University of Alberta

Physico-Chemical Processes for Oil Sands Process-Affected Water Treatment

by

Parastoo Pourrezaei

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Environmental Engineering

Department of Civil and Environmental Engineering

Spring 2013
Edmonton, Alberta

DEDICATION

This thesis is dedicated to my beloved family. They mean more than a world to me. My dearest parents have always given me their invaluable support all through my life and have inspired me time and again. My beautiful sisters, Parisa and Parinaz are the most supporting and caring sisters one could wish for. And finally my grandpa, who is not with us anymore, always encouraged me to pursue higher education.

ABSTRACT

Coagulation/Flocculation/Sedimentation (CFS), petroleum coke (PC) adsorption, and zero valent iron (ZVI) oxidation-enhanced by PC were applied for the remediation of oil sands process-affected water (OPSW), generated from oil sands operations in northern Alberta, Canada. OSPW is a complex mixture of various organic compounds [e.g., naphthenic acids (NAs)], dissolved and suspended solids, and a stable suspension of fine particles. Alum and cationic polymer, polydiallyldimethylammonium chloride (polyDADMAC), were used as the coagulant and coagulant aid, and the process was optimized to improve the efficiency of NAs and turbidity removals. Alum at 250 mg/L resulted in 96%, 10-37%, and 64-86% removal of turbidity, NAs and oxidized NAs, respectively. Destabilization of the particles occurred through charge neutralization by adsorption of the hydroxides on the surface of the particles. Analysis of the surface functional groups on flocs confirmed the removal of the NAs. Addition of polyDADMAC caused toxicity towards the benthic invertebrate, *Chironoums dilutus*, thus application of this polymer should be limited.

PC, as a waste by-product generated during the oil upgrading processes, was used for the removal of NAs and extractable organic fraction (EOF). EOF and NAs removals of 60% and 75%, respectively, were achieved at a PC dose of 200 g/L after 16 h of contact. Fourier transform infrared (FT-IR) spectra of PC suggested the physisorption of organic compounds onto the PC surface. The calculated mean free energy of adsorption (E < 8 kJ/mol) also indicated the

physisorption of organics. The hydrophobic interactions between the NAs and PC were suggested as the dominant adsorption mechanism. Speciation analysis of the leached vanadium from PC into OSPW indicated that vanadium (V) was the predominant specie.

In the presence of oxygen, ZVI at 25 g/L, added to PC, enhanced the NAs removal to 90%. PC, as an electron conductor, accelerated the electron transfer to oxygen resulting in the production of hydroxyl radicals. The hydroxyl radicals were responsible for the oxidation of NAs. Oxidized NAs concentration increased by 34% after the treatment. Toxicity of the treated OSPW to *Vibrio fischeri* bacteria, tested using Microtox® bioassay, showed a decrease in the toxic effects of the ZVI/PC treated samples.

ACKNOWLEDGEMENTS

I would like to express my deep appreciation to my supervisor, Dr. Mohamed Gamal El-Din for his guidance and support throughout this research. His encouragement was essential to accomplish this work.

I would also like to thank the post-doctoral fellows of our research group, Dr. Pamela Chelme-Ayala, Dr. Przemysław Drzewicz, Dr. Alla Alpatova, and Dr. Leonidas Perez for their support, comments, and recommendations; I greatly appreciate their valuable help.

I deeply thank my dearest friends who greatly supported me during the course of my studies: Keivan and Marjan. I sincerely appreciate all your help and presence when I most needed you. I also acknowledge the support I received from the friends and colleagues in the department of civil and environmental engineering department: Maria Demeter, Jela Burkus, Atefeh Afzal, Ahmed Moustafa, and all my colleagues. Special thanks to Warren Zubot who was generously helpful during our collaboration with Syncrude Canada Ltd.

I would like to acknowledge the financial support provided by the research grants from Alberta Innovates-Energy and Environment Solutions, Helmholtz-Alberta Initiative (HAI), and NSERC Industrial Research Chair in Oil Sands Tailings Water Treatment (Dr. Gamal El-Din). I also thank the “high resolution mass spectrometry lab” at University of Alberta, “Toxicology Centre” at University of Saskatchewan under the supervision of Dr. John P. Giesy, and Ms. Madeleine Jensen-Fontaine and Dr. X. Chris Le in the department of chemistry.

Finally, a special thanks to my dearest family for their support and sacrifices during the course of this adventure.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

Al_2O_3: Aluminium oxide

Al $(OH)_3$: Aluminum hydroxide precipitates

Alum: Aluminum sulfate

AOP: Advanced oxidation processes

As: Arsenic

BA: Benzoic acid

BET: Brunauer-Emmett-Teller

BOD: Biochemical oxygen demand

BTEX: Benzene, toluene, ethylbenzene, and xylenes

CaO: Calcium oxide

$C_{14}H_{28}O_2$:Tetradecanoic acid-1-^{13}C

CD: Cyclodextrins

CFS: Coagulation/flocculation/sedimentation

c-NAs: Classical NAs

COD: Chemical oxygen demand

CP: Chlorophenol

CT: Consolidated tailings

CZVI: Combination of PC and ZVI

DNT: Dinitro-toluene

DOC: Dissolved organic carbon

E: Mean free energy of adsorption

EOF: extractable organic fraction

E.T.C.: Estimated total concentration

FT-IR: Fourier transform infrared spectroscopy

GAC: Granular activated carbon

$H_4SiW_{12}O_{40}$: Tungstosilicic acid

$HNa_2PW_{12}O_{40}$: Phosphotungstic acid

HPLC-ICP-MS: High performance liquid chromatography-inductively coupled plasma mass spectrometer

IC: Inhibitory concentration

LC_{50}: Median lethal dose

log K_{ow}: Octanol/water partition coefficient

n: Carbon number

Na_2EDTA: Ethylenediaminetetraacetic acid disodium salt dehydrate

NaOH: Sodium hydroxide

NAs: Naphthenic acids

OSPW: Oil sands process-affected water

p=Probability

PAC: Powdered activated carbon

PACl: Polyaluminum chloride

PAH: Polyaromatic hydrocarbons

PC: Petroleum coke

polyDADMAC: Polydiallyldimethylammonium chloride

POM: Polyoxometalate

PZC: Point of zero surface charge

q_m: Adsorption capacity

R_L: Separation factor

SEM: Scanning electron microscopy

SFS: Synchronous fluorescence spectroscopy

SiO_2: Silicon dioxide

TA: Terephthalic acid

TCE: Trichloroethylene

TDS: Total dissolved solids

TGA: Thermo gravimetric analysis

TOC: Total organic carbon

UPLC: Ultra performance liquid chromatograph

UPLC/HRMS: Ultra pressure liquid chromatography/high resolution mass spectrometry

UV: Ultraviolet light

V: Vanadium

WHO's: World Health Organization's

WIP: West in-pit

XPS: X-ray photoelectron spectroscopy

Z: Degree of cyclization

ZVI: Zero valent iron

CHAPTER 1. BACKGROUND INFORMATION AND RESEARCH OBJECTIVES

1.1. Oil Sands Operations

The oil sands deposit in Alberta, Canada is the world's third largest oil deposit after Venezuela and Saudi Arabia [1-6]. The recoverable bitumen from the Athabasca oil sands is estimated at 170 billion barrels, of which 1 million barrels of oil is now produced per day [4, 6]. Rapid expansion of the industry and increases in the oil demand lead to an increase in the production of oil [4].

Unlike conventional oil, oil sands are composed of bitumen (6-16 %wt.), water (1-8 %wt.), and a mixture of sand, silt, and clay (80-87 %wt.) [6, 7]. The Clark hot water process is used for the extraction of bitumen from the oil sands ores at alkaline pH ~8 [6, 8-10]. During the extraction process, sodium hydroxide (NaOH) solution at 80 °C is mixed with the oil sands to separate the bitumen from the sands and clays [4, 6, 11]. A large volume of water is used during the extraction of bitumen. Part of the required water is supplied from fresh river water. Approximately 3 m^3 of the fresh water is taken from the Athabasca River for every m^3 of the produced oil from the oil sands and about 80-85% of the remaining required water for extraction is recycled from the generated process-affected waters [5, 6, 12]. As a result of the extraction process, 4 m^3 of the oil sands process-affected water (OSPW) is generated. Oil sands companies are not allowed to release the generated OSPW into the receiving environment [13]. Instead, OSPW is transported to the constructed tailings ponds for the long-term storage [6, 14]. The approximate surface area of the tailings ponds now exceeds 70 km^2 [4, 15]. The volume of OSPW in the tailings ponds in Athabasca region is estimated to reach more than 1 billion m^3 by 2025 [6, 16]. Continuous recycling of OSPW results in the decrease in the water quality for the extraction, which directly affects the bitumen recovery [4]. This process leads to the gradual increase in the fresh water intake from the river, which may affect the aquatic environment. Although less than 2% of the annual river flow is currently taken from the Athabasca River, it is of concern whether the low winter flow could supply the required water in the future without affecting the aquatic environment [4].

1.2. OSPW Water Quality

OSPW is composed of water, unrecoverable bitumen, sands, silts, clays, heavy metals, organic, and inorganic compounds [6, 16-18]. Although the composition of OSPW depends on the source of the ore, the extraction and upgrading processes, and its age; OSPW generally contains 1-3%wt. of residual bitumen, 20-30%wt. of solids, and the remaining portion [70-80%wt.] as water [4, 6]. On the addition of OSPW to the tailings ponds, rapidly settleable particles and solids are separated from the OSPW. This process results in the formation of a surface water layer with the low amounts of solids and a suspension layer of fine particles with ~20% (wt.) solids [4].

1.2.1. Organic Compounds

OSPW contains a complex mixture of various organic compounds including unrecovered bitumen (measured as oil and grease), naphthenic acids (NAs), polyaromatic hydrocarbons (PAH), BTEX (benzene, toluene, ethylbenzene, and xylenes), and other organic acids such as fulvic and humic acids [4, 13, 19, 20]. The bitumen concentration in OSPW ranges from 9 to 92 mg/L in Suncor and 25 mg/L in Syncrude tailings ponds [4]. The PAH and BTEX content in the tailings ponds water is ≤ 0.01 mg/L [4, 19]. The chemical oxygen demand (COD), biochemical oxygen demand (BOD), and dissolved organic carbon (DOC), used as the cumulative measures of the organic compounds, are higher in OSPW than in the Athabasca River [4]. Typical concentration of extractable organic fraction (EOF) in the tailings ponds water is in the range of 40-70 mg/L [4, 12] as compared to <1 mg/L in the surface waters [14].

Fourier transform infrared spectroscopy (FT-IR) had been previously used to measure the concentration of the NAs in OSPW. However, because of advances in analytical chemistry, it was found that NAs and oxidized NAs, as well as other acid extractable organics, can be measured together using the FT-IR instrument. This concentration is currently referred to as EOF rather than NAs [21, 22]. It is believed that NAs are associated with the toxicity of the OSPW to various organisms [4]. Among all the contaminants in OSPW, NAs compounds and remediation technologies for NAs removal have drawn significant attention because of their chemical characteristics and toxicity [5].

1.2.1.1. Naphthenic Acids

NAs are a group of polar carboxylic acids naturally present in petroleum [23, 24], crude oil or oil sands [6, 17, 25]. NAs are a mixture of saturated alicyclic carboxylic acids [8, 26]. Classical NAs (c-NAs) are represented by the general formula of $C_nH_{2n+Z}O_2$, in which n is the number of the carbon atoms and Z, a negative even integer, which when divided by -2 ($-Z/2$) represents the number of the rings resulting in a hydrogen deficiency in their structure arising from the ring formation [10, 17, 26]. The carboxylic acid group (COOH) is usually attached to a side alkyl chain rather than to the rings [13, 14]. Figure 1.1 shows the structure of some of the c-NAs based on the Z number.

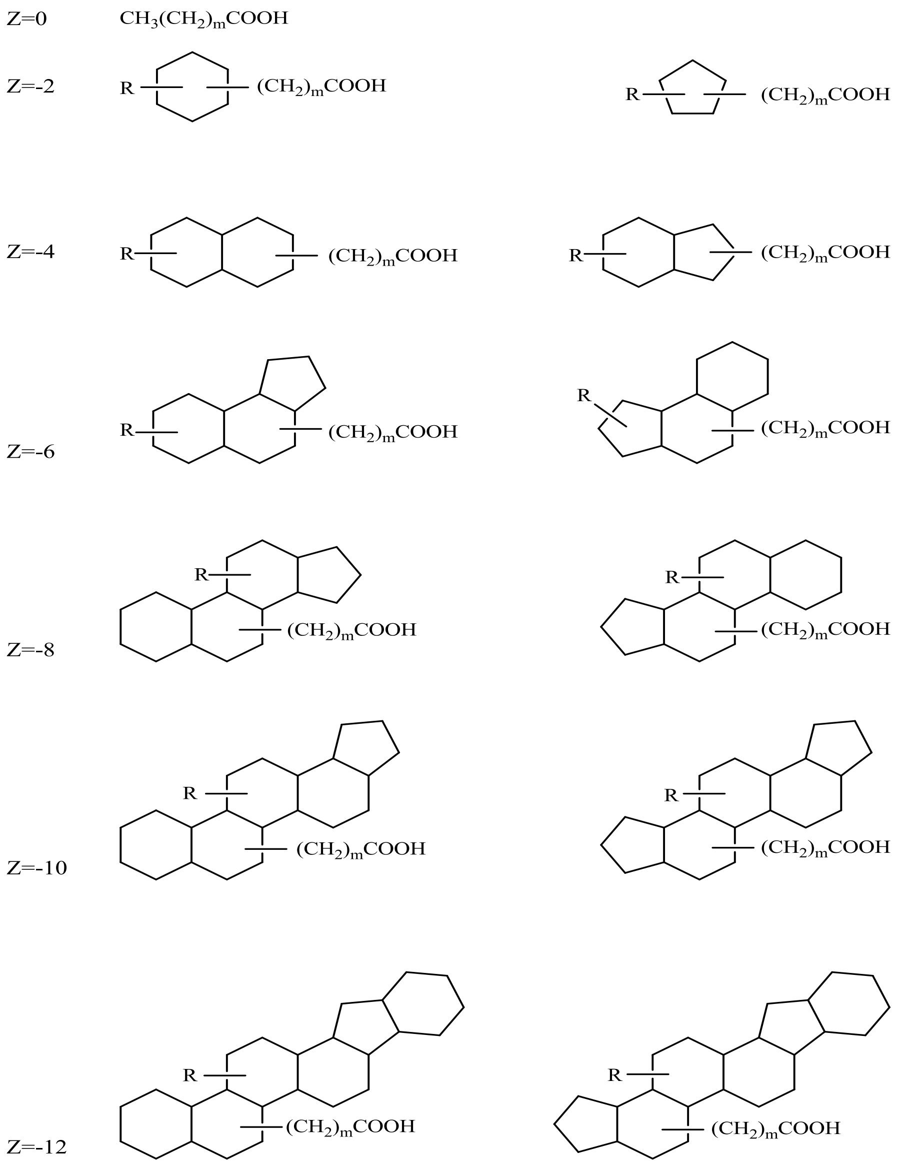

Figure 1.1. NAs structures for -*Z*=0 to 12. R represents the alkyl groups and m is the number of CH_2 units in the structure of the NAs (adopted from Clemente et al. [27] and Qian et al. [28]).

