation could be placed as an intermediate or post treatment step after some scavenger ions are removed by other processes. For example, it was reported that NH_4^+ could be consumed and pH will decrease after aerobic biological OSPW treatment process (Xue et al., 2016), which contributed to the decreasing concentration of NH_4^+ and HCO_3^-. Thus, placing ozonation as a post treatment step after aerobic biological treatment could reduce the negative effect caused by these scavenger ions. Recently Zhang et al. (Submitted) conducted ozonation treatment as a post treatment process after biofiltration process. Their results indicated that with the utilized ozone dose of 30 mg/L, 84.8% of O_2-NAs and 11.5% of oxidized NAs were removed from the biofiltrated OSPW (0.3 mg O_2-NAs NAs/mg O_3 and 0.1 mg oxidized NAs/mg O_3). However, by using the same ozone dose, the degradation of O_2-NAs and oxidized NAs from raw OSPW was 32.1% and 3.9% (0.1 mg O_2 NAs/mg O_3 and 0.0 mg oxidized NAs/mg O_3), respectively. The results from these other studies (Xue et al., 2018; Zhang et al., Submitted) supported our proposal that the ozonation efficiency would be increased if ozonation is conducted as a post treatment process after biological treatment.

In both CHA-Buffer and CHA-OSPW-IF, consumed ozone dosages declined dramatically after two minutes, which indicated that ozone was not utilized efficiently in this semi-batch system (Figure 5.2). Previous research reported that coarse bubble diffuser used in this work performed lower ozone mass transfer efficiency compared with fine bubble diffuser and impinging-jet ozone contactor in the semi-batch system (Gamal El-Din and Smith, 2002a, b). Additionally, the small reactor (2 L) used in the semi-batch system might also resulted in the high concentration of ozone in the off-gas and low ozone utilization efficiency (Wang et al., 2013). Moreover, considering the rapidly decline of ozone consumption after two minutes, an intermittent ozonation process, where ozone is intermittently spiked into OSPW may achieve higher overall ozone utilization efficiency than the continuous ozonation process. In conclusion, ozone contactor design and configuration, process optimization as well as operating conditions should be further investigated to obtain the proper scale-up factors for the development of practical ozonation applications for OSPW treatment and reclamation.

5.4 Conclusion

Ozonation of model compound CHA and NAs in OSPW with or without OSPW-IF were performed to study the influence of OSPW-IF on the ozonation of NAs. CHA removal in CHA-Buffer (14.03%, 18.25% and 30.99%) was higher than that in CHA-OSPW-IF (9.49%, 12.85% and 20.78%) after 20, 24 and 33 mg/L of ozone treatment. In addition, utilized ozone dosages in CHA-Buffer (16.91, 23.44 and 45.06 mg/L) were lower than those in CHA-OSPW-IF (20.28, 28.72 and 55.16 mg/L). This indicated that OSPW inorganic fraction consumed ozone and adversely affected the ozonation of CHA. NH_4^+, Mn^{2+}, Cl^- and HCO_3^- have found to display negative effect on CHA degradation, while Na^+, Mg^{2+}, and SO_4^{2+} did not affect CHA degradation. The removal of O_2-NAs, O_3-NAs, O_4-NAs and O_x-NAs were 86.62%, 66.70%, 55.99%, 68.70% in OSPW-OF (without inorganics), which were higher than in OSPW (with inorganics) 82.72%, 51.76%, 43.26%, 60.39%, respectively, demonstrating that the inorganic fraction have negative effect on the ozonation of NAs in OSPW. Insignificant difference for NA removal in non-filtered and filtered OSPW after ozonation was observed, indicating that ozonation of NAs in OSPW was unaffected by particles. This study implies that the presence of inorganic fraction in OSPW could affect OSPW ozonation treatment, by inhibiting NA degradation and increasing ozone demand. Therefore, it would be suggested that for the practical application of ozonation on OSPW remediation, ozonation process should be used as a post treatment in a treatment train and an intermittent ozonation process may achieve higher ozone utilization efficiency than a continuous ozonation process.

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Chapter 6 Photodegradation of Naphthenic Acids Induced by Natural Photosensitizer in Oil Sands Process Water

6.1 Introduction

Extraction of bitumen from oil sands in Northern Alberta, Canada, produces large volume of oil sands process water (OSPW), which is a complex alkaline mixture containing organics, inorganics, and particles (Wang et al., 2015). Naphthenic acids (NAs), a mixture of aliphatic and (poly-) alicyclic carboxylic acid (Klamerth et al., 2015), are responsible for the acute and sub-chronic toxicity of OSPW towards microorganisms (Zhang et al., 2011), aquatic organisms (Hughes et al., 2017), and mammals (Li et al., 2017). NAs have a general formula of $C_nH_{2n+z}O_x$, whereby n is the number of carbons, z is zero or an even negative number referring to double bonds or the number of saturated rings, and x is the number of oxygen (Wang et al., 2016).

Degradation of NAs using advanced oxidation processes (AOPs) has been investigated (Quinlan and Tam, 2015, Wang et al., 2016). Relatively high operating costs and use of energy are the principal drawbacks of traditional AOPs for full-scale applications (Oller et al., 2011). Thus, there is considerable interest in the utilization of renewable solar energy driven AOPs for OSPW remediation to remove organic contaminants (Chan et al., 2012, Hendrikse et al., 2018, Shu et al., 2014).

Generally, there are two types of photolysis processes for the degradation of organic compounds in natural water without the addition of catalysts: direct and indirect photolysis. In the direct photolysis process, organic compounds absorb photon directly for transformation. In the indirect photolysis process, photosensitizers in water absorbs light energy to product reactive radicals which induce the photodegradation of organic compounds (Liu et al., 2017). It was reported that NAs do not absorb light, which resulted in the low NA degradation efficiency by direct photolysis

(Afzal et al., 2012). Therefore, UV-based AOPs with the generation of active radicals, such as hydroxyl radicals (•OH), sulfate radicals ($SO_4•^-$), and chlorine radicals (•Cl), initiated by H_2O_2 (Afzal et al., 2012), $S_2O_8^{2-}$ (Fang et al., 2018) and HOCl (Shu et al., 2014), have been studied to improve the organic contaminants degradation efficiency for OSPW treatment. In addition, light-absorbing molecules such as natural organic matters, humic acids, nitrite and nitrate in the water matrix could act as photosensitizers to adsorb UV/visible light to produce reactive radicals to achieve the indirect photolysis of organic contaminants (Li et al., 2018, Liu et al., 2017). Hereby, the photodegradation of organic contaminant in aquatic environments is directly related to water matrix.

There are a variety of inorganic ions existing in OSPW, including Na^{2+}, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, and some trace metals. To date, no research has been conducted to investigate whether any inorganic species in OSPW could induce or enhance the photodegradation of organic compounds in OSPW. Understanding whether there are photosensitizers existing in OSPW could provide information about the photochemical processes upon OSPW and the possibility of photodegradation of organic compounds by the passive solar remediation without the addition of external catalysts.

The main objectives of this study were to: 1) Study the influence of inorganic fraction in OSPW on the photodegradation of NAs; 2) Identify the specific inorganic species present in OSPW that could induce or enhance the photodegradation of a model NA 1-adamantanecarboxylic acid (ACA) and suggest the possible degradation pathways.

6.2 Material and Methods

6.2.1 Chemicals and Materials

Sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium nitrate ($NaNO_3$), copper sulfate ($CuSO_4$), zinc sulfate ($ZnSO_4$), magnesium sulfate ($MgSO_4$), sodium chloride (NaCl), sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), manganese sulfate ($MnSO_4$), allyl alcohol (AA), *tert*-butylalcohol (TBA) and optima-grade methanol were purchased from Fisher Scientific Co. Canada. Model compound 1-adamantanecarboxylic acid (ACA) were obtained from Sigma-Aldrich Co. Canada. Granular activated carbon (GAC) was purchased from Calgon Carbon Corporation, PA, USA. Oasis HLB cartridge (6 mL, 500 mg) was obtained from Waters Co., ON., Canada. 0.2 µm nylon membrane (Whatman) were purchased from Fisher Scientific Co. Canada. OSPW was collected from a tailing pond located in Fort McMurray, Alberta, and stored in polyvinyl chloride barrels at 4 °C. The OSPW was allowed to reach room temperature (20 ± 2 °C) before it was used for any experiment.

6.2.2 Sample Preparation

6.2.2.1 Extraction of Inorganics and Organics Only from OSPW

OSPW containing only inorganic fraction (OSPW-IF) and extraction of OSPW organic fraction (OSPW-OF) were obtained using the procedures outline in Chapter 3 section 3.3.2. In summary the OSPW-IF was obtained after the organics were adsorbed onto GAC, while the OSPW-OF was extracted by SPE using HLB cartridge. The concentrations of NAs species in OSPW and OSPW-OF are presented in Table 6.1

Table 6.1 NA concentration (mg/L) in OSPW and OSPW-OF

Samples	O_2-NAs	O_3-NAs	O_4-NAs	O_5-NAs	O_6-NAs	O_x -NAs
OSPW	20.11	11.94	10.02	2.09	0.81	44.96
OSPW-OF	16.52	10.97	10.44	2.09	0.81	40.83

6.2.2.2 Preparation of Model Compound ACA in Buffer with Individual Ions And in OSPW-IF

40 mg/L of ACA in OSPW-IF (ACA-OSPW-IF) or 3mM $NaHCO_3$ buffer (ACA-Buffer) was prepared by adding ACA directly into OSPW-IF or buffer. Owing to the low solubility of ACA in water, the solutions were stirred for 24 h (covered with aluminum foil) to ensure that ACA was completely dissolved. The pH of ACA-Buffer was adjusted to 8.7 using NaOH as to be consistent with the pH of ACA-OSPW-IF. Appropriate volume of $NaNO_3$, $CuSO_4$, $ZnSO_4$, $MgSO_4$, $MnSO_4$, NaCl, $NaHCO_3$ and Na_2SO_4 from individual stock solutions were added into 40 mg/L ACA-Buffer to obtain ACA-Buffer with individual ions whose concentrations were similar with those in real OSPW (Table 6.2). For example, 18 mg/L-NO_3^- (0.3 mM) of $NaNO_3$ in ACA-Buffer was prepared based on the nitrate concentration in real OSPW. All samples were filtered with 0.2 μm nylon membrane before photodegradation experiments and analysis.

Table 6.2 Properties of OSPW and OSPW-IF[a]

Properties	OSPW	OSPW-IF
pH	8.83±0.01	8.81±0.03
Alkalinity (mg/L-$CaCO_3$)	465±5	481±6
Conductivity (μS/cm)	2.740±0.028	2.854±0.059
DOC (mg/L)	52.64±0.11	1.81±0.03
Analytes / Ions (mg/L)		
Lithium (Li)	0.206±0.006	0.229±0.005
Boron (B)	1.923±0.009	1.200±0.004
Sodium (Na)	615.086±3.503	651.556±8.464
Magnesium (Mg)	24.604±0.086	23.37±0.269
Aluminum (Al)	0.028±0.001	0.179±0.051
Silicon (Si)	3.650±0.042	3.915±0.017
Potassium (K)	27.614±0.054	28.657±0.186
Calcium (Ca)	15.641±0.046	15.196±0.052
Titanium (Ti)	0.006±0.000	0.006±0.000
Vanadium(V)	0.009±0.000	0.018±0.000
Chromium (Cr)	0.013±0.001	0.015±0.000
Manganese (Mn)	0.001±0.000	0.001±0.001
Nickel (Ni)	0.007±0.000	0.002±0.000
Copper (Cu)	0.042±0.000	0.035±0.000
Zinc (Zn)	0.002±0.000	0.001±0.001
Arsenic (As)	0.005±0.000	0.009±0.000
Selenium (Se)	0.002±0.000	0.002±0.001
Rubidium (Rb)	0.034±0.000	0.035±0.000
Strontium (Sr)	0.791±0.004	0.754±0.016
Molybdenum (Mo)	0.089±0.001	0.096±0.001
Antimony (Sb)	0.003±0.000	0.003±0.000
Barium (Ba)	0.057±0.001	0.081±0.002
Tungsten (W)	0.005±0.000	0.004±0.000
Uranium (U)	0.009±0.000	0.014±0.000
Anions (mg/L)		
Fluoride (F^-)	2.869±0.007	3.147±0.046
Chloride (Cl^-)	348.516±0.411	364.854±0.554
Sulfate (SO_4^{2-})	433.297±0.749	450.845±0.428
Nitrate (NO_3^-)	17.942±0.323	16.581±0.312
Nitrite (NO_2^-)	<0.05	<0.05

[a] OSPW containing only inorganic fraction (OSPW-IF) was obtained after the organics were adsorbed by activated carbon with a final TOC of 1.81±0.03 mg/L.