NAs in OSPW are a complex mixture of c-NAs and oxidized NAs [13, 22, 29]. Oxidized NAs ($C_nH_{2n+Z}O_x$, x=3-5) contain three or more oxygen atoms in their structures [8, 13]. In addition to the NAs, there are other acid extractable organic compounds in OSPW, which are measured together with NAs using FT-IR spectroscopy. It was found that only less than 50% of the acid extractable organics were c-NAs or oxidized NAs [22]. NAs with two 2 ($-Z$=4) and 3 ($-Z$=6) number of rings and carbon numbers of 11 to 15 are the most predominant species in OSPW [22, 30], whereas, acyclic NAs, mainly palmitic and stearic acids, are mainly found in surface waters [22].

The volatility of NAs is quite low [31], which results in their high chemical stability in OSPW [6, 32]. The molecular weights of the NAs in OSPW were reported to be in the range of 150-300 g/mol [33]. Lower molecular weight NAs (compounds with fewer number of carbons and rings) are the most soluble compounds [34], while increasing the molecular weights of NAs and cyclicity results in lower polarity and higher hydrophobicity [14, 25]. The boiling point of the NAs is in the range of 250-350 °C [35].

1.2.1.2. Toxicity of NAs

NAs are believed to be one of the causes of the toxicity of OSPW [4, 13, 36]. OSPW NAs are shown to be toxic to a variety of organisms, including plants [37, 38], fish [36, 39], mammals [31], and amphibians [40]. Garcia-Garcia et al. [41] showed that OSPW NAs had adverse effects on the immune system of mice, which resulted in a poor immune ability of their organs against diseases. The lethal NAs dose for humans has been reported to be 11 g/kg [42]. NAs are classified as surfactants with hydrophobic ends, which can penetrate through the membrane wall of the organisms' cells to cause toxicity [26, 31, 34, 36]. NAs concentrations in natural waters are usually lower than the detection limits (1 mg/L) [43]. The concentration of NAs in the Athabasca River is less than 1 mg/L. However, in the limestone and basal aquifers, it can reach a high level of 55 mg/L [14].

NAs with lower molecular weights are more susceptible to natural biodegradation [12]. This process results in the accumulation of the recalcitrant high molecular weight compounds with more carbons and rings [6, 12, 17, 27]. The NAs biodegradation rate with more rings and alkyl branching has been shown to be very slow [6, 9]. However, the carbon number effect on the biodegradation rate was found to be insignificant, except for NAs with three rings ($-Z=6$). NAs with a higher number of carbons ($n>22$) have been shown to be less toxic than those with lower molecular weights ($n=13\text{-}16$) [12].

1.2.2. Inorganic Compounds

Besides the organic compounds in OSPW, there are elevated concentrations of inorganic contaminants that could also contribute to the OSPW toxicity [4]. OSPW is alkaline with pH in the range of 7.9-8.5 [4]. A high alkalinity of OSPW, in the form of bicarbonate and carbonate ions results in its high buffering capacity [4]. OSPW is classified as brackish water because of the high level of total dissolved solids (TDS) (2000-2500 mg/L). Bicarbonate (700-1000 mg/L), sodium (500-700 mg/L), sulfate (200-300 mg/L), and chloride (75-550 mg/L) have the highest concentrations among all dissolved solids present in OSPW. The concentration of these solids, as well as ammonia (4-14 mg/L), is significantly higher than in the Athabasca River [21]. Trace metals, which are present in the ores, could also be released into OSPW during the extraction process. Depending on the ore and the extraction process, the concentration of some of the trace metals, such as aluminum, nickel, arsenic, copper, zinc, and chromium in OSPW, might exceed the levels in the Athabasca River.

1.3. Petroleum Coke

Petroleum coke (PC) is produced as a by-product during the bitumen upgrading to synthetic crude oil [21, 44]. At Syncrude Canada Ltd., high molecular weight hydrocarbons are thermally cracked into lower molecular weight compounds in the fluid cokers using hot generated PC (~600°C) [21]. Volatile hydrocarbons are removed from the top of the cokers and the generated

PC is deposited on the coker wall and is further withdrawn from the bottom of the cokers. The PC is transferred to the burners, in which a partial combustion of the PC occurs. The hot PC is then returned to the fluid cokers to provide the required heat for the thermal hydrocracking. The excess of PC is withdrawn from the burners and mixed with the generated OSPW. At Syncrude Canada Ltd., this slurry is hydraulically transported to the tailings ponds through a series of pipelines for the long-term storage [21]. The typical PC production from the bitumen feed is 20 kg for every barrel of produced oil [21]. Specifically, at Syncrude Canada Ltd., approximately 2-2.5 million tonnes of PC/year are produced. In 2010, the inventory of the PC in Alberta had reached 68 million tonnes [45]. The generated PC, as a by-product in the petroleum industry, is currently stockpiled on site [46] and a practical application of PC could include the application of PC for the treatment of generated process affected waters.

Fluid PC from Syncrude Canada Ltd. has an onion-like spherical shape with particle sizes between 100 μm and 1000 μm and specific gravity in the range of 1.50-1.65 [21, 47-49]. PC is mainly composed of fixed carbon, and the volatile and ash content of PC is relatively low [21]. The moisture content of PC is also less than 1% (wt.). PC has high amounts of sulfur (~6-7% wt.), which results in the limited application of PC as a heat source [50]. Silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3) comprise the highest ash content of the PC as indicated by the ash analysis [21]. In addition, the concentrations of vanadium and nickel are relatively high among all other elements. These elements, which exist in the oil sands bitumen feed, are accumulated in the PC matrix during the upgrading processes.

1.4. OSPW Treatment Options

OSPW is a complex mixture of various organic and inorganic compounds, which can contribute to its toxicity [4, 13, 36]. OSPW is currently accumulated in the tailings ponds, and the volume of the OSPW inventory is continually increasing [13]. Accumulation of the OSPW in the tailings ponds has raised several environmental concerns [21]. Because of the vicinity of the ponds to the

Athabasca River, there might be leaching of the contaminants into the river, which can endanger the aquatic biota [4, 5, 22]. In addition, more lands are being exploited for the OSPW accumulation as tailings ponds. All the disturbed lands used for the oil sands operations, such as tailings ponds, should be eventually reclaimed; therefore, the oil sands companies have to remediate OSPW for safe discharge into the environment to decrease the OPSW inventory [4]. Moreover, in order to minimize the fresh water intake from the Athabasca River, the treatment technologies should be optimized to treat the OSPW to a level suitable for the utilities and other operational needs [4]. For the release of OSPW into the nearby rivers, the quality of the treated OSPW should meet the standard guidelines, and the removal of the NAs and other organic compounds should be considered as the highest treatment priority [5]. To achieve this, a series of consecutive treatment processes is needed to remove all the contaminants including suspended and dissolved solids, insoluble hydrocarbons, and dissolved organic compounds [21]. There are relatively few studies investigating the applicability of various treatment methods for OSPW remediation. Adsorption, membrane filtration, biological treatment, advanced oxidation, and constructed wetlands have been studied as the treatment options for the OSPW [5, 13, 16, 20, 34, 43, 44, 51-62]. There are still significant research gaps considering the effectiveness and applicability of the proposed treatment technologies for the OSPW remediation at an industrial scale.

Natural remediation is not a viable option for OSPW treatment because of its very low rate and incomplete degradation of the organic compounds [4, 34]. Higher molecular weight NAs are more persistent to biodegradation. The NAs concentration in the tailings ponds was shown to decrease by 16% per year over the first 5 years arising from the biodegradation, after which insignificant biodegradation was observed [4]. The consolidation of the fine tailings to reach 30-35% (wt.) of solids was also anticipated to take 125-150 years [6, 63]. In spite of the decrease in the acute toxicity of OSPW, the chronic toxicity to aquatic organisms remained high. The application of natural or constructed wetlands was also proposed as the reclamation methods for OSPW [6, 20, 51, 52]. NAs removal of 40% from consolidated tailings (CT) was achieved in the small constructed ponds [5, 53]. It was reported that a long residence time is required for the biodegradation of the NAs [63, 64]. The cold climate and leaching of the organic and inorganic compounds to the ground waters are environmental concerns that limit applicability of wetlands for the OSPW remediation [5, 52]. In addition, it is still of concern whether the wet landscape can support the aquatic biota [4].

Biological treatment processes have also been investigated as a treatment option for the oil refinery produced waters [5, 16, 55-57]. In conventional biological treatments, such as activated sludge, microorganisms are more sensitive to the feed water characteristics such as salinity and toxicity. However, the microorganisms are shown to be more resistant to the toxicity in the fixed growth systems [5, 65]. Although microbial biodegradation processes are low-cost treatments compared to other processes, such as advanced treatment processes, they have been shown to be very slow and hence cannot be used effectively as a remediation method for OSPW NAs, especially with the current huge amount of OSPW production and storage rate. The biodegradation half-life of NAs in OSPW was found to be 12.8-13.6 yrs [66]. In addition, the complete removal of NAs was not achieved using biodegradation [34, 43], since large molecular weight NAs are more recalcitrant to biodegradation. More in depth research is required to investigate the effectiveness of biological treatment systems for OSPW remediation in regards to their ability to achieve complete NAs degradation and the degradation of other organic compounds. Therefore, biodegradation should be considered as a polishing treatment following the removal of large molecular weight recalcitrant NAs [6].

Effective sand filtration requires the NAs to be acidified to less than their pK_as to be adsorbed onto the filter media [5]. Membrane filtration has also been shown to be used effectively for the removal of organic and inorganic compounds from oil refinery generated waters [54, 62, 68, 69]. Nanofiltration was shown to remove more than 95% of NAs from OSPW [54]. In addition, a high removal of cations (sodium, calcium, and magnesium) and anions (chloride, sulfate, and bicarbonate) was achieved. However, reversible fouling arising from the presence of the suspended solids and colloidal particles decreased the permeate flux. Membrane fouling, durability, and cost have been considered as the main concerns affecting the selection of this treatment technology for large-scale applications [5, 68].

Advanced oxidation processes (e.g., O_3/H_2O_2, UV/O_3, UV/H_2O_2), in turn, are suitable treatment options for toxic waters containing recalcitrant organic compounds, such as those in OSPW [5]. Photocatalytic oxidation was shown to be an effective treatment for the degradation of NAs [5, 70-73]. However, the presence of the certain compounds that compete for the surface sites on the catalyst and the solution pH could affect the efficiency of the process [5, 73]. Chloride and bicarbonate ions are among the radical scavengers that can decrease the effectiveness of the photocatalytic processes and the production of the radicals [5, 74]. Light-based oxidation processes are also effective treatment options for waters with low levels of suspended solids [6]. Because of a light penetration limitation, which limits the light to the top layers of the water, a large surface area is required for effective treatment. The proposed treatment technologies should have the capability for the large-scale applications considering the huge amounts of OSPW accumulated in the tailings ponds. Therefore, the major challenge for the oil sands companies is to find effective treatment methods, for the stored OSPW, that are environmentally and technically reliable and cost effective [6, 12].

Currently, there is no viable economical and practical treatment technology, on an industrial scale, to handle the huge amounts of generated waste by-products (OSPW and PC) from the oil sands industry, which results in serious environmental issues [22, 34]. The presence of low combustible volatiles and relatively inactive carbon forms [79, 80], makes PC less effective in heat generation as compared to coal. The high sulfur content raises significant environmental concern over its potential use as an alternative energy source [46].

Therefore, the continuing accumulation and stock piling of large quantities of PC require the development of innovative strategies for the effective utilization of this carbon-reach material on an industrial scale. Considering the abundance of PC in the oil sands industry, it could be applied effectively for adsorptive treatment of OSPW. This application of PC, which is essentially free-of-charge, would not require large investments by the oil sands industry. In addition, this adsorption process, which uses two already generated waste streams, will not result in the production of more solid wastes after the treatment.

1.4.1. Physico-Chemical Treatments

Physical treatment processes, including sedimentation and filtration, have been evaluated for the removal of suspended solids and particles [64]. Because of the small particle size and surface charges, effective sedimentation would require a long period of time [64]. Therefore, addition of chemicals could destabilize particles and enhance their agglomeration for the effective settling in a reasonable period of time [36]. In addition, the presence of these particles causes the membrane filters to clog quickly. Therefore, for effective application of membrane technology, the OSPW should be free of particles.