6.2.3 UV Irradiation Test

UV irradiation experiments were conducted in a 100 mL beaker (5.4 cm diameter) with 80 mL sample solution. The beaker was placed on a magnetic stirrer under a collimated beam generated by a UV apparatus (Model PSI-I-120, Calgon Carbon Corporation, PA, USA) equipped with a medium pressure Hg-lamp with the emission wavelength from 200 nm to 530 nm shown in Figure 6.1. The irradiance was measured by a calibrated UV detector (International Light, model SEL 240, Peabody, MA, USA) connected to a radiometer (International Light, Model IL 1400A, Peabody, MA, USA) and set at 2.92 mW/cm^2 for all the irradiation experiments.

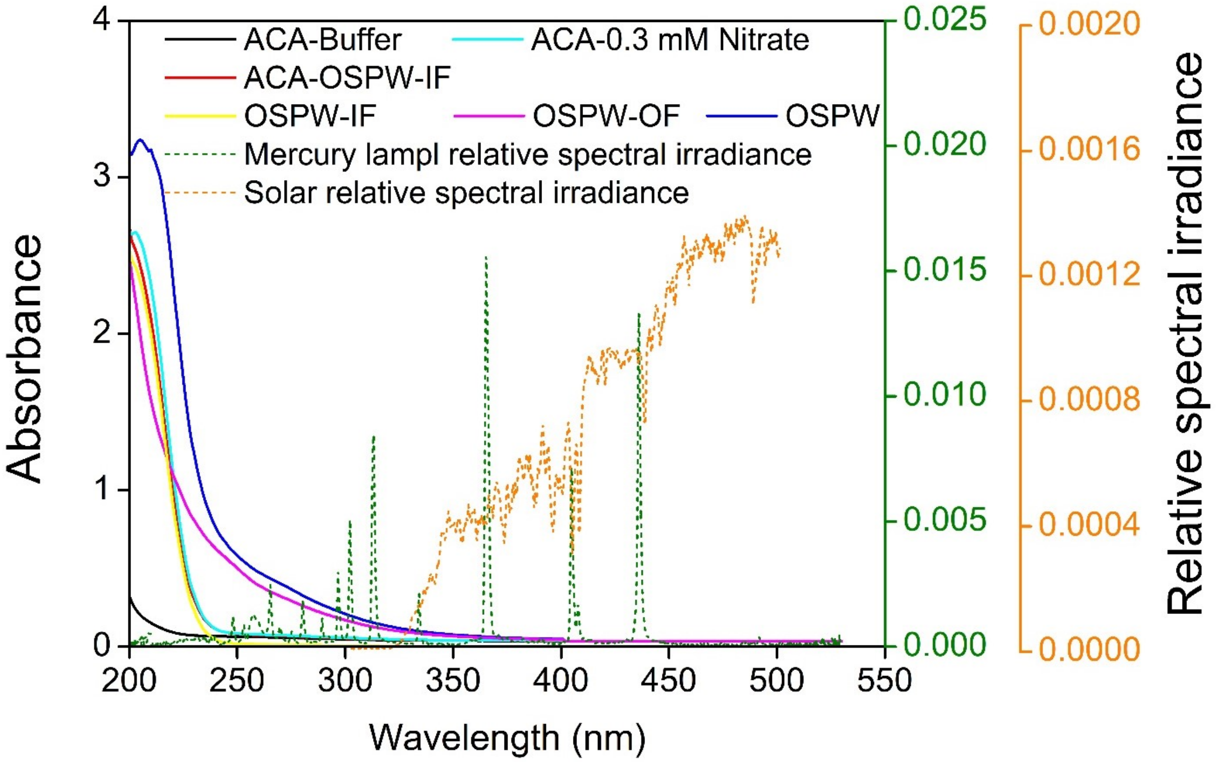

Figure 6.1 Absorbance of ACA-Buffer and ACA- OSPW-IF, ACA-0.3mM nitrate, OSPW and the relative spectral irradiance of the medium pressure mercury lamp and solar.

6.2.4 Analytical Methods

The concentration of model compound 1-adamantanecarboxylic acid (ACA) was determined by ultra-performance liquid chromatography coupled with a single quadrupole mass spectrometry (UPLC-MS) (SQ Detector 2, Waters, ON, Canada). The concentration of NAs in OSPW OSPW-OF was measured by ultra-performance liquid chromatography coupled with time-of-flight mass spectrometry (UPLC-TOF-MS) (Synapt G2, Waters, ON, Canada). NA concentration was measured by an ultra-performance liquid chromatograph time-of-flight mass spectrometry (UPLC-TOF-MS) (Synapt G2, Waters, ON). 1 mL of each water sample was centrifuged at 10 000 RPM for 10 min. The injection solution was prepared with 500 μL of the supernatant, 100 μL of 4.0 mg/L internal standard (ISTD) compound (Myristic acid-1-^{13}C) in methanol, and 400 μL methanol to reach a final sample volume of 1 mL. The samples were analyzed using UPLC-TOF-MS in high-resolution mode (mass resolution = 40000 FWHM at 1431 m/z) at mass range of 100-600 (m/z). The chromatographic separation was achieved by a method developed in our previous reports for the separation of NAs (Huang et al., 2015). The electrospray ionization source was operated in the negative mode to measure NAs in the samples. Data acquisition was controlled using MassLynx (Waters, ON) and data analysis was performed using TargetLynx (Waters, ON). One raw OSPW sample has been used as the quality control sample to ensure the method stability. This method was developed previously for semi-quantification of NAs based on the signal of a compound versus the signal of spiked ISTD. By-products analysis was also conducted using UPLC-TOF-MS operated at ESI negative mode using MS scan over the mass range of 50-1200 Da in high resolution mode. Leucine enkephalin (*m/z*=554.2615) was used as lock mass for the mass correction and was continuously infused via the lockspray ESI prode. The chromatographic method was the same for both NAs and by-products analysis. The analysis of anion concentrations was conducted by ion chromatography (ICS-2000 and 2500, Dionex, Sunnyvale, CA, USA). The concentrations of trace elements were quantified by inductively coupled plasma mass spectrometry (ICP-MS, Elan 6000 ICP mass spectrometer, PerkinElmer, Waltham, MA, USA). Dissolved organic carbon (DOC) was measured using a Total Organic Carbon Analyzer (Shimadzu, TOC-V CHS/CSN).

6.3 Results and Discussion

6.3.1 Direct Photolysis of OSPW and OSPW-OF for The Removal of Natural NA Mixture

Direct photolysis of OSPW and OSPW-OF were conducted to study the degradation of natural NA mixture in the presence and absence of OSPW inorganic fraction. 24.3% of O_x-NAs of that 46.4% of O_2-NAs, 11.2% of O_3-NAs, and 9.9% of O_4-NAs in OSPW; and 12.4% of O_x-NAs of that 29.6% of O_2-NAs, 2.5% of O_3-NAs, and 1.6% of O_4-NAs in OSPW-OF were degraded after 60 mins of direct UV exposure (Figure 6.2a). The lower NA degradation in OSPW-OF was expected as previous research shown that NAs do not absorb light in the solar wavelength and photolysis of NAs in the absence of photosensitizers or photocatalysts leaded to low degradation efficiency (Afzal et al., 2012, McMartin et al., 2004). The higher NA degradation in OSPW (24.3%) as compared to OSPW-OF (12.4%) indicated that some inorganic species in OSPW acted as photosensitizer(s) that induced or enhanced the photodegradation of NAs. In addition, higher degradation for NAs with higher carbon number and double bond equivalent (DBE) were observed (Figure 6.1b), which was consistent with previous study about the degradation of NAs in OSPW in the presence of •OH (Afzal et al., 2012).

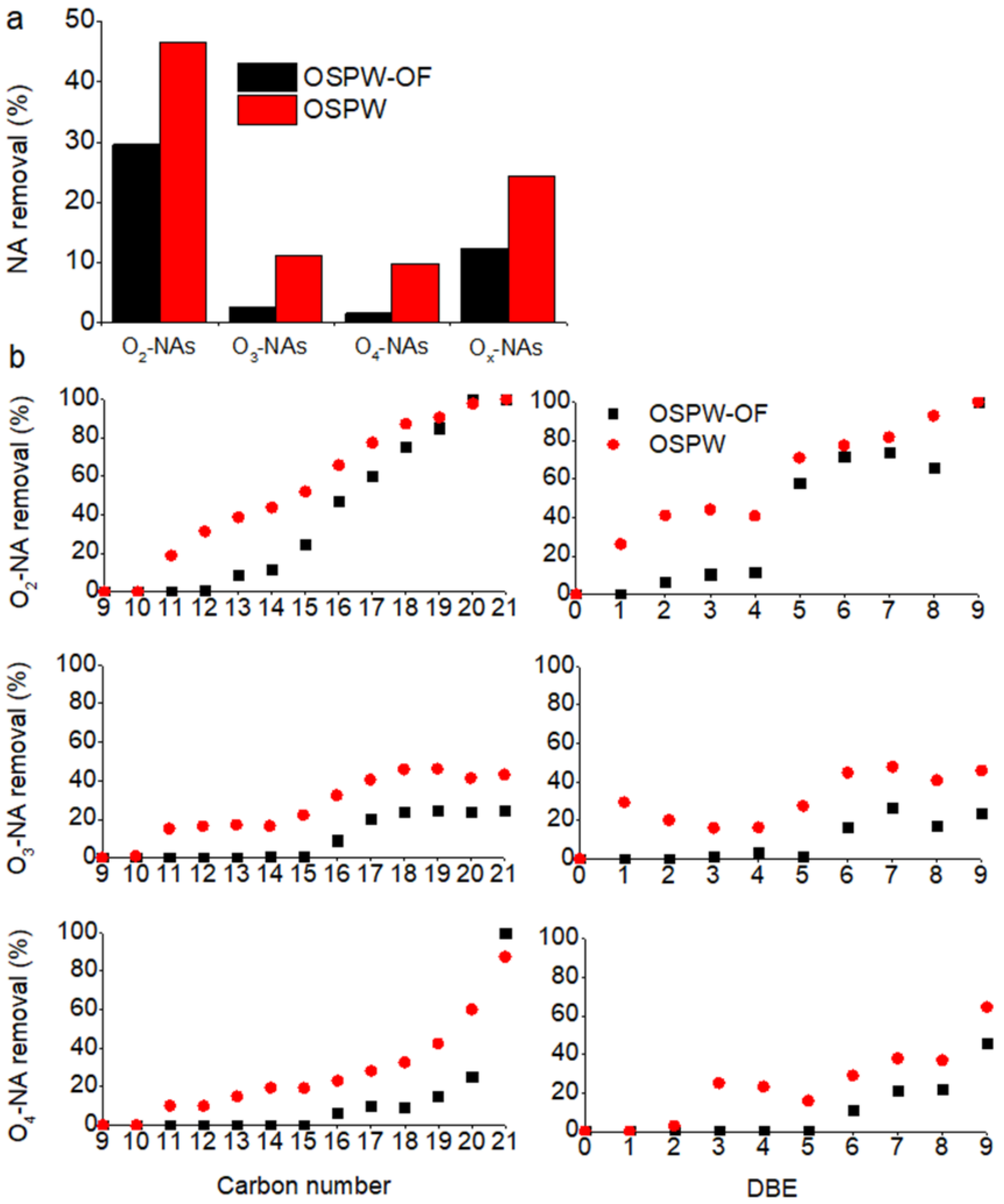

Figure 6.2 NA removal in OSPW-OF (extracted OSPW organics re-dissolved in 3 mM $NaHCO_3$ buffer, in the absence of inorganics) and OSPW (in the presence of inorganics) (a) and NA removal with respect to carbon number and DBE (b) after 60 min of 2.92 mW/cm^2 UV irradiation at pH of 8.7. (Note: O_x-NAs is the sum of O_2-, O_3-, O_4-, O_5-, and O_6-NAs. Initial concentration of NA species in OSPW and OSPW-OF is listed in Table 6-1).

6.3.2 The Effect of OSPW Inorganic Fraction on The Photodegradation of a Model NA

OSPW containing only inorganic fraction (OSPW-IF) was obtained to study its effect on the photodegradation of a model compound ACA. The chemical and physical properties of OSPW and OSPW-IF are listed in Table 6.2. Dissolved organic carbon (DOC) in OSPW-IF was 1.81 ± 0.03 mg/L after DOC was removed by GAC. There was no significant difference in terms of the main anions and cations concentration, pH, conductivity and alkalinity between OSPW and OSPW-IF, indicating that the obtained OSPW-IF was able to represent the condition of real OSPW for the following experiments.

Solution of ACA (40 mg/L) in either 3 mM $NaHCO_3$ buffer (ACA-Buffer) or OSPW-IF (ACA-OSPW-IF) was exposed under UV irradiation to further investigate the role of OSPW-IF on the photodegradation of a model NA. The resulted showed a 30.9% degradation of ACA in ACA-OSPW-IF, while no degradation of ACA in ACA-buffer solution was observed after 60 min of UV exposure (Figure 6.2), indicating that the OSPW-IF induced the photodegradation of ACA. The results demonstrated the presence of photosensitizers in OSPW, which could produce reactive radicals and induce the degradation of ACA. In addition, the higher absorbance of ACA-OSPW-IF compared to ACA-Buffer (Figure 6.1) also confirmed the existing of photosensitizers in OSPW-IF.

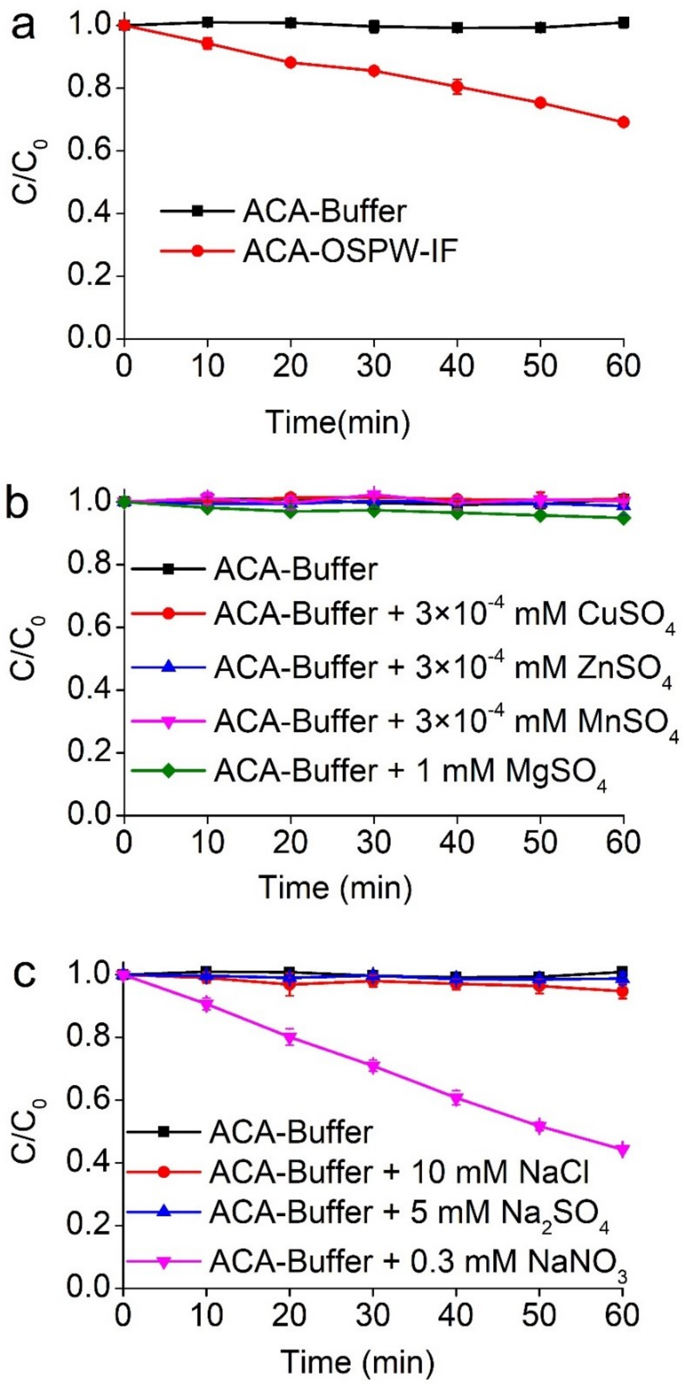

Figure 6.3 Photodegradation of model compound 1-Adamantanecarboxylic acid (ACA) in the presence of (a) OSPW inorganics, (b) individual cations, and (c) anions with the irradiation intensity of 2.92 mW/cm^2 at pH 8.7. [ACA]$_0$=40 mg/L. (Note: Buffer is 3 mM of $NaHCO_3$ solution; The concentration of each ion is similar with their concentration in OSPW).

In order to clarify the specific ions in OSPW that induced the photodegradation of ACA, main ions with similar concentration in OSPW were individually spiked into each ACA-Buffer and exposed under UV irradiation. The results (Figures 6.3b and 6.3c) showed that all cations as well as Cl^- and SO_4^{2-} demonstrated no effect on the photodegradation of ACA, while NO_3^- induced the photodegradation of ACA. Previous work showed that the addition of Cl^- to pure water increased the photolytic rate of thiamphenicol and florfenicol under UV-vis irradiation due to the formation of $^1O_2$ (Ge et al., 2009). However, the promotion effect of Cl^- on the photodegradation of ACA was not observed in this study. Sanches et al. (2011) reported that experiments conducted with different target compounds in different matrices may show contradictory effects in terms of the influence of chloride on the degradation efficiency. Thus, no ACA degradation was observed in this study with the addition of Cl^- may due to the low reactivity of ACA to $^1O_2$ or the low production of $^1O_2$ in our system.

Previous work pointed out that nitrate is an important photosensitizer that is ubiquitous and also the key source of the •OH in natural waters (Brezonik and Fulkerson-Brekken, 1998, Jacobs et al., 2008). Consistent with the previous work about the initiation effect of nitrate on the photodegradation of other organic compounds (e.g., benzophenone, atenolol, PAHs, and chlorotoluron) (Ge et al., 2019, Jacobs et al., 2008, Ji et al., 2012, Nélieu et al., 2009), this study demonstrated the induced effect of nitrate on the indirect photolysis of ACA. In addition, light absorption by the ACA sample in OSPW-IF (ACA-OSPW-IF) showed that nearly all the light-absorbing properties of the inorganic fraction in OSPW appeared to be dominated by nitrate when compared to the UV-vis absorbance spectrum of ACA in 0.3 mM nitrate solution (ACA-0.3 mM nitrate) (Figure 6.1), which demonstrated that nitrate was the dominant inorganic photosensitizer in OSPW.

The fluence-based pseudo-first-order decay rate constants (k, cm^2/J) of ACA in 0.3 mM nitrate and OSPW-IF is indicated by a linear plot of ln (C/C_0) versus the UV dose of fluence (Figure 6.4). The rate equation was expressed as

$$\frac{-d[C]}{dF} = k\,[C] \qquad (1)$$

The rate constant of ACA in 0.3 mM nitrate was 0.0734 cm^2/J, which was higher than that in OSPW-IF (0.0332 cm^2/J), indicating that the presence of other water matrix in OSPW-IF may inhibit nitrate-induced photodegradation of ACA.

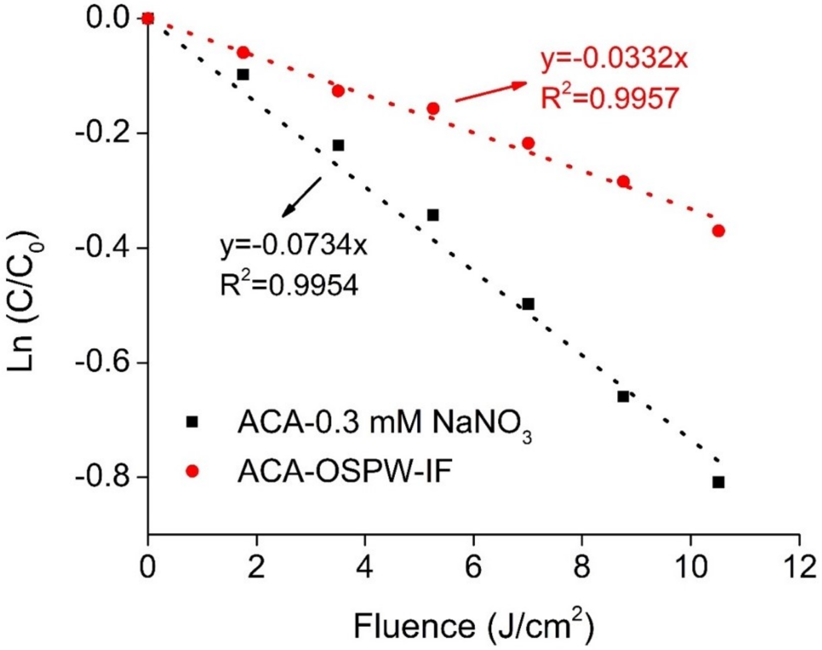

Figure 6.4 Photodegradation of ACA as a function of fluence in the presence of 0.3 mM nitrate and OSPW inorganic fraction at irradiation intensity of 2.92 mW/cm^2 and pH of 8.7, $[ACA]_0$=40 mg/L.