1.4.1.1. Coagulation/Flocculation/Sedimentation

Coagulation/flocculation/sedimentation (CFS) is a common pre-treatment process for the removal of the suspended solids and colloidal particles, as well as insoluble hydrocarbons [81, 82]. As an enhanced coagulation, CFS has also the ability to decrease the concentrations of high molecular weight dissolved organic compounds in water and wastewaters [81, 83, 84]. Because of their small size and surface charge, suspended particles cannot be removed properly by sedimentation or filtration in a reasonable period of time. In addition, suspended solids and insoluble hydrocarbons have negative impacts on other treatment processes, including membrane filtration, biological treatments, and ultraviolet light (UV)-based advanced oxidation processes [85, 86]. Therefore, it is hypothesized that the removal of these contaminants would effectively enhance the performance and efficiency of the subsequent treatment processes. Depending on the water and particle characteristics, the particles usually have negative surface charges that cause them to repel each other and form a stable suspension [81]. Chemical additives could be used to neutralize the surface charge of the particles to facilitate their agglomeration for subsequent sedimentation.

CFS was found to be an effective treatment process for petroleum refining wastewaters in a large-scale application [30, 85]. The petroleum refining industry generally produces large volumes of wastewaters containing insoluble hydrocarbons, sulfur and nitrogen compounds, dissolved or suspended organic and inorganic contaminants [85, 86]. In a study by Santo et al. [85], CFS was applied for the treatment of petroleum refining wastewater using polyaluminum chloride, alum, and ferric sulfate. Increasing the coagulant concentration showed an increasing trend for COD removal. The highest COD removal of 87% was achieved using 27.2 mg/L of polyaluminum chloride to treat the sample with an initial COD of 580 mg/L. Alum and ferric sulfate resulted in COD removals of 87% and 85% at relatively higher concentrations of 40 and 56 mg/L, respectively. Similar total organic carbon (TOC) removals of 84%, 83%, and 82% were obtained by the addition of the same concentrations of the polyaluminum chloride, alum and ferric sulfate, respectively to treat the sample with an initial TOC of 97.5 mg/L. High turbidity reduction of >73% was obtained with the addition of the coagulants. In addition, further increase in the coagulant concentrations did not enhance the removal efficiency over what was observed. A high molecular weight polyacrylamide was also tested as a flocculant in combination with the coagulants. Larger flocs were formed upon the addition of the flocculant and the best combination was found to be the addition of 4.2 mg/L of the flocculant to the 34 mg/L of polyaluminum chloride, which resulted in 97% COD, 90% TOC, and 88% turbidity removals.

Demirci et al. [86] also suggested that the application of 100 mg alum/L in combination with a clay at 100 mg/L, as the coagulant aid, resulted in ~90% COD and turbidity removals for a wastewater from a petroleum refinery plant. Ferric chloride, ferric sulfate, and calcium oxide (CaO) showed similar removals as did alum. Additionally, cationic and anionic polyelectrolytes were shown to be more effective than clay with >70% and ~95% COD and turbidity removals, respectively. A 61-96% removal of trace metals (Mn, Ni and Zn) were also achieved after the treatment. Terephthalic acid (TA) wastewater generated from the TA petrochemical production plant, mainly composed of the aromatic carboxylic acids, such as benzoic acid, toluic acid, phthalic acid, and TA [30, 87] was treated by CFS [30]. A COD removal of 76% was obtained by the addition of 3 g/L of ferric chloride. The BOD_5/COD ratio increased after the CFS treatment, due to the decrease in COD concentration, indicating the suitability of the treated TA wastewater for biological treatment.

The impact of pH adjustment, using sulfuric acid, for the removal of the EOF from the consolidated tailings (CT) water from Syncrude Canada Ltd. was studied by Marr et al. [64]. The objective of the conducted study was to investigate whether the acidification followed by alum addition and sand filtration could remove naphthenates from CT waters to the residual concentration in the range of 30-50 mg/L. The pH of the CT samples decreased to <5 by sulfuric acid in the range of 0-1000 mg/L to form insoluble naphthenates. Alum was added for the coagulation of the pH-adjusted samples. The chemically treated samples were filtered using fine sand filtration (0.1 mm) columns in an up-flow configuration. Depending on the initial condition of the CT, the required sulfuric acid concentration was found to be in the range of 200-500 mg/L. The pH adjustment resulted in the precipitation of the naphthenates from the CT waters enhancing their physical entrapment by the filter media. The average initial values for pH and EOF concentration were 8.3 and 75 mg/L, respectively. Acidification alone at 490 mg/L sulfuric acid followed by sand filtration, decreased the EOF to 46-48 mg/L. Acidification followed by coagulation using 100-200 mg alum/L and sand filtration resulted in a lower EOF concentration of 37-42 mg/L. Acidification alone increased the turbidity of the CT from 0.1 to 57 NTU, which again decreased to a similar initial value after the sand filtration. This indicated the increase in the concentration of the insoluble naphthenates after acid addition and physical entrapment by the filter media. Evaluation of the effect of initial EOF concentration in the range of 50-200 mg/L, by spiking the samples to reach the desired concentrations, also showed a higher concentration of sulfuric acid is required by increasing the EOF concentration. However, EOF removal was not enhanced by the addition of more than 490 mg sulfuric acid/L at all the initial EOF concentrations. The addition of the 490 mg sulfuric acid/L and 100-200 mg alum/L resulted in the formation of insoluble naphthenates, which were then successfully removed by the sand filtration media to result in a 44-51% EOF removal from the CT water.

CFS is a potential pre-treatment option for OSPW for the removal of suspended solids and colloidal particles. In addition, enhanced CFS may decrease the concentration of the naphthenic acids (NAs). CFS is not affected by the toxicity of the wastewaters, which is an advantage for its application in the OSPW treatment containing NAs as one of the principal toxicants [88].

1.4.1.2. Adsorption

Adsorption is an important process affecting the fate and transport of environmental contaminants [89]. An adsorption phenomenon is the process of attachment of the adsorbates (e.g., ions or molecules) from one phase (e.g., gas or liquid) onto the surface of an adsorbent (i.e., solid substance). Adsorption is generally used to remove natural and synthetic organic chemicals, inorganic compounds, and heavy metals from liquid or gas phases. Among all the adsorbents, carbonaceous materials such as activated carbons, carbon blacks, carbon nanotubes, zeolites and synthetic polymers are the most commonly used sorbents [5]. Adsorption of the NAs and other organic contaminants, as well as inorganics, from OSPW using various types of natural and engineered sorbents, is a promising treatment process for OSPW remediation. Potential applicability of adsorption treatment of OSPW has not been studied comprehensively [6]. There are few studies evaluating the adsorption of NAs and EOF from OSPW using fresh and activated PC and a synthesized copolymer [13, 21, 44, 57]. As compared to other treatment technologies, adsorption process results in the minimum waste production and has less negative impacts on the environment [5, 21].

Zubot et al. [21] investigated the impact of PC adsorption for the removal of NAs from the OSPW. OSPW and fluid PC from Syncrude Canada Ltd. were used for the experiments. The results indicated that after 4 h of mixing, high removals of the NAs (64-96%) were obtained by the addition of 9-39%wt. PC to OSPW. The adsorption process was reported to occur through a two-step uptake, with an initial rapid removal rate followed by a slower removal rate, which was related to the diffusion into micropores or adsorption onto the lower reactive sites. The PC surface area was found to affect the adsorption of the NAs [44]. The surface area of the non-activated PC was reported to be 5.7 m^2/g [5]; whereas, steam activation of PC was shown to significantly increase the surface area to 494 m^2/g as reported by Small et al. [44]. Non-activated PC at 30%wt. in OSPW, removed up to 77% of the EOF from filtered OSPW. For the case of activated PC, this amount was reduced to 5%wt. and resulted in a 92% EOF removal. The concentration of calcium and magnesium decreased with increasing the PC dose because of adsorption onto the PC surface; while, silicon, molybdenum, and vanadium contents increased by increasing the PC dose as a result of leaching form PC [21, 44]. However, vanadium was shown to be re-adsorbed onto the PC over the longer contact times of approximately one year [21]. The leached vanadium concentration also increased after activation, as compared to non-activated PC [44], since vanadium was shown to be the most abundant trace metal in the PC composition [21]. In addition, PC adsorption was found to be an effective treatment to remove the toxicity of OSPW to *Vibrio fischeri* bacteria tested using the Microtox® bioassay [21].

Cyclodextrins (CD) have been shown to form stable complexes with alicyclic carboxylic acids [13, 90-92]. In addition, the incorporation of β-CDs into copolymers was shown to be effective for the sequestration of the organic compounds. Synthetically engineered β-CD copolymers were tested as a potential adsorbent for the removal of NAs extracted from OSPW in an alkaline solution

[13]. The copolymers with aromatic monomers in their structures showed lower NAs adsorption capacity, whereas aliphatic linkers attached to the copolymers resulted in higher adsorption capacity. The adsorption capacity of the copolymers also increased with increasing the initial NAs concentration in the solution. The adsorption capacity of the copolymers at pH=9 and room temperature was found to be in the range of 25.5-77.1 mg/g. However, the high surface area of the granular activated carbon (GAC) (1000 m^2/g), as compared to the copolymers (100 m^2/g), resulted in a higher NAs adsorption capacity (147 mg/g).

1.4.1.3. Zero Valent Iron

Zero valent iron (ZVI) has been used for wastewater and ground water remediation since 1990 [95, 96]. It was initially applied as permeable reactive barriers (PRB) for the removal of chlorinated solvents from ground waters [93, 95-98]. Wastewater treatment using ZVI is a novel, cost-effective and environmentally friendly process [99, 100].

The successful application of ZVI for the removal of refractory organic compounds [101], nitroaromatics [102, 103], halogenated compounds [104-106], and metals [107-109] from aqueous solutions and wastewaters has been reported. The petroleum refinery wastewater, which is high in organic and inorganic contaminants, was treated with nano size ZVI (nZVI) using ultrasonication [99]. Ultrasonication was performed for 60 min on 20 mL of wastewater containing 0.05 g nZVI. More than 90% COD removal was achieved after 50 min of sonication in the presence of nZVI as compared to 40% removal in the absence of nZVI after 60 min of sonication. A pH 5 was found to be the optimum pH for the COD removal. In addition, COD removal increased with an increase in nZVI concentration. Biphasic kinetics was observed for COD removal, with a fast degradation rate up to the first 7 min followed by a slower rate. The availability of more of fresh nZVI surface for the reaction was suggested as a reason for the initial fast reaction rate. These results suggested that sonication could enhance the degradation of the organic compounds from petroleum refinery wastewater using the nZVI technology. The addition of 6.8 g ZVI into 5 mL of aqueous solution containing 2,4-dinitro-toluene (DNT) resulted in the complete removal of DNT in 60 min [93]. Dinitrotoluene was formed as a result of the DNT reduction within 10 min of reaction, and its concentration after 3 h treatment reached 90% of the initial DNT concentration.

The actual removal mechanism using ZVI has not been understood completely [110-112]. Depending on the environmental conditions (e.g., pH of the water and oxygen availability), the possible removal mechanisms include adsorption, co-precipitation, direct or indirect reduction, and oxidation of the contaminants [94-96, 110, 113]. ZVI is unstable [114], and it is quickly oxidized to Fe^{2+} [95]. In the pH range of $5 < pH < 9$, Fe^{2+} is oxidized to Fe^{3+} and could subsequently form various forms of iron oxy/hydroxides (FeO, FeOOH, Fe_2O_3) [95]. The surfaces of these oxide products serve as adsorption sites for the contaminants [94, 101, 115]. Co-precipitation of the dissolved contaminants also occurs by their mechanical entrapment in the hydroxide structures [95, 116]. The formation of the mixed crystals by incorporation of the contaminants into the lattice of the hydroxides is another form of co-precipitation, mainly for the inorganic compounds and metals [95]. Unlike surface adsorption, entrapment of the compounds into the hydroxides structures results in their immobilization, as long as the hydroxides are insoluble [95]. During the oxidation of ZVI, the generated electrons could be used to reduce contaminants. In the presence of oxygen, the generated electrons are transferred to oxygen molecules, which results in the production of H_2O_2 [117]. Further reaction of H_2O_2 with Fe^{2+} in a Fenton-type reaction forms highly reactive hydroxyl radicals, which could be involved in the oxidation of the organic compounds.

Organic compounds could undergo oxidation reactions in the presence of ZVI and oxygen [118]. The oxidation of a carboxylic acid, benzoic acid (BA), into *p*-hydroxybenzoic acid (*p*-HBA) using nZVI in the presence of oxygen at pH 3 was investigated by Joo et al. [118]. The possible reaction pathways on addition of nZVI into the BA solution include:

$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2$ (1)

$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + 2OH^-$ (2)

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\circ}OH + OH^-$ (3)

The reactions which involve electron transfer occur mainly on the ZVI surface [118, 119]. The oxidants production rate is fast in the initial stages, which then decreases with increasing formation of the oxide products on the surface [118, 120]. As a result, production of *p*-HBA was rapid in the initial stages and gradually decreased during 1 day of contact. Increasing the initial BA concentration from 50 μM to 5 mM at pH 3 and 0.9 mM nZVI resulted in a higher production of *p*-HBA. In addition, the *p*-HBA production increased with increasing the nZVI from 0.2 to 5 mM at a 10 mM initial BA concentration.

The effect of pH increase on the oxidizing ability of nZVI was investigated at two BA concentrations of 50 μM and 10 mM. Although the results showed a decrease in the production rate of oxidants by increasing pH, the oxidation reactions was shown to continue up to pH 8 as the formation of the *p*-HBA indicated. It was hypothesized that the affinity of the ZVI surface for Fe^{2+} increased at high pH resulting in an increase in the thickness of the passivating layer. Oxygen was also assumed to compete with H_2O_2 for Fe^{2+}, which results in the formation of lower amounts of reactive radicals. The addition of competing compounds, including humic acid, phenol, aniline, and *o*-hydroxybenzoic acid in the presence of 10 mM BA at pH 3, showed that the *p*-HBA production yield decreased by increasing the concentration of these competitors. The relative reaction rate constants of these compounds with hydroxyl radicals were higher than for BA. The application of different ZVI particle sizes for the oxidation of 10 mM BA at pH 3 showed that, although nZVI resulted in a higher oxidation of BA, the *p*-HBA production rate using fine powder, powder, and granular ZVI was significant as well. The fine powder was shown to be the most effective BA oxidant.