Influence of abundance anions existing in OSPW (Cl^-, HCO_3^-, and SO_4^{2-}) on the nitrate-induced photodegradation of ACA was studied. The results showed that Cl^- and SO_4^{2-} played a negligible role on the photodegradation of ACA in the presence of nitrate, while HCO_3^- inhibited the degradation of ACA (Figure 6.5). Similar inhibition effect of HCO_3^- was obtained on the photodegradation of oxytetracycline in the presence of NO_3^- in another study by Li et al. (2018). The inhibition effect of HCO_3^- owes to its function as a •OH scavenger via the following equations (Eq.2). In addition, hydrolysis of HCO_3^- produces CO_3^{2-}, which is highly reactive with •OH (Eq.3) (Liu et al. 2017).

$$HCO_3^- + \bullet\,\mathrm{OH} \rightarrow CO_3\bullet + H_2O \quad [k_{\mathrm{HCO_3^-,\bullet OH}} = 8.5 \times 10^6\ \mathrm{M^{-1}S^{-1}}] \qquad (2)$$

$$CO_3^{2-} + \bullet\,\mathrm{OH} \rightarrow CO_3\bullet + OH^- \quad [k_{\mathrm{CO_3^{2-},\bullet OH}} = 3.9 \times 10^8\ \mathrm{M^{-1}S^{-1}}] \qquad (3)$$

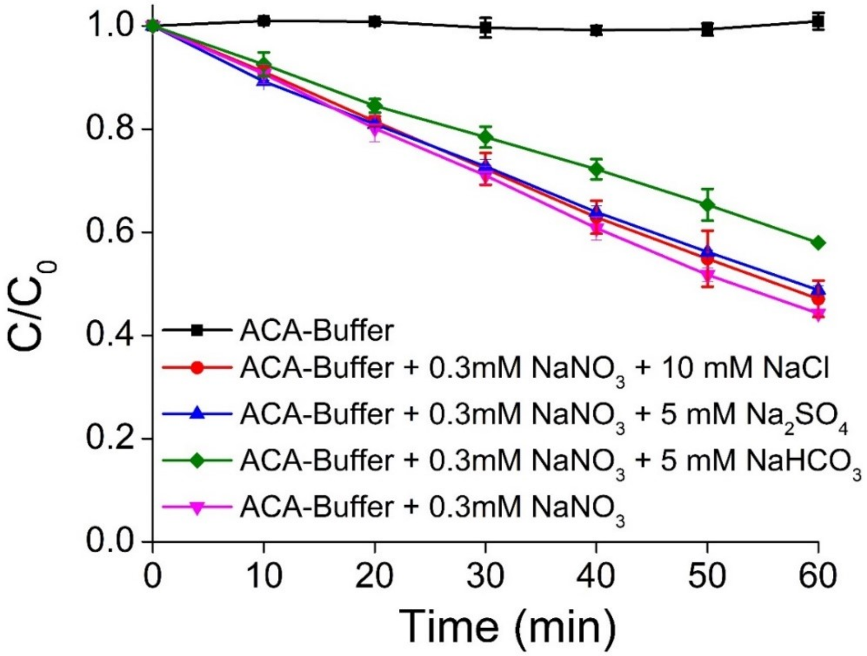

Figure 6.5 The comprehensive influence of NO_3^-, HCO_3^-, SO_4^{2-} and Cl^- on the photodegradation of ACA at irradiation intensity of 2.92 mW/cm^2 and pH of 8.7 ($[ACA]_0$ = 40 mg/L).

6.3.3 Exploration of The Reaction Mechanism of The Nitrate Induced Photodegradation of ACA

6.3.3.1 Effect of •OH on The NO_3^- Induced Photodegradation of ACA

NO_3^- can absorb light and act as a photosensitizer to promote the photoreaction (Vione et al. 2005). The photolysis of NO_3^- leads to the formation of both •OH and reactive nitrogen species (RNS: NO• and NO_2•) via the following photochemical processes (Eq. 4-7) (Nélieu et al. 2009). The NO_2• could then recombined to form N_2O_4 which would degrade back into NO_3^- and NO_2^- (Eq. 8 & 9) and continue the photolysis process.

$$\mathrm{NO_3^-} + \mathrm{H_2O} + \mathrm{h}v \rightarrow NO_2 \bullet + \ \bullet \mathrm{OH} + \mathrm{OH^-} \qquad (4)$$

$$\mathrm{NO_3^-} + \mathrm{h}v \rightarrow \mathrm{NO_2^-} + \ \mathrm{O(^3P)} \qquad (5)$$

$$\mathrm{NO_2^-} + \mathrm{H_2O} + \mathrm{h}v \rightarrow \mathrm{NO} \bullet + \bullet \mathrm{OH} + \mathrm{OH^-} \qquad (6)$$

$$\mathrm{NO_2^-} + \bullet \mathrm{OH} \rightarrow NO_2 \bullet + \mathrm{OH^-} \qquad (7)$$

$$2\ \mathrm{NO_2} \bullet \rightarrow \mathrm{N_2O_4} \qquad (8)$$

$$\mathrm{N_2O_4} + \mathrm{H_2O} \rightarrow \ 2\mathrm{H^+} + \mathrm{NO_2^-} + \mathrm{NO_3^-} \qquad (9)$$

The produced •OH and RNS from photolysis of NO_3^- could oxidize ACA and contribute to the indirect photolysis of ACA. To identify the dominant radicals responsible for the ACA degradation in the presence of NO_3^-, two radical quenching agents, TBA and AA, were added into the ACA solution with 0.3 mM NO_3^- to capture hydroxyl and nitrate radicals. The two scavengers have been reported of different reactivity with •OH and •NO_3. Specifically, the rate constants of TBA and AA with •OH and •NO_3 are as following (Anbar and Neta 1967, Feng et al. 2015, Mezyk et al. 2017):

$$\mathrm{TBA} + \bullet \mathrm{OH} \rightarrow \mathrm{intermediates}\ (k = 2.8 \times 10^8\ \mathrm{M^{-1}}S^{-1}) \qquad (10)$$

$\mathrm{TBA} + \bullet\,\mathrm{NO_3} \rightarrow \mathrm{intermediates}\ (k = 5.7 \pm 1.3\ \times 10^4\ \mathrm{M^{-1}}S^{-1})$ (11)

$\mathrm{AA} + \bullet\,\mathrm{OH} \rightarrow \mathrm{intermediates}\ (k = 1.2\ \times 10^9\ \mathrm{M^{-1}}S^{-1})$ (12)

$\mathrm{AA} + \bullet\,\mathrm{NO_3} \rightarrow \mathrm{intermediates}\ (k = 2.2 \pm 0.2\ \times 10^8\ \mathrm{M^{-1}}S^{-1})$ (13)

Based on these characteristics, TBA was selected to scavenge •OH, whereas AA was used to scavenge both •OH and RNS. As shown in Figure 6.6a, the addition of 10 mM AA completely inhibited the photodegradation of ACA and 10 mM TBA diminishing ACA removal to 12.8% after 60 min UV exposure. The restrained effect of TBA was enhanced with increasing concentration. The result indicated that ACA was predominantly oxidized by •OH. Similar findings were also obtained by Ji et al. (2012), where it was suggested that •OH was the dominated radical in the nitrate-induced photodegradation of atenolol. The completed inhibition of the photodegradation of ACA in the presence of AA indicated that RNS could oxidize ACA, although at a much slower rate than •OH, which was expected due to the much lower redox potential of 1.03 V for NO_2• as compared to •OH (1.8 - 2.7 V) (Ji et al. 2017). Moreover, as RNS were involved in the regeneration of NO_2^- and NO_3^- for the continuous production of •OH (Eq. 4-9), the scavenging of both RNS and •OH by AA completely quenched the reactive radicals in the system, which completely inhibited the photodegradation of ACA.

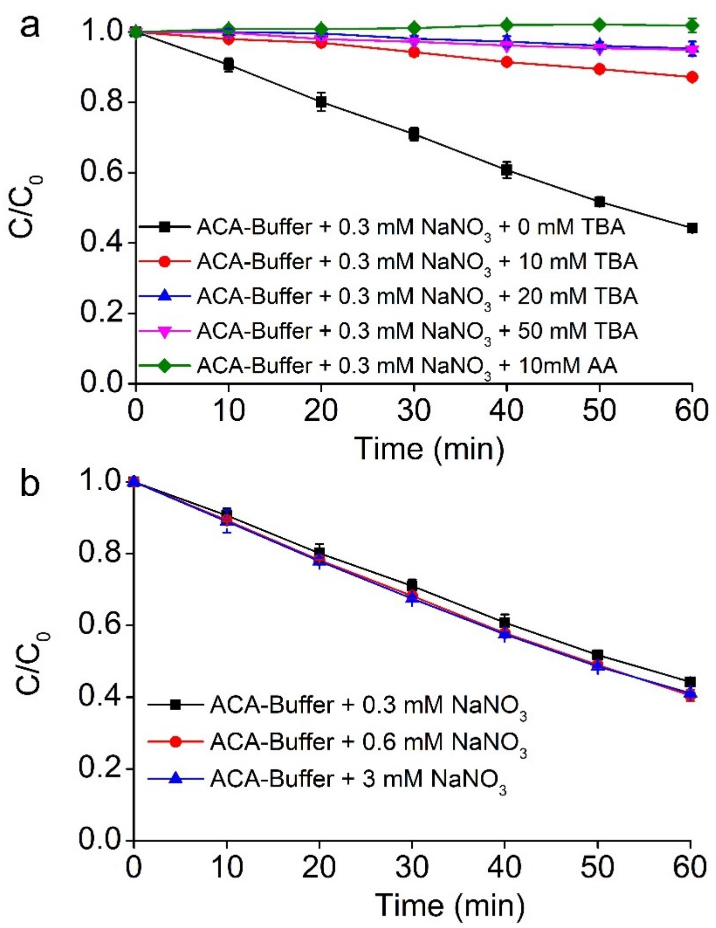

Figure 6.6 Effect of *tert*-butyl alcohol (TBA), allyl alcohol (AA) and $NaNO_3$ concentration on the photodegradation degradation of 1-Adamantanecarboxylic acid (ACA) with the irradiation intensity of 2.92 mW/cm^2 at pH 8.7. $[ACA]_0$=40 mg/L.

A positive correlation between nitrate concentration and the production of •OH under the exposure of UV lamp was reported previously (Brezonik and Fulkerson-Brekken 1998). Therefore, it was expected that increasing the NO_3^- concentration would increasing the production of •OH and enhance the degradation of ACA. However, our results showed that with the increasing of NO_3^- concentration from 0.3 mM to 3 mM, insignificance increase of ACA degradation was observed (Figure 6.6b). It may be explained by the scavenging effect of NO_2^- on •OH. With the increasing concentration of NO_3^-, excessively NO_2^- was generated, which consumed •OH and resulted in negligible enhanced ACA degradation (Eq.7) (Anbar and Neta 1967, Liu et al. 2017). Moreover, the formation of N_2O_4 during the photolysis of NO_3^- process contributing to the yield back of NO_3^- and NO_2^- (Eq. 8 and 9). The regenerated NO_3^- would continue to initiate the production of •OH under UV exposure (Li et al. 2018, Vione et al. 2005). The result also suggested that natural occurrence concentration of nitrate in OSPW was enough and of advantage for the nitrate-induced photodegradation of the model compound. The results showed that NO_3^- acted as an initiator for the indirect photolysis of ACA. After initiation process, the propagation of radicals in the system would continue with the auto oxidation of ACA or the regeneration of NO_3^-. Thus, in our study, NO_3^- concentration was not a key factor on the rate of ACA photodegradation. This result also demonstrated that the nitrate-induced photo-oxidation could potentially be used as a low-cost passive system for OSPW remediation in terms of the degradation of organic contaminants. However, study involving more organic compounds would be required. In addition, the study by Ji et al. 2017 has also shown similar trend where the increase in nitrite (NO_2^-) concentration did not increase the rate of degradation of phenol, but the authors found that the number and concentration of nitroaromatic compounds increased with increasing nitrite concentration. Thus, it is also important to investigate the by-products formation from the nitrate-induced photodegradation of ACA.

6.3.3.2 Identification of Degradation By-products and Pathways

Samples of ACA-Buffer in the presence of NO_3^- (100 mg/L ACA and 0.8mM NO_3^-) before and after UV irradiation was analyzed by UPLC-TOF-MS to identify the by-products of the nitrate-induced photodegradation of ACA. A longer irradiation time of 120 min and higher concentration of ACA (100 mg/L) and NO_3^- (0.8 mM) were used to ensure high enough concentration of the by-products were produced for the identification of the by-products.

Meanwhile, difference in the by-products produced between a short and long irradiation time may be observed with a longer irradiation time. Three new peaks in the total chromatogram (TIC) were observed at 4.26, 4.54 and 4.84 min after the UV irradiation (Figure 6.7), indicating that at least three by-products were formed. Based on the elemental formula generated from the measured mass (±5 ppm) of the new peaks, by-products with 6 different molecular formula were produced (Table 6.3), in which one isomer was presented for illustration proposes. The corresponding theoretical and observed isotope ratio of the proposed by-products are listed in Appendix B Figure B.1-B.6.