In another study by Joo et al. [121], the degradation of the herbicide molinate, using nZVI was investigated in the absence and presence of oxygen. The molinate removal at pH 4 and in the absence of oxygen was negligible; whereas, 70% removal was achieved in aerated samples. Vigorous shaking was also reported to result in the same degree of removal as aerated samples. The reason could be a continuous removal of the passivating layer on the ZVI, which results in more effective electron transfer from ZVI to the contaminants/oxygen [122]. In addition, vigorous mixing may facilitate oxygen uptake by the solution and increase the oxygen transfer to the ZVI surface for radical formation. Investigation of reaction by-products revealed that molinate degradation occurred through oxidative rather than reductive reactions. Pseudo-first-order kinetics described well the behavior of the molinate oxidation. Increasing the ZVI loading resulted in an increase in the observed rate constant, and a linear relationship was found between the rate constant and the ZVI concentration. Although in some studies it has been shown that the degradation rate of the contaminants decreased to a great extent by increasing the pH, Joo et al. [121] observed 60% molinate removal in a carbonated buffered sample at pH 8 as compared to 65% removal at pH 4.

A 27% of Bangladesh aquifers are contaminated with arsenic (As), which is a toxic element [123, 124]. The arsenic concentration in these aquifers (50 μg/L), which is used as drinking water in rural areas [125], is well above the World Health Organization's (WHO's) guidelines of 10 μg/L [124]. ZVI, which was shown to be an effective treatment technology for the removal of As from ground waters [109, 126], was applied for the remediation of the Bangladesh ground waters [123]. Batch test experiments indicated that 99% As removal was achieved by the addition of 2 g/L of ZVI after 15 h of contact in the presence of oxygen at neutral pH. The results of this study suggested that ZVI can be used as a reliable treatment process for decontamination of surface and ground waters.

1.4.1.3.1. Electron Shuttling Effect

Electron transfer plays a significant role in all oxidation/reduction reactions occurring in the ZVI/water system. Therefore, the application of an electron conductor to accelerate the electron transfer could result in an increase in the reaction rates to enhance the process efficiency [127-131]. Carbonaceous materials have been known to have electron conducting ability [89, 106, 132]. The reductions of hexahydro-1,3,5-trinitro-1,3,5-triazine by sulfide [127] and 2,4-dinitrotoluene by dithiothreitol [128] were reported to be accelerated in the presence of black carbon. The graphite-like structures of the black carbon play the role of both adsorption sites and electron conductor for the molecules to be reduced [127, 128]. Activated carbon was also shown to enhance the removal of 1,1,2,2-tetrachloroethane [129] and hexachlorocyclohexane [130] from aqueous solutions.

nZVI was impregnated onto the surface of the GAC to prepare the GAC-ZVI composites for the reduction of trichloroethylene (TCE) in the aqueous solutions [133]. GAC-ZVI composites exploit the advantages of being adsorption sites for TCE with the reductive ability of the embedded ZVI to dechlorinate the physically adsorbed TCE [89, 133]. At 5 g/L of GAC-ZVI, the TCE concentration decreased rapidly over the 50 min treatment time with complete removal after 300 min, as compared to the incomplete degradation of TCE (~40%) by 0.15 g/L ZVI. The adsorption/dechlorination of the TCE fit well to a pseudo first-order kinetic model.

Metal-oxygen cluster anion compounds, also known as polyoxometalate (POM), including tungstosilicic acid ($H_4SiW_{12}O_{40}$) and phosphotungstic acid ($HNa_2PW_{12}O_{40}$), have been used as an electron shuttle to enhance the oxidation of 4-chlorophenol (4-CP) [131]. A 40% removal of 4-CP was obtained in ZVI alone system after 4 h contact time, which shows the oxidative ability of ZVI as also reported by another study [118]. The addition of POMs increased the removal of 4-CP to more than 80% with the simultaneous production of chloride, confirming the oxidation pathway of 4-CP rather than just adsorption on the ZVI surface.

Increasing the ZVI concentration from 0 to 2 g/L was shown to increase the 4-CP removal as also reported for the reduction/oxidation of other contaminants using ZVI [94, 102, 118, 121, 130]. No removal observed in the absence of ZVI indicating the inability of POM alone to oxidize the 4-CP. In addition, the 4-CP oxidation rate was faster by increasing the POM concentration up to 2 mM. Fenton-type reactions are more efficient at lower pH [130]. Increasing the pH was shown to have a decreasing effect on the 4-CP removal in the ZVI alone system. However, the addition of POM accelerated the oxidation rate and widened the range of effective pH for the 4-CP degradation. Joo et al. [118] also observed the progression of the oxidation reactions up to pH 8.

1.5. Objectives and Scope of the Research

As discussed earlier, the generation of the waste by-products from the oil sands industry, including OSPW and PC, is continually increasing. Accumulation of these wastes has raised environmental problems, which necessitates the development of viable treatment strategies for OSPW and PC on an industrial scale. In order to do so, a series of consecutive treatment processes is needed to remove all the contaminants from OSPW. There are few studies investigating the applicability of different treatment processes for OSPW, and yet there are significant research gaps considering the effectiveness and applicability of the proposed treatment technologies for OSPW remediation. Based on these needs, this research study focused on assessing the feasibility and efficiency of CFS, PC adsorption, and PC mediated-ZVI oxidation processes for the removal of the different types of contaminants, including suspended solids and dissolved organic compounds, from OSPW.

The objectives of this research were achieved through the application of CFS, PC adsorption, and ZVI oxidation processes in different phases. These objectives were:

1) To determine the effectiveness of CFS pre-treatment for the removal of the suspended particles and organic compounds, mainly NAs, from OSPW (Chapter 2);
2) To identify the coagulation mechanism, assess the floc properties, such as structure, size, and surface functional groups, and to determine the toxicity of the non-treated and treated OSPW towards invertebrates (Chapter 2);
3) To investigate the efficiency of the PC adsorption process for the removals of EOF and NAs from OSPW without any pre-treatment (Chapter 3);
4) To determine the mechanisms of NAs adsorption on the PC surface and to study the effect of physico-chemical properties of PC on the adsorption of NAs (Chapter 3);
5) To investigate the vanadium leaching from PC during the adsorption process and its speciation (Chapter 3);
6) To investigate the effectiveness of ZVI for the removal of the organic compounds, including NAs, flourophore organic compounds, and EOF and metals from OSPW.
7) To understand the potential role of PC, as an electron conductor, on the improvement of the organic compounds removal in the presence and absence of oxygen (Chapter 4).
8) To study the impact of the contact time and ZVI concentration on the removal of organic compounds and metals from OSPW and to determine the removal mechanisms of organic compounds and metals (Chapter 4).

By achieving these research objectives, this research study will provide a unique opportunity to treat the high amount of different wastes generated by the oil sands industry. The performed study will provide the valuable information regarding the effectiveness and removal mechanisms, and more importantly, the applicability of the proposed treatment options on an industrial scale.

1.6. Thesis Organization

The general overview regarding the oil sands operations and generation of the waste by-products, and the proposed treatment processes for waste by-products are presented in Chapter 1. The experimental methodologies and the obtained results of the various phases of this research are presented in Chapters 2-4. Chapter 2 presents the application of the CFS process as a pre-treatment for the removal of the suspended solids and organic compounds by the use of different metallic salt coagulants. Synthetic organic polymers were also tested as coagulant aids or flocculants. The effect of various operational factors, including chemical types and concentrations, rapid and slow mixing times and intensities on the removal of the target contaminants were investigated. The turbidity was measured as a surrogate for the suspended solids and colloidal particles. The TOC and NAs were measured to investigate changes in the concentration of the organic compounds. The toxicity of OSPW to invertebrates before and after CFS treatment was also investigated.

Chapter 3 includes a comprehensive evaluation of the adsorption of various organic contaminant fractions (COD, EOF and NAs) on PC; determination of the adsorption mechanisms of the NAs on the PC; study of the effect of physico-chemical properties of PC on the adsorption of NAs; and investigation of the speciation and leaching of vanadium from PC during the adsorption process.

In Chapter 4, ZVI was investigated as a source of electron in combination with PC, for the enhanced removal of fluorophore organic compounds, EOF, NAs, and metals from OSPW. PC was used as an electron conductor to provide a simultaneous adsorption and oxidation sites to enhance the removal of the contaminants. The effect of the ZVI concentration and the contact time on the fluorophore organic compounds, EOF, NAs, and metals removals was also investigated.

In Chapter 5, general conclusions of the performed research and recommendations for the future work are presented. Some of the experimental methodologies and supplementary graphs and tables to support the obtained results are presented in the Appendix sections attached at the end of the Thesis.

1.7. References

1. Board, E. R. C., ST98–2009: Alberta’s energy reserves 2008 and supply/demand outlook 2009–2018;. In Alberta, G. o., Ed. Calgary, AB, Canada, 2008; p 220.

2. Gray, M.; Xu, Z. H.; Masliyah, J., Physics in the oil sands of Alberta. *Physics Today* 2009, *62*, (3), 31-35.

3. Watkins, E., PDVSA, Eni initiate heavy oil, refinery projects in Venezuela. *Oil & Gas Journal* 2010, *108*, (46), 41-42.

4. Allen, E. W., Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. *Journal of Environmental Engineering and Science* 2008, *7*, (2), 123-138.

5. Allen, E. W., Process water treatment in Canada's oil sands industry: II. A review of emerging technologies. *Journal of Environmental Engineering and Science* 2008, *7*, (5), 499-524.

6. Kannel, P. R.; Gan, T. Y., Naphthenic acids degradation and toxicity mitigation in tailings wastewater systems and aquatic environments: A review. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering* 2012, *47*, (1), 1-21.

7. Liu, J. J.; Xu, Z. H.; Masliyah, J., Processability of oil sand ores in Alberta. *Energy & Fuels* 2005, *19*, (5), 2056-2063.

8. Clemente, J. S.; Fedorak, P. M., A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids. *Chemosphere* 2005, *60*, (5), 585-600.

9. Han, X. M.; Scott, A. C.; Fedorak, P. M.; Bataineh, M.; Martin, J. W., Influence of molecular structure on the biodegradability of naphthenic acids. *Environmental Science & Technology* 2008, *42*, (4), 1290-1295.

10. Frank, R. A.; Fischer, K.; Kavanagh, R.; Burnison, B. K.; Arsenault, G.; Headley, J. V.; Peru, K. M.; Van der Kraak, G.; Solomon, K. R., Effect of carboxylic acid content on the acute toxicity of oil sands naphthenic acids. *Environmental Science & Technology* 2009, *43*, (2), 266-271.

11. Chalaturnyk, R. J.; Scott, J. D.; Ozum, B., Management of oil sands tailings. *Petroleum Science and Technology* 2002, *20*, (9-10), 1025-1046.

12. Holowenko, F. M.; MacKinnon, M. D.; Fedorak, P. M., Characterization of naphthenic acids in oil sands wastewaters by gas chromatography-mass spectrometry. *Water Research* 2002, *36*, (11), 2843-2855.

13. Mohamed, M. H.; Wilson, L. D.; Headley, J. V.; Peru, K. M., Sequestration of naphthenic acids from aqueous solution using beta-cyclodextrin-based polyurethanes. *Physical Chemistry Chemical Physics* 2011, *13*, (3), 1112-1122.

14. Headley, J. V.; McMartin, D. W., A review of the occurrence and fate of naphthenic acids in aquatic environments. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering* 2004, *39*, (8), 1989-2010.

15. Dominski, M., Surface mined oil sand: tailings practices, per-formance, and projections. In *The 3rd International Heavy Oil Conference*, Alberta Energy and Utilities Board: Calgary, AB, 2007.

16. Herman, D. C.; Fedorak, P. M.; Mackinnon, M. D.; Costerton, J. W., Biodegradation of naphthenic acids by microbial-populations indigenous to oil sands tailings. *Canadian Journal of Microbiology* 1994, *40*, (6), 467-477.

17. Scott, A. C.; MacKinnon, M. D.; Fedorak, P. M., Naphthenic acids in athabasca oil sands tailings waters are less biodegradable than commercial naphthenic acids. *Environmental Science & Technology* 2005, *39*, (21), 8388-8394.

18. Mikula, R. J.; Kasperski, K. L.; Burns, R. D.; MacKinnon, M. D., Nature and fate of oil sands fine tailings. *Suspensions: Fundamentals and Applications in the Petroleum Industry* 1996, *251*, 677-723.

19. Rogers, V. V.; Liber, K.; MacKinnon, M. D., Isolation and characterization of naphthenic acids from Athabasca oil sands tailings pond water. *Chemosphere* 2002, *48*, (5), 519-527.

20. Madill, R. E. A.; Orzechowski, M. T.; Chen, G. S.; Brownlee, B. G.; Bunce, N. J., Preliminary risk assessment of the wet landscape option for reclamation of oil sands mine tailings: Bioassays with mature fine tailings pore water. *Environmental Toxicology* 2001, *16*, (3), 197-208.

21. Zubot, W. A. Removal of naphthenic acids from oil sands process water using petroleum coke. M.Sc. Dissertation. University of Alberta, Edmonton, Alberta, Canada;, 2010.

22. Grewer, D. M.; Young, R. F.; Whittal, R. M.; Fedorak, P. M., Naphthenic acids and other acid-extractables in water samples from Alberta: What is being measured? *Science of the Total Environment* 2010, *408*, (23), 5997-6010.

23. Fan, T. P., Characterization of naphthenic acids in petroleum by fast-atom-bombardment mass-spectrometry. *Energy & Fuels* 1991, *5*, (3), 371-375.

24. Seifert, W. K.; Teeter, R. M., Carboxylic acids in a California petroleum-Identification of structural types. *Chemistry & Industry* 1969, (41), 1464-&.

25. Herman, D. C.; Fedorak, P. M.; Costerton, J. W., Biodegradation of cycloalkane carboxylic-acids in oil sand tailings. *Canadian Journal of Microbiology* 1993, *39*, (6), 576-580.

26. Smith, B. E.; Lewis, C. A.; Belt, S. T.; Whitby, C.; Rowland, S. J., Effects of alkyl chain branching on the biotransformation of naphthenic acids. *Environmental Science & Technology* 2008, *42*, (24), 9323-9328.

27. Clemente, J. S.; MacKinnon, M. D.; Fedorak, P. M., Aerobic biodegradation of two commercial naphthenic acids preparations. *Environmental Science & Technology* 2004, *38*, (4), 1009-1016.

28. Qian, K. N.; Robbins, W. K.; Hughey, C. A.; Cooper, H. J.; Rodgers, R. P.; Marshall, A. G., Resolution and identification of elemental compositions for more than 3000 crude acids in heavy petroleum by negative-ion microelectrospray high-field Fourier transform ion cyclotron resonance mass spectrometry. *Energy & Fuels* 2001, *15*, (6), 1505-1511.

29. Rowland, S. J.; Scarlett, A. G.; Jones, D.; West, C. E.; Frank, R. A., Diamonds in the rough: Identification of individual naphthenic acids in oil sands process water. *Environmental Science & Technology* 2011, *45*, (7), 3154-3159.

30. Verrna, S.; Prasad, B.; Mishra, I. M., Pretreatment of petrochemical wastewater by coagulation and flocculation and the sludge characteristics. *Journal of Hazardous Materials* 2010, *178*, (1-3), 1055-1064.

31. Rogers, V. V.; Wickstrom, M.; Liber, K.; MacKinnon, M. D., Acute and subchronic mammalian toxicity of naphthenic acids from oil sands tailings. *Toxicological Sciences* 2002, *66*, (2), 347-355.

32. Kanicky, J. R.; Poniatowski, A. F.; Mehta, N. R.; Shah, D. O., Cooperativity among molecules at interfaces in relation to various technological processes: Effect of chain length on the pK(a) of fatty acid salt solutions. *Langmuir* 2000, *16*, (1), 172-177.

33. Mohammed, M. A.; Sorbie, K. S., Naphthenic acid extraction and characterization from naphthenate field deposits and crude oils using ESMS and APCI-MS. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 2009, *349*, (1-3), 1-18.

34. Quagraine, E. K.; Peterson, H. G.; Headley, J. V., In situ bioremediation of naphthenic acids contaminated tailing pond waters in the Athabasca oil sands region-demonstrated field studies and plausible options: A review. *Journal of*

Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering 2005, *40*, (3), 685-722.

35. Brient, J. A., Wessner, P.J., Doly, M.N. , Naphthenic acids. In *Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I., Ed. John Wiley and Sons: New York, 1995; Vol. 16, pp 1017-1029.

36. Mackinnon, M. D.; Boerger, H., Description of two treatment methods for detoxifying oil sands tailings pond water. *Water Pollution Research Journal of Canada* 1986, *21*, (4), 496-512.

37. Wort, D. J.; Patel, K. M., Response of plants to naphthenic and cycloalkane carboxylic acids. *Agronomy Journal* 1970, *62*, (5), 644-&.

38. Kamaluddin, M.; Zwiazek, J. J., Naphthenic acids inhibit root water transport, gas exchange and leaf growth in aspen (Populus tremuloides) seedlings. *Tree Physiology* 2002, *22*, (17), 1265-1270.

39. Dokholyan, B. K.; Magomedov, A. K., The effect of sodium naphthenate on the viability and physiological and biochemical indices of fish. *Voprosy Ikhtiologii* 1984, *23*, (6), 1013-1019.

40. Pollet, I.; Bendell-Young, L. I., Amphibians as indicators of wetland quality in wetlands formed from oil sands effluent. *Environmental Toxicology and Chemistry* 2000, *19*, (10), 2589-2597.

41. Garcia-Garcia, E.; Pun, J.; Perez-Estrada, L. A.; Din, M. G. E.; Smith, D. W.; Martin, J. W.; Belosevic, M., Commercial naphthenic acids and the organic fraction of oil sands process water downregulate pro-inflammatory gene expression and macrophage antimicrobial responses. *Toxicology Letters* 2011, *203*, (1), 62-73.

42. Rockhold, W., Toxicity of naphthenic acids and their metal salts. *A.M.A. Arch. Ind. Health* 1955, *12*, 477-482.

43. Headley, J. V.; Peru, K. M.; Adenugba, A. A.; Du, J. L.; McMartin, D. W., Dissipation of naphthenic acids mixtures by lake biofilms. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering* 2010, *45*, (9), 1027-1036.

44. Small, C. C., Ulrich, A.C., Hashisho, Z., Adsorption of acid extractable oil sands tailings organics onto raw and activated oil sands coke. *Journal of Environmental Engineering and Science* 2012, DOI 10.1061/(ASCE)EE.1943-7870.0000543.

45. Board, E. R. C., ST98- 2011: Alberta's Energy Reserves 2010 and Supply/Demand Outlook 2011- 2020. In Alberta, G. o., Ed. Calgary, AB, Canada, 2011; p 74.

46. Lee, S. H.; Choi, C. S., Chemical activation of high sulfur petroleum cokes by alkali metal compounds. *Fuel Processing Technology* 2000, *64*, (1-3), 141-153.

47. Bejarano, C. A.; Jia, C. Q.; Chung, K. H., A study on carbothermal reduction of sulfur dioxide to elemental sulfur using oilsands fluid coke. *Environmental Science & Technology* 2001, *35*, (4), 800-804.

48. Fedorak, P. M.; Coy, D. L., Oil sands cokes affect microbial activities. *Fuel* 2006, *85*, (12-13), 1642-1651.

49. Furimsky, E., Gasification of oil sand coke: Review. *Fuel Processing Technology* 1998, *56*, (3), 263-290.

50. Squires, A. J. Ecotoxicological assessment of using coke in aquatic reclamation strategies at the Alberta oil sands. University of Saskatchewan, Saskatoon, Saskatchewan, Canada, 2005.

51. Leung, S. S.; MacKinnon, M. D.; Smith, R. E. H., The ecological effects of naphthenic acids and salts on phytoplankton from the Athabasca oil sands region. *Aquatic Toxicology* 2003, *62*, (1), 11-26.

52. Knight, R. L.; Kadlec, R. H.; Ohlendorf, H. M., The use of treatment wetlands for petroleum industry effluents. *Environmental Science & Technology* 1999, *33*, (7), 973-980.

53. MacKinnon, M. D., Gulley, J.R., and Van Meer, T. Role of wetlands in attenuation of process-related components. Environmental Research Group (EnRG) Research Symposium, 3 May 2001, Edmonton, AB http://www.conrad.ab.ca/ seminars/research_sym/Agenda.htm

54. Peng, H.; Volchek, K.; MacKinnon, M.; Wong, W. P.; Brown, C. E., Application of nanofiltration to water management options for oil sands operations. *Desalination* 2004, *170*, (2), 137-150.

55. Del Rio, L. F.; Hadwin, A. K. M.; Pinto, L. J.; MacKinnon, M. D.; Moore, M. M., Degradation of naphthenic acids by sediment micro-organisms. *Journal of Applied Microbiology* 2006, *101*, (5), 1049-1061.

56. Golby, S.; Ceri, H.; Gieg, L. M.; Chatterjee, I.; Marques, L. L. R.; Turner, R. J., Evaluation of microbial biofilm communities from an Alberta oil sands tailings pond. *Fems Microbiology Ecology* 2012, *79*, (1), 240-250.

57. Zubot, W.; MacKinnon, M. D.; Chelme-Ayala, P.; Smith, D. W.; El-Din, M. G., Petroleum coke adsorption as a water management option for oil sands process-affected water. *Science of the Total Environment* 2012, *427*, 364-372.

58. Scott, A. C.; Zubot, W.; MacKinnon, M. D.; Smith, D. W.; Fedorak, P. M., Ozonation of oil sands process water removes naphthenic acids and toxicity. *Chemosphere* 2008, *71*, (1), 156-160.

59. Martin, J. W.; Barri, T.; Han, X. M.; Fedorak, P. M.; El-Din, M. G.; Perez, L.; Scott, A. C.; Jiang, J. T., Ozonation of oil sands process-affected water accelerates microbial bioremediation. *Environmental Science & Technology* 2010, *44*, (21), 8350-8356.

60. El-Din, M. G.; Fu, H. J.; Wang, N.; Chelme-Ayala, P.; Perez-Estrada, L.; Drzewicz, P.; Martin, J. W.; Zubot, W.; Smith, D. W., Naphthenic acids speciation and removal during petroleum-coke adsorption and ozonation of oil sands process-affected water. *Science of the Total Environment* 2011, *409*, (23), 5119-5125.

61. Liang, X. M.; Zhu, X. D.; Butler, E. C., Comparison of four advanced oxidation processes for the removal of naphthenic acids from model oil sands process water. *Journal of Hazardous Materials* 2011, *190*, (1-3), 168-176.

62. Kim, E. S.; Liu, Y.; El-Din, M. G., The effects of pretreatment on nanofiltration and reverse osmosis membrane filtration for desalination of oil sands process-affected water. *Separation and Purification Technology* 2011, *81*, (3), 418-428.

63. Eckert, W. F.; Masliyah, J. H.; Gray, M. R.; Fedorak, P. M., Prediction of sedimentation and consolidation of fine tails. *Aiche Journal* 1996, *42*, (4), 960-972.

64. Marr, J. B., Mohammed, P., MacKinnon, M., Rogers, M. Removal of Naphthenic Acid from Water via pH Adjustment, Coagulation and Sand Filtration International. In *Water Conference Proceeding*; 1996; pp 738-754.

65. Moore, M. M., Del Rio, L., Hadwin, A., and Pinto, L. Enhancing oil sands reclamation technologies by optimizing the microbial degradation of naphthenic acids. *Report prepared for the Alberta Energy Research Institute*, Edmonton, AB: 2002.

66. Gruber, W., Cegene's biotreatment technology: destroying organic compounds with an in-line, on-site treatment system. *EI Digest. November* 1993, 17–20.

67. Han, X. M.; MacKinnon, M. D.; Martin, J. W., Estimating the in situ biodegradation of naphthenic acids in oil sands process waters by HPLC/HRMS. *Chemosphere* 2009, *76*, (1), 63-70.

68. Farnand, B. A.; Krug, T. A., Oil removal from oil field-produced water by cross flow ultrafiltration. *Journal of Canadian Petroleum Technology* 1989, *28*, (6), 18-24.

69. Zaidi, A.; Simms, K.; Kok, S., The use of micro/ultrafiltration for the removal of oil and suspended-solids from oil-field brines. *Water Science and Technology* 1992, *25*, (10), 163-176.

70. Herrmann, J. M., Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis Today* 1999, *53*, (1), 115-129.

71. Mazzarino, I.; Piccinini, P., Photocatalytic oxidation of organic acids in aqueous media by a supported catalyst. *Chemical Engineering Science* 1999, *54*, (15-16), 3107-3111.

72. Mazzarino, I.; Piccinini, P.; Spinelli, L., Degradation of organic pollutants in water by photochemical reactors. *Catalysis Today* 1999, *48*, (1-4), 315-321.

73. Trillas, M.; Peral, J.; Domenech, X., Photocatalyzed degradation of phenol, 2,4-dichlorophenol, phenoxyacetic acid and 2,4-dichlorophenoxyacetic acid over supported TiO_2 in a flow system. *Journal of Chemical Technology and Biotechnology* 1996, *67*, (3), 237-242.

74. Bekbolet, M.; Lindner, M.; Weichgrebe, D.; Bahnemann, D. W., Photocatalytic detoxification with the thin-film fixed-bed reactor (TFFBR): Clean-up of highly polluted landfill effluents using a novel TiO_2-photocatalyst. *Solar Energy* 1996, *56*, (5), 455-469.

75. Gogate, P. R.; Mujumdar, S.; Pandit, A. B., Sonochemical reactors for waste water treatment: comparison using formic acid degradation as a model reaction. *Advances in Environmental Research* 2003, *7*, (2), 283-299.

76. Bessa, E., Sant'Anna, G.L., Dezotti, J., Photocatalysis: An approach to the treatment of oil field produced waters. *Journal of Advanced Oxidation Technologies* 1999, *4*, 196-202.

77. Quagraine, E. K.; Headley, J. V.; Peterson, H. G., Is biodegradation of bitumen a source of recalcitrant naphthenic acid mixtures in oil sands tailing pond waters? *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering* 2005, *40*, (3), 671-684.

78. Giesy, J. P.; Anderson, J. C.; Wiseman, S. B., Alberta oil sands development. *Proceedings of the National Academy of Sciences of the United States of America* 2010, *107*, (3), 951-952.

79. Parmar, B. S.; Tollefson, E. L., Desulfurization of oil sands coke. *Canadian Journal of Chemical Engineering* 1977, *55*, (2), 185-191.

80. Friedrich, F. D.; Lee, G. K.; Desai, D. L., Fluidized-bed combustion of petroleum coke. *Mechanical Engineering* 1983, *105*, (1), 81-81.

81. Duan, J. M.; Gregory, J., Coagulation by hydrolysing metal salts. *Advances in Colloid and Interface Science* 2003, *100*, 475-502.

82. Tansel, B.; Regula, J., Coagulation enhanced centrifugation for treatment of petroleum hydrocarbon contaminated waters. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering* 2000, *35*, (9), 1557-1575.

83. Jarvis, P.; Jefferson, B.; Parsons, S. A., Characterising natural organic matter flocs. *Natural Organic Material Research: Innovations and Applications for Drinking Water* 2004, *4*, (4), 79-87.

84. Jarvis, P.; Jefferson, B.; Parsons, S. A., How the natural organic matter to coagulant ratio impacts on floc structural properties. *Environmental Science & Technology* 2005, *39*, (22), 8919-8924.