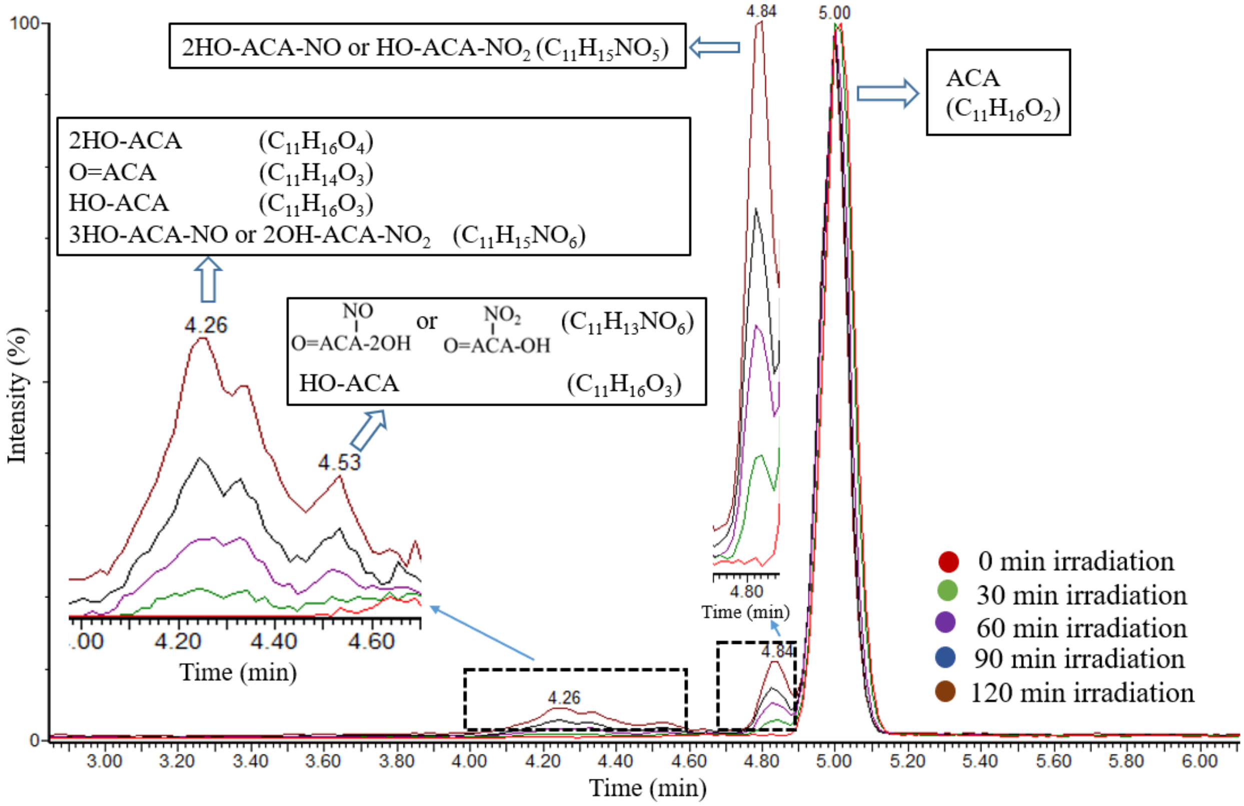

Figure 6.7 UPLC-TOF-MS total ion chromatograms (TICs) of ACA samples after different irradiation times (0 min to 120 min with 30 min interval) in ESI negative mode.

Table 6.3 Proposed molecular formulas and structures of the by-products of nitrate-induced photodegradation of 1-Adamantanecarboxylic acid (ACA) via mass spectra

Retention time (min)	Observed *m/z* [M-H]$^-$	ΔPPM^a	Molecular Formula
4.26	193.0847	4.7	$C_{11}H_{14}O_3$
4.54	195.1027	3.1	$C_{11}H_{16}O_3$
4.26	195.1028	3.6	
4.26	211.0980	4.7	$C_{11}H_{16}O_4$
4.84	240.0881	3.7	$C_{11}H_{15}NO_5$
4.54	254.0674	3.5	$C_{11}H_{13}NO_6$
4.26	256.0826	2.0	$C_{11}H_{15}NO_6$

a: ΔPPM shows the difference between the observed mass and the theoretical mass of the proposed by-products molecules, which indicates the accuracy of mass. ΔPPM= $\frac{observed\ mass - theoretical\ mass}{theoretical\ mass} \times 10^6$.

The possible degradation pathways with 120 min exposure were proposed in Figure 6.8. In Pathway I, the •OH attacked a secondary carbon forming a carbon radical which would then react with dissolved oxygen to form carbonylated-ACA (P1, Figure 6.8) and hydroxylated-ACA (P2-1, Figure 6.8). In Pathway II, the •OH would attack a tertiary carbon forming a carbon radical which react with another •OH to form hydroxylated-ACA (P2-2, Figure 6.8), where the hydroxyl was substituted at a tertiary carbon instead of a secondary carbon in P2-1. Then, •OH continued to attack P2-2 at another tertiary carbon to form the hydroxylated-ACA radical which then combined with NO_2• to form one hydroxyl and one nitro substituent by-product (P4-1, Figure 6.8). Moreover, the reaction between the •OH and secondary carbon would continue to form by-products with one carbonyl, one hydroxyl, and one nitro substituents (P5-1) as well as two hydroxyl and one nitro substituents (P6-1, Figure 6.8). Meanwhile, for pathway III, the reaction between the •OH and secondary or tertiary carbon would continue to form by-products with two hydroxyl substituents (P3, Figure 6.8). Then, in the presence of NO•, a two hydroxyl and one nitroso substituents by-products (P4-2, Figure 6.8) and finally three hydroxyl and one nitroso substituents (P5-2, Figure 6.8) as well as two hydroxyl, one carbonyl and one nitroso substituents (P6, Figure 6.8) were formed. As •OH is more reactivity towards tertiary carbon due to the formation of more stable intermediate radicals after hydrogen atom abstractions (Afzal et al., 2012, Anbar et al., 1966), the by-products proposed in pathway II and III had the substituents at the tertiary carbon.

The degradation pathways agreed with our earlier finding (Section 6.3.3.1) that •OH was the key oxidizing species and the change of nitrate concentration has little impact on the degradation rate of ACA, as the initial step for all the proposed pathways would be the formation ACA radical through an electron transfer by •OH. The plausible reason that the substitution of only one nitro (NO_2) or nitroso (NO) occurred in step 2 in pathway II and step 3 in pathway III was that the reactivity of RNS was lower than •OH, where the reactivity to ACA be proposed to be •OH> NO_2•> NO•. As no three hydroxyls only substituent was detected, it could suggest that pathway II and III were stepwise reaction instead of a simultaneous reaction, where the substitution of a third hydroxyl group was not favorable. P5 and P6 were only detected in the samples that were exposed under UV irradiance for 90 and 120 min, while not observed in the samples exposed for 30 and 60 min. The result strongly suggested that P5 and P6 were formed after the H abstraction happened at secondary carbon where the reactivity is lower than that at tertiary carbon. The formation of nitroso and nitro substituted by-products also suggested the possibility of the formation of potentially toxic and carcinogenic by-product such as nitroaromatic in the presence of aromatic and nitrosamine if an amine is present in the structure. Thus, further study on the formation of nitrosamine from nitrate induce photo-oxidation should be conducted and the toxicity and carcinogenicity of the treated water should be tested.

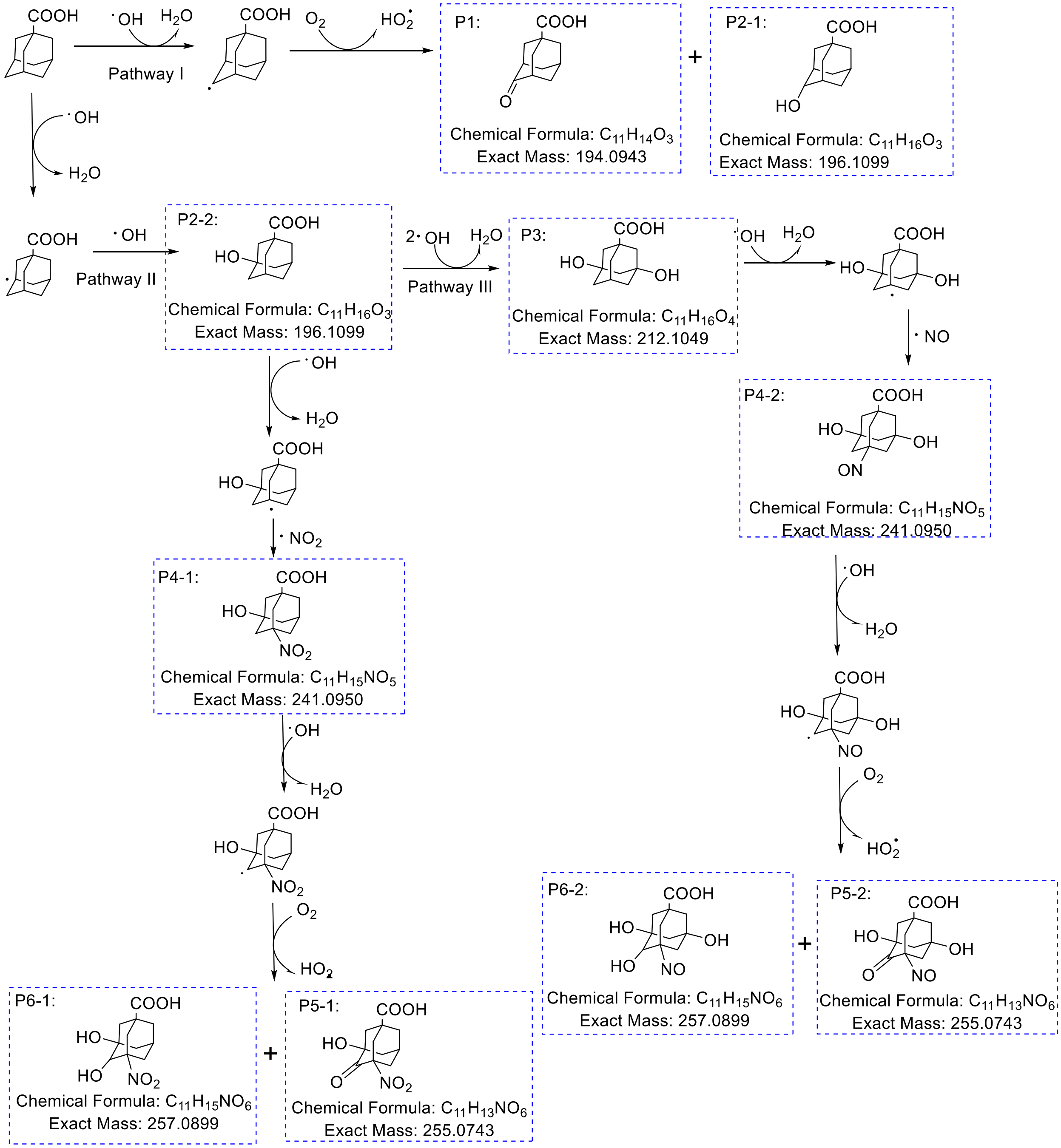

Figure 6.8 Possible transformation pathways of nitrate induced photodegradation of 1-Adamantanecarboxylic acid (ACA). Structure highlighted were detected with UPLC-TOF-MS.

6.4 Conclusions

After 60 min of direct exposure under UV irradiation of 2.92 mW/cm^2, higher degradation of NAs in OSPW (24.3%) as compared to that in OSPW-OF (12.4%) showed that some inorganic species in OSPW enhanced the photodegradation of NAs. NAs with higher carbon number and DBE were preferentially degraded during the OSPW direct photo-oxidation process. It was also confirmed that some inorganic species in OSPW could induce the photodegradation of a model compound ACA which was not degradable by the direct photolysis process. It was found that NO_3^- was the inorganic ion responsible for the induced photodegradation process as no photodegradation of ACA was observed in the presence of other major ions in OSPW. Abundance ions in OSPW such as Cl^- and SO_4^{2-} showed negligible effect on the nitrate-induced photodegradation of ACA, while HCO_3^- inhibited the photodegradation of ACA. Both •OH and RNS were generated during the nitrate-induced ACA photodegradation process, where •OH was demonstrated to be the dominant reactive species that contribute to the degradation of ACA. Ten by-products (including a pair of isomers) were proposed to be formed during the nitrate induced ACA photodegradation process through three different pathways.

This study showed that the nitrate could be utilized as a natural photosensitizer to induce photo-oxidation of organic contaminants in OSPW and could potentially be used as a low-cost passive system for the remediation of OSPW. As nitrate is known to be ubiquitous in natural aquatic environment, nitrate-induced photodegradation could also be used in other wastewater treatment system such as waste stabilization pond and wetland remediation where the wastewaters are exposed for natural degradation. In conclusion, the results of this research suggest that the photodegradation efficiency of OSPW treatment strategies can be enhanced in presence of the inorganic species in OSPW.

6.5 References

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Chapter 7 Conclusions and Recommendations

7.1 Thesis Overview

Large volume of oil sands process water (OSPW) generated from oil sands industry has caused environmental concern. To eliminate the potential environmental risks and to allow the release of treated OSPW into the environment, remediation processes such as physical, chemical, biological and their combinations have been investigated to remove the contaminants in OSPW and the toxic effect of OSPW towards organisms. Advanced oxidation processes (AOPs) have the capacity to oxidize biological recalcitrant compounds and enhance their biodegradability. Thus, AOPs are potential treatment processes for the practical remediation of OSPW. Considering the presence of varieties of inorganic ions in OSPW, it is crucial to systematically investigate how these inorganic ions affect OSPW oxidation treatment efficiency in terms of the degradation of organic contaminants and to provide fundamental information for the implementation of oxidation treatment on the remediation of OSPW at large scale.

To better understand the influence of inorganic ions in OSPW on the oxidation of organic contaminants, Chapter 3 of this research was to develop methods to isolate OSPW inorganic and organic fractions. Moreover, Ag-ion SPE was used to fractionate OSPW organic components into aliphatic O_2−NA, aromatic O_2−NA, O_3−NA, and O_4−NA to study their ozonation reactivity in Chapter 4.

As described in Chapter 5, in this research, the impact of water matrix (inorganic components and particles) in OSPW on the ozonation of both model NA and the natural NA mixture was investigated to provide fundamental information for the practical implementation of ozonation on OSPW remediation. In addition, the impact of OSPW inorganic fraction on the photo-oxidation of NAs was also studied in this research (Chapter 6) to clarify whether any inorganic ions present in

OSPW could be utilized as a photosensitizer to induce the photodegradation of organic contaminants, which could provide information for the application of passive solar photolysis of OSPW without the addition of external catalysts.

7.2 Conclusions

The main conclusions of this research based on different projects are listed as follows:

Separation of OSPW inorganics and organics

- HLB SPE process achieved the highest DOC and NA recovery (95.41% DOC, 89.98% O_x-NAs) as compared to other SPE cartridges and DCM LLE (48.84% DOC, 81.05% O_x-NAs). SPE using HLB cartridge with one step methanol elution is a convenient method to extract OSPW organics and achieved higher recovery efficiency.
- After GAC adsorption, DOC of the effluent was 2.04 ± 0.11mg/L, with 96.13% of DOC removed. Insignificant properties difference between original OSPW and the GAC effluent was observed. The adsorption and leaching of ions after the GAC adsorption were negligible. Thus, GAC adsorption was able to isolate OSPW inorganic fraction representable to real OSPW.
- As OSPW is composed of complex mixture with some organic occurring at trace concentration, and thus it is difficult to analyze and identify the organic compounds individually. Extraction is, therefore, required before the organic compounds analysis using methods such as ^{1}H nuclear magnetic resonance, Fourier transform infrared spectroscopy and high resolution mass spectrometry analysis. SPE using HLB cartridge with methanol elution is recommended as an alternative for the extraction of organics from OSPW for the analysis of OSPW organic components.

Fractionation of OSPW NA species and their ozonation reactivity

- OSPW organics were fractionated to aliphatic O_2-NA, aromatic O_2-NA, O_3-NA, and O_4-NA species using Ag-ion SPE. 16.8 mg/L ozone treatment on the NA species achieved the removal of aliphatic O_2-NAs, aromatic O_2-NAs, O_3-NAs, and O_4-NAs to be 97.2%, 94.7%, 59.4% and 44.7%, respectively. O_2- and oxidized NAs with larger carbon number were favorably removed during ozonation treatment.
- The degradation of oxidized NAs consumed more ozone in the molar ratio than the degradation of aliphatic and aromatic O_2-NAs. Thus, the reactivity of oxidized NAs was lower than that of O_2-NAs.

Impact of inorganic fraction and particles on the ozonation of NAs

- CHA removal in buffer (14.03%, 18.25% and 30.99%) was higher than that in the solution of OSPW-IF (9.49%, 12.85% and 20.78%) after 20 mg/L, 24 mg/L and 33 mg/L of ozone treatment, while the utilized ozone dosages in buffer (16.91 mg/L, 23.44 mg/L and 45.06 mg/L) were lower than those in the solution of OSPW-IF (20.28 mg/L, 28.72 mg/L and 55.16 mg/L). It was concluded that OSPW-IF consumed ozone and adversely affected the ozonation of CHA. NH_4^+, Mn^{2+}, Cl^- and HCO_3^- were demonstrated to be responsible for the negative effect on CHA degradation.

- The removal of O_2-NAs, O_3-NAs, O_4-NAs and O_x-NAs in buffer (86.62%, 66.70%, 55.99%, 68.70%) were higher than that in OSPW (82.72%, 51.76%, 43.26%, 60.39%), which demonstrated the inhibition effect of inorganic fraction in OSPW on the ozonation of natural NA mixture in OSPW.

- There was insignificant difference for NA removal in non-filtered and filtered OSPW after ozonation, indicating that ozonation of NAs in OSPW was unaffected by particles.

- The presence of inorganic fraction in OSPW could affect OSPW ozonation treatment, by inhibiting NA degradation and increasing ozone demand. However, the presence of particle is not a concern for the ozonation treatment of OSPW.

- The presence of inorganic fraction in OSPW inhibited the OSPW ozonation performance in terms of NA removal. Although some pretreatment processes such as coagulation, flocculation and ion exchange could remove the inorganics and eliminate the negative effect. It is impractical to implement these pretreatment processes due to the high cost of the processes build-up and maintenance. When designing a treatment train, it is recommended to place ozonation as an intermediate or at post treatment after other treatment processes which could remove the ions that showed inhibiting effects on the ozonation of organic compounds. For example, NH_4^+ and HCO_3^-, which was proved to have the negative effect on the ozonation of model NA compounds in this study, could be consumed in an aerobic biological treatment.

Photodegradation of NAs induced by inorganic photosensitizer in OSPW

- Direct photo-oxidation achieved higher degradation of NAs in OSPW (24.3%) than the degradation of extracted NAs in buffer (12.4%), which indicated that OSPW-IF enhanced the photodegradation of NAs. NAs with higher carbon number and DBE were preferentially degraded during the OSPW direct photo-oxidation process.

- OSPW-IF induced the photodegradation of a model compound ACA. Nitrate was the most likely inorganic ion in OSPW, which was responsible for the induced photodegradation process. Both •OH and reactive nitrogen species were generated during the nitrate-induced ACA photodegradation process, where •OH was demonstrated to be the dominant reactive species that contributed to the degradation of ACA. Ten by-products (including a pair of isomers) were proposed to be formed from the nitrate-induced photodegradation of ACA.

7.3 Recommendations

Based on the results obtained in this research, the following recommendations are drawn for future studies.

- As methods to separation OSPW organic and inorganic fraction have been developed in this work, it is recommended to conduct some toxicity assays to assess how OSPW-OF, OSPW-IF and their interaction result in the toxic effects of whole OSPW.
- The influences of OSPW inorganic fraction on ozonation and photo-oxidation of NAs were investigated in this study. The influence of inorganics on other treatment processes such as biological and physical adsorption processes could also be conducted in the future to provide information for the design of the practical OSPW remediation.
- The utilization of silver-ion SPE in this work was proved to be a suitable method to fractionate OSPW NA species. Toxicity of individual NAs species towards different organisms could be assessed in the future. Other treatment processes could be conducted on the fractionated NA species to study their reactivity. Reactivity of different NA species could provide information for future studies investigating the degradation mechanism under other treatment conditions. In addition, knowing the reactivity of different NA species is crucial for the design of OSPW remediation processes targeting species with high toxicity.
- Photodegradation efficiency of OSPW treatment strategies can be enhanced in presence of some photosensitizers. Thus, photolysis of OSPW could potentially be used as a low-cost passive system for the degradation of organic compounds in OSPW. The enhanced effect of OSPW

inorganic fraction on the photodegradation of the organic contaminants under solar exposure could be further studied.

- Moreover, it is advisable to compare the relative photodegradation kinetics and identify the possible by-products of model NA compounds with diverse structures in the solution of OSPW-IF under solar exposure to better understand the NA photodegradation kinetics during the practical OSPW photolysis process.
- The degradation of NAs in OSPW-OF indicated that NA could also be degraded in the absence of inorganics. Therefore, some organic components in OSPW may absorb light and act as photosensitizer to produce reactive radicals. It is recommended that in the future, the organic photosensitizers in OSPW could be investigated so that they could be utilized for the passive solar remediation of OSPW.

Appendix

Appendix A

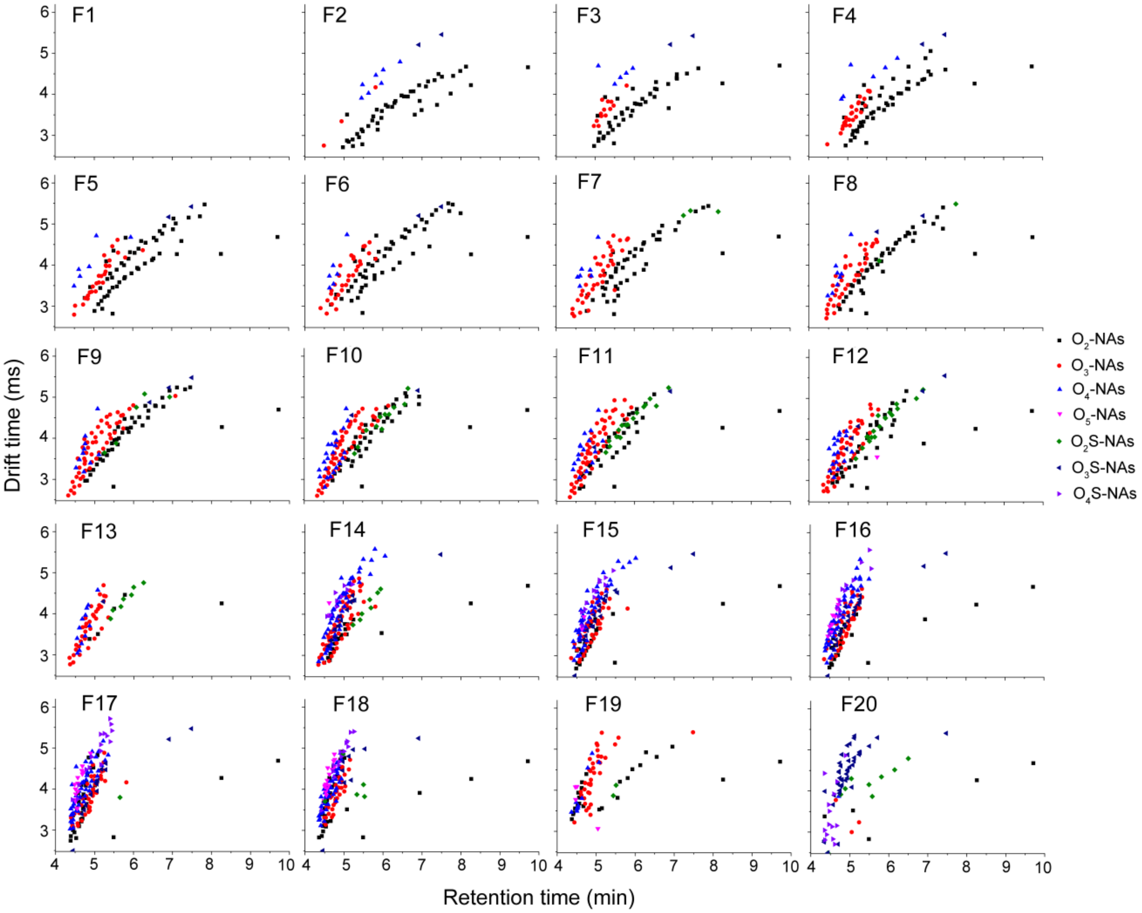

Figure A.1 O_x−NA ($2 \leq x \leq 5$) and O_yS−NA ($2 \leq y \leq 4$) species were identified on the basis of the match of accurate masses for Ag-ion SPE fractions F1−F20 from raw OSPW.