85. Santo, C. E.; Vilar, V. J. P.; Botelho, C. M. S.; Bhatnagar, A.; Kumar, E.; Boaventura, R. A. R., Optimization of coagulation-flocculation and flotation parameters for the treatment of a petroleum refinery effluent from a Portuguese plant. *Chemical Engineering Journal* 2012, *183*, 117-123.

86. Demirci, S.; Erdogan, B.; Ozcimder, R., Wastewater treatment at the petroleum refinery, Kirikkale, Turkey using some coagulants and Turkish clays as coagulant aids. *Water Research* 1998, *32*, (11), 3495-3499.

87. Zhang, X. X.; Cheng, S. P.; Wan, Y. Q.; Sun, S. L.; Zhu, C. J.; Zhao, D. Y.; Pan, W. Y., Degradability of five aromatic compounds in a pilot wastewater treatment system. *International Biodeterioration & Biodegradation* 2006, *58*, (2), 94-98.

88. Aboulhassan, M. A.; Souabi, S.; Yaacoubi, A.; Baudu, M., Removal of surfactant from industrial wastewaters by coagulation flocculation process. *International Journal of Environmental Science and Technology* 2006, *3*, (4), 327-332.

89. Tang, H.; Zhu, D. Q.; Li, T. L.; Kong, H. N.; Chen, W., Reductive dechlorination of activated carbon-adsorbed trichloroethylene by zero-valent iron: carbon as electron shuttle. *Journal of Environmental Quality* 2011, *40*, (6), 1878-1885.

90. Mohamed, M. H.; Wilson, L. D.; Headley, J. V.; Peru, K. M., A spectral displacement study of cyclodextrin/naphthenic acids inclusion complexes. *Canadian Journal of Chemistry-Revue Canadienne De Chimie* 2009, *87*, (12), 1747-1756.

91. Gadre, A.; Connors, K. A., Binding of substituted acetic acids to alpha-cyclodextrin in aqueous solution. *Journal of Pharmaceutical Sciences* 1997, *86*, (11), 1210-1214.

92. Gadre, A.; Rudiger, V.; Schneider, H. J.; Connors, K. A., Binding of cyclodextrins to alicyclic and aromatic substrates: Complex formation of alpha-,

beta-, and gamma-cyclodextrins with substituted cyclohexanecarboxylic acids and phenylalkanoic acids. *Journal of Pharmaceutical Sciences* 1997, *86*, (2), 236-243.

93. Oh, S. Y.; Cha, D. K.; Chiu, P. C., Graphite-mediated reduction of 2,4-dinitrotoluene with elemental iron. *Environmental Science & Technology* 2002, *36*, (10), 2178-2184.

94. Matheson, L. J.; Tratnyek, P. G., Reductive dehalogenation of chlorinated methanes by iron metal. *Environmental Science & Technology* 1994, *28*, (12), 2045-2053.

95. Noubactep, C., The fundamental mechanism of aqueous contaminant removal by metallic iron. *Water Sa* 2010, *36*, (5), 663-670.

96. O'Hannesin, S. F.; Gillham, R. W., Long-term performance of an in situ "iron wall" for remediation of VOCs. *Ground Water* 1998, *36*, (1), 164-170.

97. Puls, R. W.; Paul, C. J.; Powell, R. M., The application of in situ permeable reactive (zero-valent iron) barrier technology for the remediation of chromate-contaminated groundwater: a field test. *Applied Geochemistry* 1999, *14*, (8), 989-1000.

98. Puszkarewicz, A., Removal of petroleum compounds from water in coagulation process. *Environment Protection Engineering* 2008, *34*, (1), 5-14.

99. Rasheed, Q. J.; Pandian, K.; Muthukumar, K., Treatment of petroleum refinery wastewater by ultrasound-dispersed nanoscale zero-valent iron particles. *Ultrasonics Sonochemistry* 2011, *18*, (5), 1138-1142.

100. Zhang, W. X., Nanoscale iron particles for environmental remediation: An overview. *Journal of Nanoparticle Research* 2003, *5*, (3-4), 323-332.

101. Mantha, R.; Taylor, K. E.; Biswas, N.; Bewtra, J. K., A continuous system for Fe(0) reduction of nitrobenzene in synthetic wastewater. *Environmental Science & Technology* 2001, *35*, (15), 3231-3236.

102. Agrawal, A.; Tratnyek, P. G., Reduction of nitro aromatic compounds by zero-valent iron metal. *Environmental Science & Technology* 1996, *30*, (1), 153-160.

103. Devlin, J. F.; Klausen, J.; Schwarzenbach, R. P., Kinetics of nitroaromatic reduction on granular iron in recirculating batch experiments. *Environmental Science & Technology* 1998, *32*, (13), 1941-1947.

104. Orth, W. S.; Gillham, R. W., Dechlorination of trichloroethene in aqueous solution using Fe-O. *Environmental Science & Technology* 1996, *30*, (1), 66-71.

105. Kim, Y. H.; Carraway, E. R., Dechlorination of pentachlorophenol by zero valent iron and modified zero valent irons. *Environmental Science & Technology* 2000, *34*, (10), 2014-2017.

106. Eykholt, G. R.; Davenport, D. T., Dechlorination of the chloroacetanilide herbicides alachlor and metolachlor by iron metal. *Environmental Science & Technology* 1998, *32*, (10), 1482-1487.

107. Mak, M. S. H.; Lo, I. M. C., Influences of redox transformation, metal complexation and aggregation of fulvic acid and humic acid on Cr(VI) and As(V) removal by zero-valent iron. *Chemosphere* 2011, *84*, (2), 234-240.

108. Blowes, D. W.; Ptacek, C. J.; Jambor, J. L., In-situ remediation of Cr(VI)-contaminated groundwater using permeable reactive walls: Laboratory studies. *Environmental Science & Technology* 1997, *31*, (12), 3348-3357.

109. Su, C. M.; Puls, R. W., Arsenate and arsenite removal by zerovalent iron: Effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride. *Environmental Science & Technology* 2001, *35*, (22), 4562-4568.

110. Shimizu, A.; Tokumura, M.; Nakajima, K.; Kawase, Y., Phenol removal using zero-valent iron powder in the presence of dissolved oxygen: Roles of

decomposition by the Fenton reaction and adsorption/precipitation. *Journal of Hazardous Materials* 2012, *201*, 60-67.

111. Noubactep, C.; Schoner, A., Metallic iron for environmental remediation: Learning from electrocoagulation. *Journal of Hazardous Materials* 2010, *175*, (1-3), 1075-1080.

112. Wang, K. S.; Lin, C. L.; Wei, M. C.; Liang, H. H.; Li, H. C.; Chang, C. H.; Fang, Y. T.; Chang, S. H., Effects of dissolved oxygen on dye removal by zero-valent iron. *Journal of Hazardous Materials* 2010, *182*, (1-3), 886-895.

113. Weber, E. J., Iron-mediated reductive transformations: Investigation of reaction mechanism. *Environmental Science & Technology* 1996, *30*, (2), 716-719.

114. Aleksanyan, A. Y.; Podobaev, A. N.; Reformatskaya, II, Steady-state anodic dissolution of iron in neutral and close-to-neutral media. *Protection of Metals* 2007, *43*, (1), 66-69.

115. Henderson, A. D.; Demond, A. H., Long-term performance of zero-valent iron permeable reactive barriers: A critical review. *Environmental Engineering Science* 2007, *24*, (4), 401-423.

116. Karthikeyan, K. G.; Elliott, H. A.; Cannon, F. S., Adsorption and coprecipitation of copper with the hydrous oxides of iron and aluminum. *Environmental Science & Technology* 1997, *31*, (10), 2721-2725.

117. Noubactep, C., A critical review on the process of contaminant removal in Fe-0-H2O systems. *Environmental Technology* 2008, *29*, (8), 909-920.

118. Joo, S. H.; Feitz, A. J.; Sedlak, D. L.; Waite, T. D., Quantification of the oxidizing capacity of nanoparticulate zero-valent iron. *Environmental Science & Technology* 2005, *39*, (5), 1263-1268.

119. Zecevic, S.; Drazic, D. M.; Gojkovic, S., Oxygen reduction on iron .3. An analysis of the rotating-disk ring electrode measurements in near neutral solutions. *Journal of Electroanalytical Chemistry* 1989, *265*, (1-2), 179-193.

120. Davenport, A. J.; Oblonsky, L. J.; Ryan, M. P.; Toney, M. F., The structure of the passive film that forms on iron in aqueous environments. *Journal of the Electrochemical Society* 2000, *147*, (6), 2162-2173.

121. Joo, S. H.; Feitz, A. J.; Waite, T. D., Oxidative degradation of the carbothioate herbicide, molinate, using nanoscale zero-valent iron. *Environmental Science & Technology* 2004, *38*, (7), 2242-2247.

122. Stieber, M.; Putschew, A.; Jekel, M., Treatment of pharmaceuticals and diagnostic agents using zero-valent iron - kinetic studies and assessment of transformation products assay. *Environmental Science & Technology* 2011, *45*, (11), 4944-4950.

123. Abedin, M. A.; Katsumi, T.; Inui, T.; Kamon, M., Arsenic removal from contaminated ground water by zero valent iron: A mechanistic and long-term performance study. *Soils and Foundations* 2011, *51*, (3), 369-377.

124. Khan, A. H., Rasul, S. B., Munir, A. K. M., Habibuddowla, M., Alauddin, M., Newaz, S. S. Hussam, A. , Appraisal of a simple arsenic removal method for groundwater of Bangladesh. *J Environ. Sci. Health*, 2000, *35*, 1021-1041.

125. Ahmed, F. M., An overview of arsenic removal technologiesin Bangladesh and India, Technologies for Arsenic Removal fromDrinking Water. In 2001; pp 251-269.

126. Manning, B. A.; Hunt, M. L.; Amrhein, C.; Yarmoff, J. A., Arsenic(III) and Arsenic(V) reactions with zerovalent iron corrosion products. *Environmental Science & Technology* 2002, *36*, (24), 5455-5461.

127. Kemper, J. M.; Ammar, E.; Mitch, W. A., Abiotic degradation of hexahydro-1,3,5-trinitro-1,3,5-triazine in the presence of hydrogen sulfide and black carbon. *Environmental Science & Technology* 2008, *42*, (6), 2118-2123.

128. Oh, S. Y.; Chiu, P. C., Graphite- and soot-mediated reduction of 2,4-dinitrotoluene and hexahydro-1,3,5-trinitro-1,3,5-triazine. *Environmental Science & Technology* 2009, *43*, (18), 6983-6988.

129. Mackenzie, K.; Battke, J.; Koehler, R.; Kopinke, F. D., Catalytic effects of activated carbon on hydrolysis reactions of chlorinated organic compounds - Part 2. 1,1,2,2-tetrachloroethane. *Applied Catalysis B-Environmental* 2005, *59*, (3-4), 171-179.

130. MacKenzie, K.; Battke, J.; Kopinke, F. D., Catalytic effects of activated carbon on hydrolysis reactions of chlorinated organic compounds - Part 1. gamma-hexachlorocyclohexane. *Catalysis Today* 2005, *102*, 148-153.

131. Lee, J.; Kim, J.; Choi, W., Oxidation on zerovalent iron promoted by polyoxometalate as an electron shuttle. *Environmental Science & Technology* 2007, *41*, (9), 3335-3340.

132. Leon, C.; Radovic, L. R., Interfacial chemistry and electrochemistry of carbon surfaces. *Chemistry and Physics of Carbon, Vol 24* 1994, *24*, 213-310.

133. Tseng, H. H.; Su, J. G.; Liang, C. J., Synthesis of granular activated carbon/zero valent iron composites for simultaneous adsorption/dechlorination of trichloroethylene. *Journal of Hazardous Materials* 2011, *192*, (2), 500-506.

CHAPTER 2. THE IMPACT OF METALLIC COAGULATNS ON THE REMOVAL OF ORGANIC COMPOUNDS FROM OIL SANDS PROCESS-AFFECTED WATER[1]

2.1. Introduction

Coagulation/Flocculation/Sedimentation (CFS) is among the most widely used processes to remove suspended and colloidal particles from water and wastewater. Additionally, it is used to decrease concentrations of dissolved organic matter [1-3]. Because of their small size and surface charge, without any pre-treatment, suspended particles are difficult to remove by filtration or sedimentation. Moreover, suspended solids may interfere with ultraviolet light (UV)-based advanced oxidation processes (UV/O_3, UV/H_2O_2) by scattering light, thus reducing the efficiency of these processes [4]. Therefore, removal of the suspended particles may improve the performance of filtration, advanced oxidation, and membrane separation processes [4-6].

CFS is a potential pre-treatment option for treating oil sands process-affected water (OSPW) generated from oil sands operations in northern Alberta, Canada. OSPW, generated after Clark hot water extraction, contains a complex mixture of organic compounds, salts and a stable suspension of fine particles [5, 7]. Among the complex mixtures of organics in OSPW is a class of water-soluble, alicyclic compounds, collectively classified as naphthenic acids (NAs) [8]. Their general formula is $C_nH_{2n+Z}O_2$, where n represents the number of carbon atoms and Z is a negative even integer representing the number of rings [9, 10].

Numerous studies have focused on the application of secondary and tertiary treatment technologies, including biological treatments, advanced oxidation processes (AOP) and membrane filtration for treatment of OSPW [6, 7, 10-14]. Bioremediation has recently been studied for the removal of organic

---

[1] A version of this chapter has been published. Pourrezaei et al. *Environmental Science and Technology*. 45, (19), 8452-8459.

compounds from OSPW [7, 14, 15]. Microbial degradation has proved to be a very slow process due to the toxicity and persistency of NAs [10]. Ozonation was shown to not only incompletely degrade NAs, but also to generate more oxidized NAs [10, 13]. Some oxidized NAs might resemble the sex steroids compounds that may show endocrine disrupting activity [16, 17]. Nanofiltration successfully removed more than 95% of NAs and divalent ions from OSPW without any pre-treatment [6]. However, reversible fouling caused by suspended solids decreased the permeate flux and life cycle of the membrane, which limited the practical application of nanofiltration [6]. It was expected that CFS pre-treatment of OSPW would decrease the particle and organic loading on the subsequent treatment processes and enhance the performance of remediation processes.