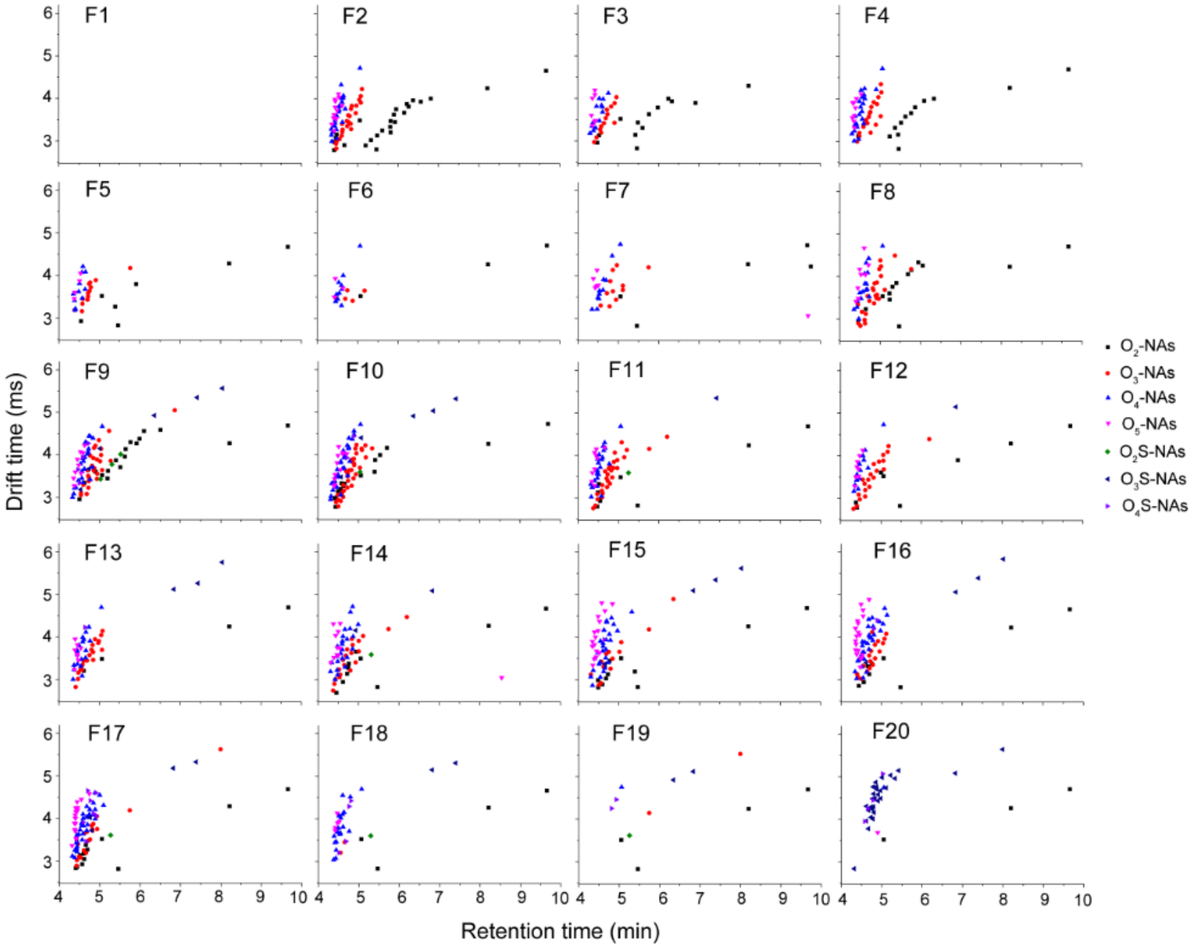

Figure A.2 O_x−NA ($2 \leq x \leq 5$) and O_yS−NA ($2 \leq y \leq 4$) species were identified based on the match of accurate masses for Ag-ion SPE fractions F1−F20 from ozonated OSPW with the applied ozone dosage 16.8 mg/L

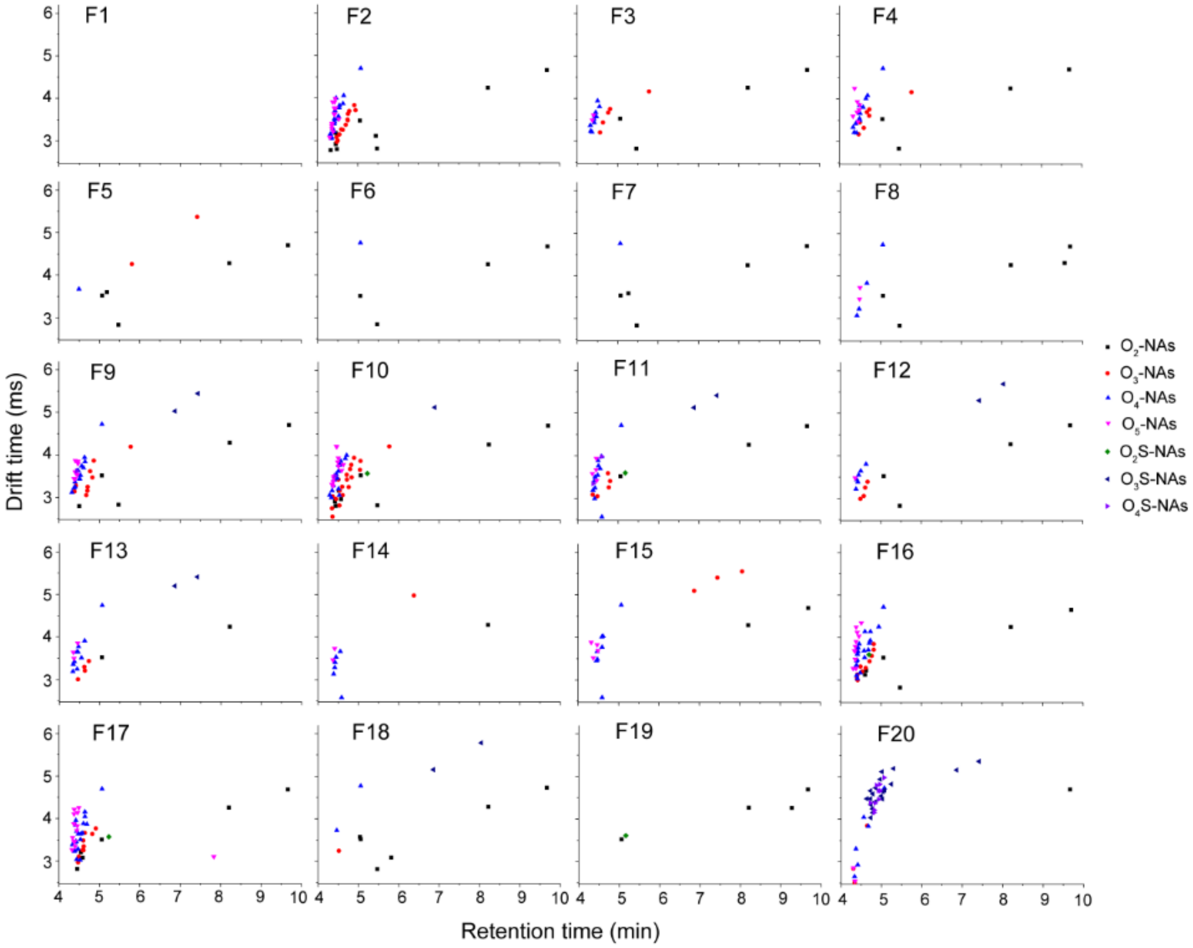

Figure A.3 O_x−NA ($2 \leq x \leq 5$) and O_yS−NA ($2 \leq y \leq 4$) species were identified on the basis of the match of accurate masses for Ag-ion SPE fractions F1−F20 from ozonated OSPW with the applied ozone dosage 33.6 mg/L.

Appendix B

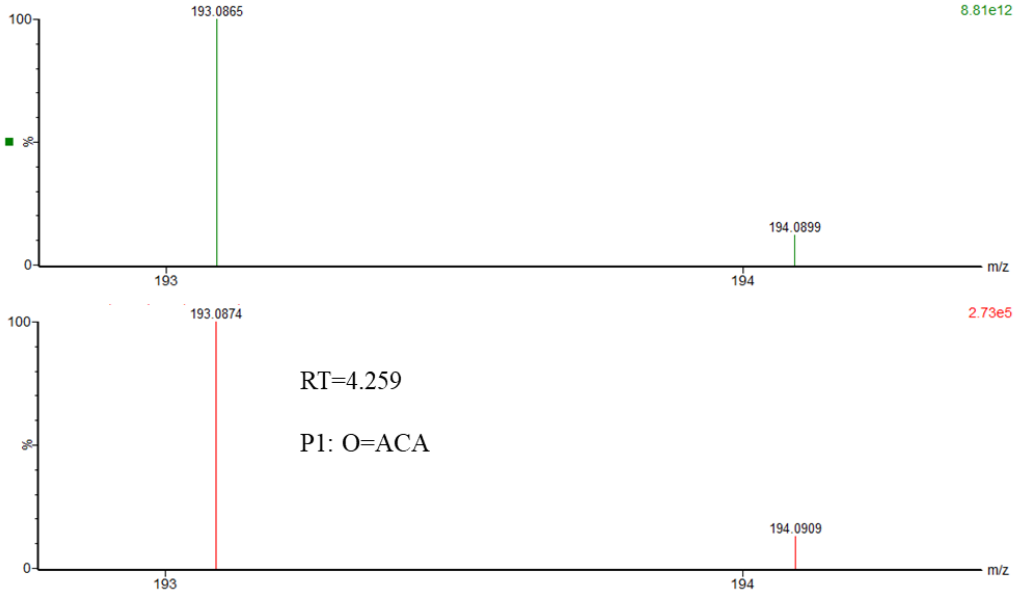

Figure B.1 Theoretical (green)and observed (red) isotope ration of proposed by-product P1.