Chemical coagulants can be effective if they can destabilize charged particles to facilitate agglomeration. Aluminum sulfate (alum) is among the most commonly used coagulants in wastewater treatment processes because of its availability and low cost [3, 18, 19]. The successful use of iron salts and polyaluminum chloride (PACl) was also reported [2, 19-21]. PACl has been shown to be a stable compound with the minimum effect on the pH of the water [3]. Flocculants, which are mainly synthetic organic polymers, have been extensively used to enhance coagulation performance [18, 22]. Among flocculants, cationic polymers have been reported to be more effective than anionic or non-ionic polymers. Addition of the polymers may intensify membrane fouling, whereas it could enhance the granular filtration performance by increasing the particle attachment to the filter media [18].

Depending on the coagulant concentration and water characteristics, various mechanisms, such as charge neutralization, adsorption, and sweep flocculation can be responsible for the removal of organic compounds and particles [3, 18]. Elevated concentrations of the residual ions in the treated water, arising from coagulant addition, necessitate further treatments. Therefore, careful monitoring of the coagulant dose is required to obtain the lowest concentration of the residual ions, which can be achieved through measurement of charge and ion concentrations. Zeta potential analysis is a critical evaluation for the characterization and quantification of the charge, with which it is possible to better understand the CFS performance and identify the removal mechanism.

In the present study, the hypothesis that the application of CFS as a pre-treatment for OSPW decreases the concentrations of the various constituents present in OSPW was tested. In order to achieve this, the effectiveness of using metallic salt coagulants of alum, ferric sulfate, ferric chloride, and three organic polymers (cationic, anionic, and non-ionic) for the removal of the particles and organic compounds and also changes in concentrations of NAs were determined. Moreover, identification of coagulation mechanism by zeta potential measurement and assessment of the properties of the flocs, such as size and surface functional groups were performed.

2.2. Materials and Methods

2.2.1. Sampling

OSPW was collected on October 2009 from the west in-pit (WIP) tailings pond located at the Syncrude Canada Ltd. facility, Fort McMurray, Alberta, Canada. OSPW was received and stored at 4 ºC. Before conducting the experiments, OSPW was slowly brought to room temperature. A complete characterization of the OSPW is presented in Table 2.1.

Table 2.1. Complete characterization of the OSPW.

Parameters	Average Value
pH	8.5
Turbidity (NTU)	180
TOC (mg/L)	51
COD (mg/L)	240
NAs (mg/L)	23.6
Oxidized NAs (mg/L)	31.6
Alkalinity (mg/L)	630
Conductivity (µS/cm)	3750
Sodium (mg/L)	827
Chloride (mg/L)	515
Sulfate (mg/L)	513
Ammonium (mg/L)	22
Aluminum (mg/L)	8.5
Iron (mg/L)	3.3
Vanadium (mg/L)	0.018
Barium (mg/L)	0.35

2.2.2. Coagulation and Flocculation

All the CFS experiments were conducted at room temperature (19-22 °C) and the natural pH of the OSPW. Experiments were performed in triplicates and parameters of the process water, detailed below, were measured before and after treatment based on standard methods [23]. Turbidity and TOC were measured before and after the establishment of optimum condition. Quantification of NAs and oxidized NAs, scanning electron microscopy (SEM) imaging, surface functional groups characterization of the flocs, and water quality analyses were measured for the optimum condition.

2.2.3. Coagulant

The initial step in optimization of the process was selection of the coagulant type. Metallic salt coagulants of alum, ferric sulfate, and ferric chloride (Fisher Scientific, New Jersey, USA) were separately applied in each jar to form a series of concentration of: 0, 20, 50, 80, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, and 600 mg/L. Coagulants were added at the beginning of the experiments. Initial coagulation conditions were 30 s of rapid mixing at 120 rpm followed by 30 min of slow mixing at 30 rpm. Any flocs formed were allowed to settle for 60 min. Based on the total organic carbon (TOC) removal and turbidity reduction, alum and ferric sulfate showed superior performance compared to ferric chloride (Figure B1 and B2 in the Appendix B). Alum and ferric sulfate resulted in the same removal efficiencies. However, addition of the ferric salts resulted in a reddish color of treated OSPW with higher color intensity at higher coagulant concentration. OSPW contains organic compounds which act as complexing agents toward iron (III) to improve its solubility [24]. As a result of formation of these complexes, a color change in the range of yellow to brown is observed. Because the experiments were performed at pH higher than the optimum pH (~7) and high concentration of ferric salts was added to achieve satisfactory TOC removal, an increase in the intensity of the yellow-brown color was observed. Since this might require additional treatment for color removal, alum, the most commonly used coagulant, was chosen for further optimization. Because the increment of the alum concentration showed an increasing trend of TOC removal and turbidity reduction, to investigate the effect of other factors, including organic polymer type, concentration and addition time of organic polymer, as well as mixing intensity and time, optimization experiments were performed at 100, 250, and 500 mg alum/L.

2.2.4. Polymer

The cationic polymer polydiallyldimethylammonium chloride (polyDADMAC), the anionic polymer polyacrylamide, and the nonionic polymer polyacrylamide (ClearTech, Edmonton, Canada) were used as flocculants.

PolyDADMAC is a low molecular weight polymer with a 100% cationic content [25]. There are two possible polymeric structures of polyDADMAC including *N*-substituted piperidine and *N*-substituted pyrrolidine [26]. Additionally, polyDADMAC has a stable positive charge below pH 10 [18], thus a change in the pH during the process does not affect the polymer charge.

To investigate the effect of the cationic polymer at each concentration of alum, a 3^2 factorial design experiment was applied at three dosages and addition times. The three concentrations of polymer were 2, 5, and 10 mg/L, and the polymer addition time during the coagulation was 0, 15, and 30 sec. A similar procedure was utilized for the anionic and nonionic polymer.

2.2.5. Mixing Intensity and Time

Once the optimum conditions for polymer were determined, the effect of rapid mixing intensity at 80, 120, and 220 rpm was investigated while other factors were kept fixed. At all three concentrations of alum, mixing at 120 rpm resulted in higher TOC removal and turbidity reduction. The effect of slow mixing time on the coagulation performance was also investigated by varying this parameter from 0 to 60 min while all the other factors were kept at the optimized condition.

2.2.6. Equipment

A Phipps & Bird jar test apparatus, equipped with a paddle stirrer and square Plexiglas beakers, was used to perform the coagulation experiments. Quantification of the NAs was performed by ultra pressure liquid chromatography/high resolution mass spectrometry (UPLC/HRMS), as described by Martin et al. [10]. Zeta potential measurements were conducted using a ZetaPALS, Brookhaven Inc. apparatus. All measurements were performed in triplicate for non-filtered samples. Diffuse Reflectance Fourier Transform Infra Red (FT-IR, BioRad FTS 6000) spectrophotometer was used to identify the surface functional groups of the flocs. SEM of the flocs was performed using a HITACHI S-2500 instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed using an AXIS 165 spectrometer (Kratos Analytical). Details of the quantification methods for pH, turbidity, TOC, alkalinity, major ions, trace metals, and other water quality analyses are provided in the Appendix A.

2.2.7. Analysis of NAs by High-Resolution Mass Spectrometry

Samples were filtered through 0.22 µm syringe filters (Millex GS, Millipore). Tetradecanoic acid-1-^{13}C ($C_{14}H_{28}O_2$) was added to each sample (0.2 µg/mL), as internal standard, to correct for sensitivity and retention time drift. Instrumental analysis was performed by a Waters Acquity UPLC System (Waters, MA, USA), employed for rapid and efficient chromatographic separation of the NAs and their oxidized products. High-resolution measurements were performed in-line with a high resolution (~10,000) QSTAR Pulsar i mass spectrometer equipped with a TurboIon Spray source (Applied Biosystem/ MDS Sciex, Concord, ON, Canada) operated in negative mode.

Chromatographic separations were run on an Acquity phenyl BEH column (150x1 mm, 1.7 µm ID) using a gradient mobile phase of (A) 10 mM ammonium acetate solution prepared in Optima-grade water and (B) 10 mM ammonium acetate in 50% methanol and 50% acetonitrile, both Optima-grade. Gradient elution was: 1% B for 2 min, ramped to 60% B by 3 min, to 70% B by 7 min, to 95% B by 13 min, holding it until 14 min and finally returned to 1% B followed y an equilibration time of 5.8 minutes. The flow was constant at 0.110 mL/min and column temperature was 50 ºC. The chromatographic system separated NA based on carbon number (*n*), degree of cyclization (*Z*), and extent of alkyl branching. Relative response to the internal standard for each NA isomer class was plotted over time to determine the concentration and NAs profile. A blank was run at the beginning of the batch to subtract background effects from the samples. As well, a blank was placed as the last sample batch to assess any carry-over effect.

2.2.8. Invertebrate Toxicity Tests

Chironomus dilutus larvae (13-14 days post-oviposition) were exposed to fresh water as a control sample, OSPW, OSPW treated with 250 mg/L alum, and OSPW treated with 250 mg alum/L plus 5 mg cationic polymer polyDADMAC/L. Prior to the initiation of exposures, the OSPW and treated samples were aerated as required (3-4 weeks) to minimize ammonia concentrations. Ten animals were randomly assigned to 300 mL glass beakers, containing approximately 1 cm of silica sand (particle size 200-400 µm) and 250 mL of the respective water samples. Animals were fed 0.67 mg dry weight/individual daily with TetraFin® fish food slurry (Tetra Company, Blacksburg, VA) and water changes (50% renewal) were performed every 2 days. A constant stream of air was bubbled into each beaker. Water samples were collected prior to the water change for assessment of water chemistry. Temperature and pH readings were taken daily from one randomly-selected row of beakers to monitor general water quality. The exposure was performed for 10 days in an environmental chamber maintained at 23 ^{o}C and all exposures were performed in quadruplicate. The toxicity tests were performed in the toxicology centre, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, under the supervision of Dr. John P. Giesy following the established methodology developed for the toxicity tests to invertebrates.

2.3. Results and Discussion

2.3.1. Optimization

The application of nonionic and anionic polymers showed adverse or no effect on the TOC removal. The optimal time for the addition of cationic polymer was 15 s from the beginning of the coagulation. Addition of the polymer at the beginning of the coagulation may affect the performance of the alum and also its addition at 30 s might not provide sufficient interaction with the particles due to the charge neutralization mechanism discussed later. For 100, 250, and 500 mg alum/L, the optimal cationic polymer concentrations were found to be 10, 5, and 2 mg/L, respectively. Rapid mixing intensity at 80 rpm might not be enough to provide necessary contact between the chemicals and the particles, and high intensity mixing at 220 rpm may cause the breakage of the flocs [21]. For slow mixing, TOC removal was the same for all the mixing times less than 30 min. Increasing the mixing time to higher than 30 min decreased the TOC removal. This could be explained by the effect of the prolonged mixing on the breakage of the flocs due to the cleavage of the bonds in the precipitated hydroxides [27, 28]. Therefore, 10 min was chosen for the slow mixing time at 30 rpm.

OSPW was characterized before and after CFS treatment (Table 2.2). The conductivity of the samples did not change, indicating the inability of CFS treatment to remove inorganic dissolved solids. The pH value decreased slightly after addition of the coagulant. Turbidity reduction was greater than 90% at all three concentrations of alum and reached 99% at 500 mg/L of alum. The addition of the cationic polymer at each concentration of alum slightly improved the removal of TOC. Dissolved aluminum ion has been suggested to contribute to the Alzheimer’s disease [18, 29]. However, aluminum concentration decreased up to 96% from its initial concentration due to formation of aluminum hydroxide as the dominant species. Therefore, coagulation-flocculation treatment did not increase its concentration in the OSPW, which eliminate any possible link with Alzheimer’s disease.

OSPW treated with 250 mg alum/L, 250 mg alum/L plus 5 mg polymer/L, and 500 mg alum/L were analyzed for concentrations of NAs and the results showed no differences in the removal of NAs and oxidized NAs. Addition of 500 mg/L of alum increased the salinity of OSPW by 50% after the process. There was no difference in the removal of TOC and turbidity in OSPW treated with 100 mg alum/L, compared to OSPW treated with 250 mg alum/L. Nevertheless, 250 mg alum/L was chosen as the optimum condition to allocate the safety range for suspended solids and TOC fluctuations in OSPW [5].

Table 2.2. Complete water quality analysis results before and after CFS treatment for optimum conditions using alum as the main coagulant and cationic polymer polyDADMAC as the coagulant aid.

Optimum Conditions	pH	Turbidity Removal (%)	TOC Removal (%)	Conductivity (µS/cm)	Sulfate Increase (%)	Aluminum Removal (%)	Iron Removal (%)	Vanadium Removal (%)	Barium Removal (%)
100 mg/L AS*	7.4	96	8	3770	7	81	82	72	54
100 mg/L AS + 10 mg/L CP*	7.4	98	12	3720	23	96	87	67	56
250 mg/L AS	7.1	97	12	3795	24	80	86	72	62
250 mg/L AS + 5 mg/L CP	7.0	99	14	3795	24	95	89	72	63
500 mg/L AS	6.5	98	14	3790	49	72	87	72	60
500 mg/L AS + 2 mg/L CP	6.5	99	17	3775	50	94	91	72	63

*AS and CP indicate aluminum sulfate (alum) and cationic polymer polyDADMAC, respectively.

2.3.2. Removal Mechanisms

2.3.2.1. Metallic Salt Coagulant

Distribution of aluminum species depends on the pH of minimum solubility and total aluminum concentration. Speciation distribution for aluminum after the addition of 90 mg alum/L showed that over pH range of 4.5 to 9, aluminum hydroxide precipitates ($Al(OH)_3$) are the predominant species [18, 30]. The surface charge of the precipitates is determined by their isoelectric point [3], which is approximately 8 for aluminum hydroxides. Thus, at the operational pH used in this study, the surface of the precipitates was positively charged.