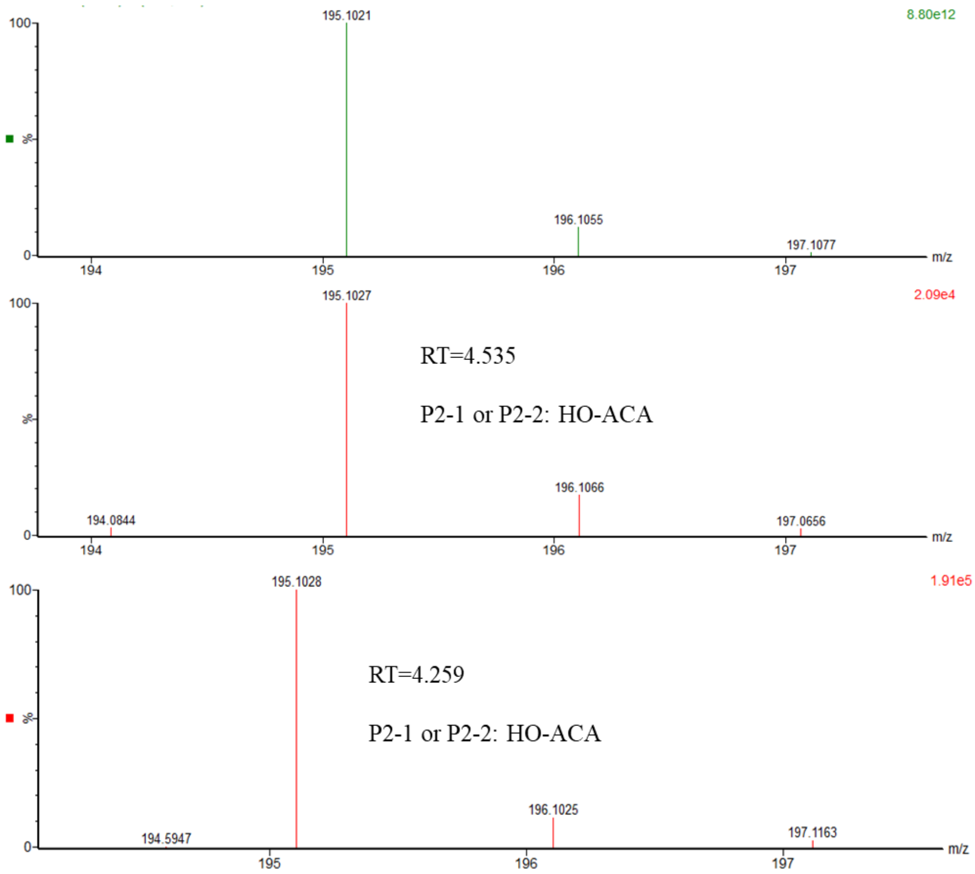

Figure B.2 Theoretical (green) and observed (red) isotope ration of proposed by-product P2-1&2

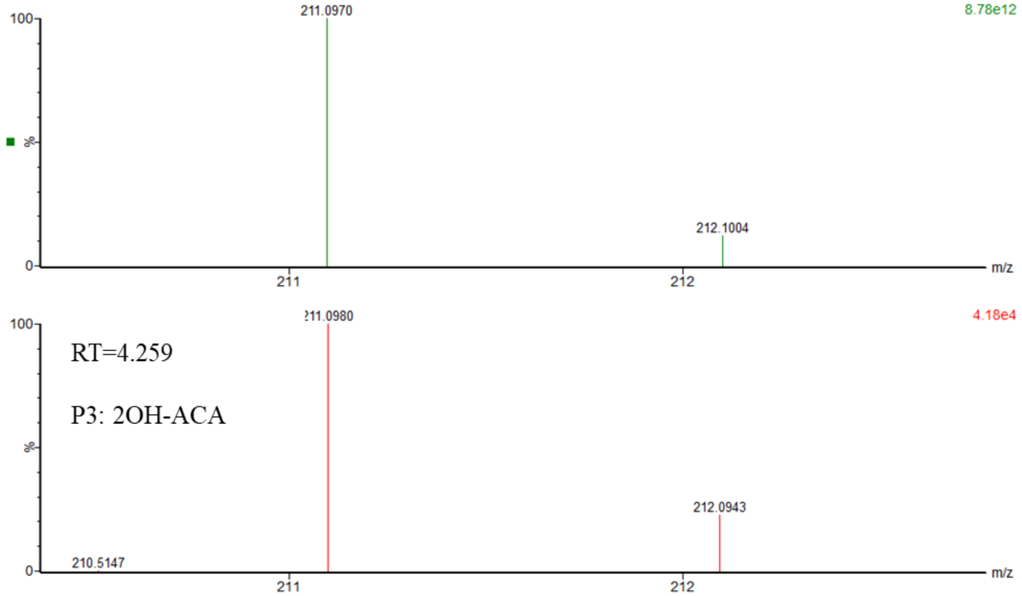

Figure B.3 Theoretical (green) and observed (red) isotope ration of proposed by-product P3

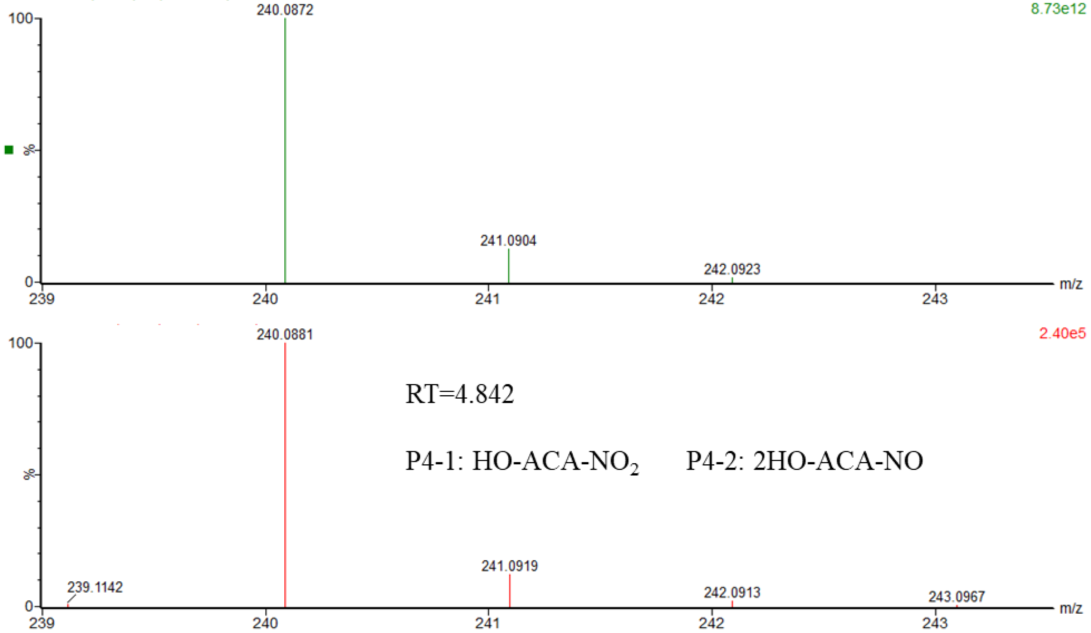

Figure B.4 Theoretical (green) and observed (red) isotope ration of proposed by-product P4-1&2.

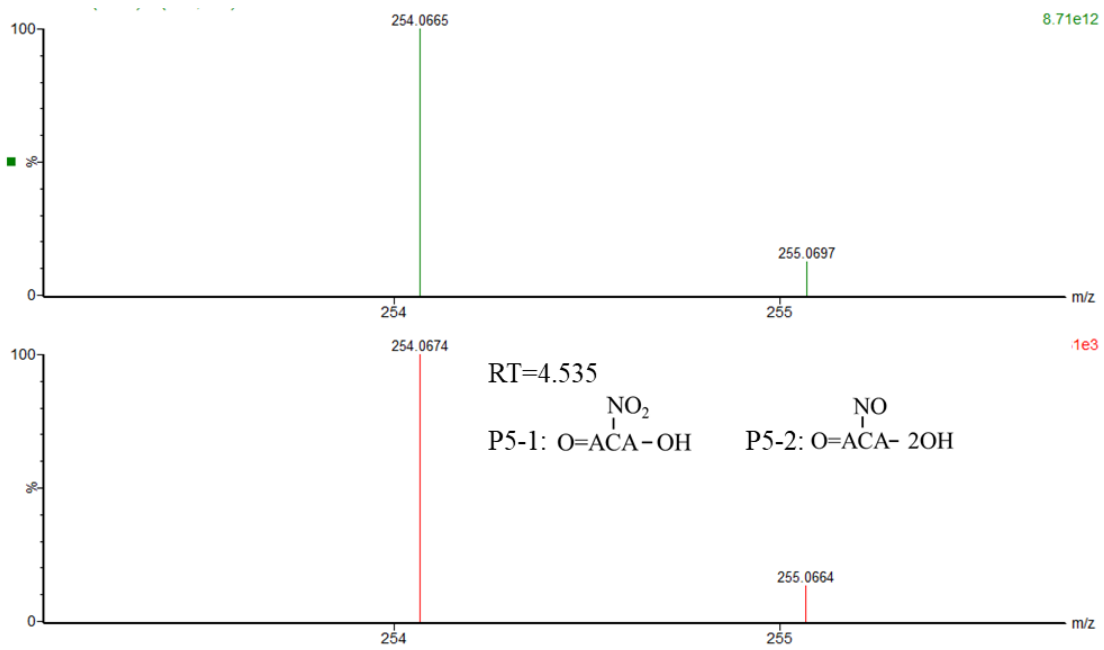

Figure B.5 Theoretical (green) and observed (red) isotope ration of proposed by-products P5-1&2.

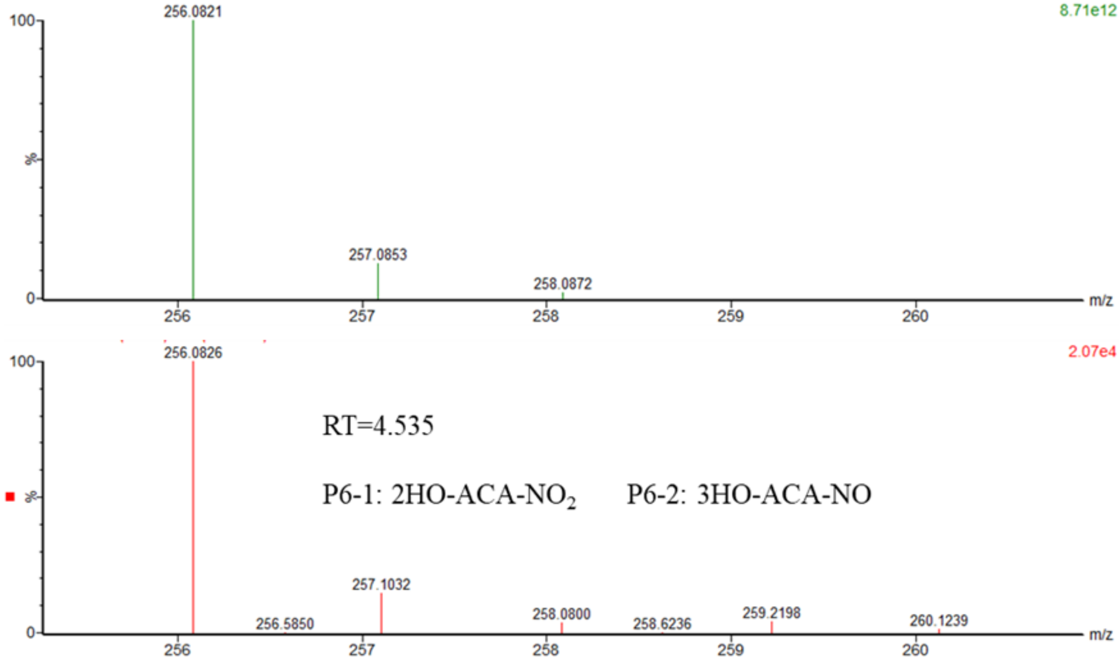

Figure B.6 Theoretical (green) and observed (red) isotope ration of proposed by-products 6.

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