Positively charged hydroxide precipitates contribute to the destabilization of the particles [3, 22, 30]. Destabilization occurs by deposition of the hydroxides on the surface of the negatively charged particles through adsorption and hetero-coagulation. This process results in charge neutralization of the particles. Dissolved organic compounds could be also adsorbed and neutralized by the positively charged precipitates resulting in their lower solubility and precipitation.

Phenolic and carboxylic functional groups of organic compounds could also be neutralized by the positively-charged hydrolysis products of alum ($Al(OH)^{2+}$, $Al(OH)_2^{+}$), which exist in smaller concentrations compared to hydroxides. This process results in lower solubility and subsequent removal [3]. In addition, these functional groups might form complexes with Al^{3+} ions [18], and removal of the organic compounds and particles coated with organic compounds result in the reduction of their concentration.

Zeta potential measurement was used to characterize and quantify the charge of the particles, to better understand the performance of CFS and determine the removal mechanism. Measurement of changes in zeta potential and turbidity, caused by the increase of alum concentration, showed that the zero zeta potential point was not reached (Figure 2.1). Therefore, at the optimum concentration of alum, only charge neutralization through adsorption could be the removal mechanism [30]. However, to reach complete charge neutralization higher concentration of alum should be applied, which would not be economically and practically justifiable due to the additional associated problems such as increasing the concentrations of sulfate ions.

By increasing the concentration of alum, a reduction in the turbidity was observed, yet the zeta potential remained negative and slowly approached zero. A similar trend has been reported previously [3]. The authors of that report proposed an adsorption mechanism of the organic compounds on the surface of the precipitates [30]. The zeta potential reached the point of charge neutralization by adding 1000 mg alum/L, after which a slight increase in the turbidity was observed. An increase in the concentration of positively-charged hydrolysis products may cause the restabilization of the suspension.

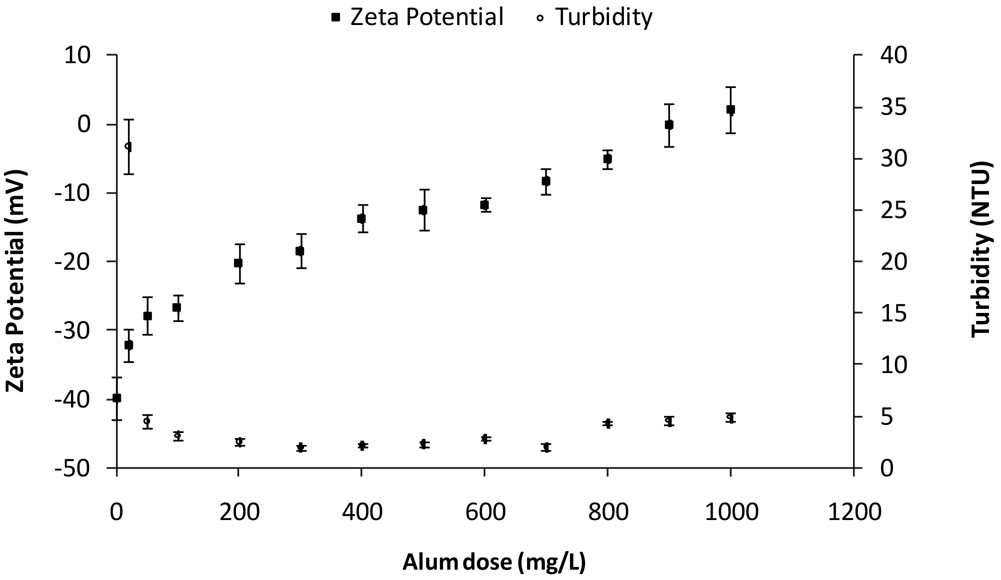

Figure 2.1. Zeta potential and turbidity residual (± std. of 5 replicates) vs. amount of alum added.

2.3.2.2. Effect of Cationic Polymer Addition

Among the advantages of cationic polymer application are the decrease in the concentration of metallic salt coagulant, alkalinity consumption, and sludge production [31]. Due to the high charge density and low molecular weight of the polyDADMAC, charge neutralization is the proposed removal mechanism. SEM images of the flocs, (Figure 2.2) indicate that the flocs formed by the addition of both alum and alum plus polymer are small and compact [32-34]. Therefore, it can be concluded that charge neutralization is the removal mechanism [34]. Although addition of the polymer resulted in slightly greater removal of TOC, it also resulted in greater toxicity of the treated OSPW (see section 2.3.5).

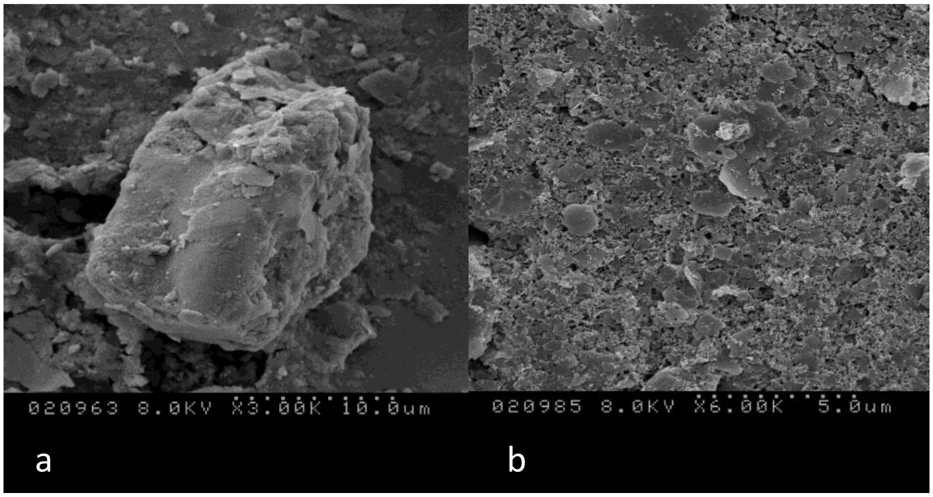

Figure 2.2. SEM images of the flocs formed by (a) 250 mg/L alum, (b) 250 mg/L alum with 5 mg/L cationic polymer.

2.3.2.3. Removal of Trace Metals

Concentrations of vanadium and barium decreased by 67–78% and 42–63%, respectively. Removal mechanisms of vanadium and barium might involve either adsorption of soluble metals to the active sites of the hydroxide or formation of complexes with organic compounds and co-precipitation [35]. Also, vanadium (V) could form insoluble precipitates, such as $AlVO_4$, with aluminum ions. Due to the high concentration of added sulfate and the negligible solubility of barium sulfate in water, barium removal could be related to the formation of the insoluble salt.

2.3.3. Naphthenic Acids

CFS is mostly suitable for removing suspended solids. However, in the current study, it was found that the concentration of dissolved NAs was significantly less in OSPW treated by CFS. Similar results for the removal of an anionic surfactant (which had similar properties and structure to NAs) using alum have been reported previously [36]. High-resolution MS analysis of NAs and oxidized NAs, before and after treatment with 250 mg alum/L are shown in Figure 2.3. High resolution MS analysis of NAs after CFS treatment has not been reported to date. OSPW is a complex mixture and the concentration of its constituents may vary [5]. In this case, the concentration of oxidized NAs ($C_nH_{2n+Z}O_3$) was 34% higher than the NAs ($C_nH_{2n+Z}O_2$). Therefore, removal of both kinds of NAs should be considered of similar importance.

After CFS treatment, NAs and oxidized NAs were removed by 10-37% and 64-86%, respectively. Presence of additional oxygen groups in oxidized NAs may play an important role in complexation ability toward metals and oligomerization of the complexes, and formation of flocs [37]. Residual concentration of NAs was 14.9 mg/L for NAs and 4.3 mg/L for oxidized NA. Removals of the NAs for all the -Z groups (degree of cyclicity) was 1.3-1.7 times; except for the -Z= 8 group of compounds, where removal was slightly higher, 2.2 times. Oxidized NAs were removed over the range of all carbon numbers, and compounds with a higher -Z number were preferentially removed; removal of oxidized NAs with -Z=2, 4, 6, 8, 10, and 12, was 2.2, 2.9, 20.5, 23.8, 8.7, 15.5–times, respectively. There were no differences in removal of oxidized NAs with different carbon numbers. The hydrophobicity of NAs increased by increasing their molecular weights, which is beneficial for the CFS. These results are consistent with the fact that CFS is generally more effective for the removal of organic compounds with higher molecular weight [3].

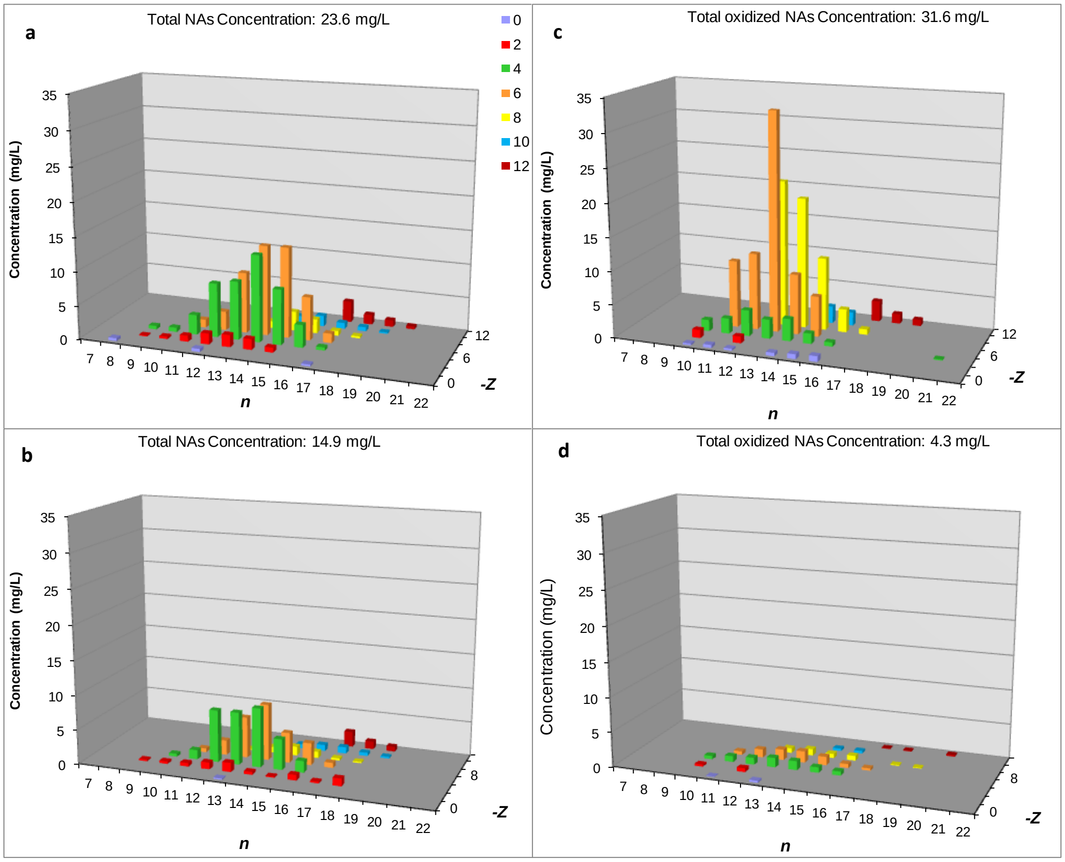

Figure 2.3. Total concentration (E.T.C.) of NAs for (a) fresh OSPW (b) after CFS treatment with 250 mg/L alum, and oxidized NAs for (c) fresh OSPW (d) after CFS treatment with OSPW treated with 250 mg/L alum.

2.3.4. FT-IR Spectral Analysis

FT–IR spectroscopy was used to characterize the surface functional groups present in the OSPW and flocs. The spectra of dried OSPW and flocs formed after treatment with 250 mg alum/L are presented in Figure 2.4. The observed spectra of the dried OSPW and OSPW treated with alum were similar, with a slight shift in peak positions, which indicated the removal of the compounds from the OSPW into the flocs.

The broad absorption band in the region of 3700–3000 cm^{-1} indicated the presence of OH functional groups [38]. These might be related either to water in the samples or the hydroxyl groups. Although samples were air dried, the absorption band may be related to the presence of trapped water inside the flocs. Alternatively, the broad absorption band indicating hydroxyl groups could be related to the presence of the oxidized NAs in the dried OSPW and flocs.

Spectra for carboxylic acids consist of three absorption bands [38]. An absorption band near 1400 cm^{-1} was characteristic of C–O stretching vibration and the second was observed near 1700 cm^{-1}, which was characteristic of C=O stretching vibration. These observations, together with the absorption band of OH groups in the region of 3300–2500 cm^{-1} indicated the presence of the carboxylic groups in the compounds. It also confirmed the presence of NAs and oxidized NAs in the samples. Therefore, these findings confirmed the removal of these compounds from OSPW to the formed flocs.

To confirm the removal of these compounds from OSPW to the formed flocs, XPS analysis was performed on the flocs. Peak deconvolution of Al_{2p} spectrum of the flocs (Figure B3) showed a peak at ∼73.4 eV, which indicated the presence of the Al oxide–oxyhydroxides based on the information from other researchers [39, 40]. Peak deconvolution of the O_{1s} spectrum (Figure B4) showed oxygen peaks with E_b at ~530.7 eV and 534.4 eV, representing the presence of C=O bond of the carboxyls and C–OH/COOH, respectively [41].

C-H functional groups present in the halogenated compounds, hydrocarbon oil, and carboxylic acids are characterized by the peak at ~285 eV (Figure B5) [42-46]. The chemical composition analysis by XPS also showed that oxygen, carbon and aluminum were the major elements in the flocs by the mass concentration of 46.2, 17.5, and 20%, respectively. Together with FT-IR analysis, it indicated the presence of the NAs as well as the aluminum hydroxide and sulfates in the flocs. Moreover, the removal of the NAs was confirmed by the analysis using the UPLC/HRMS.

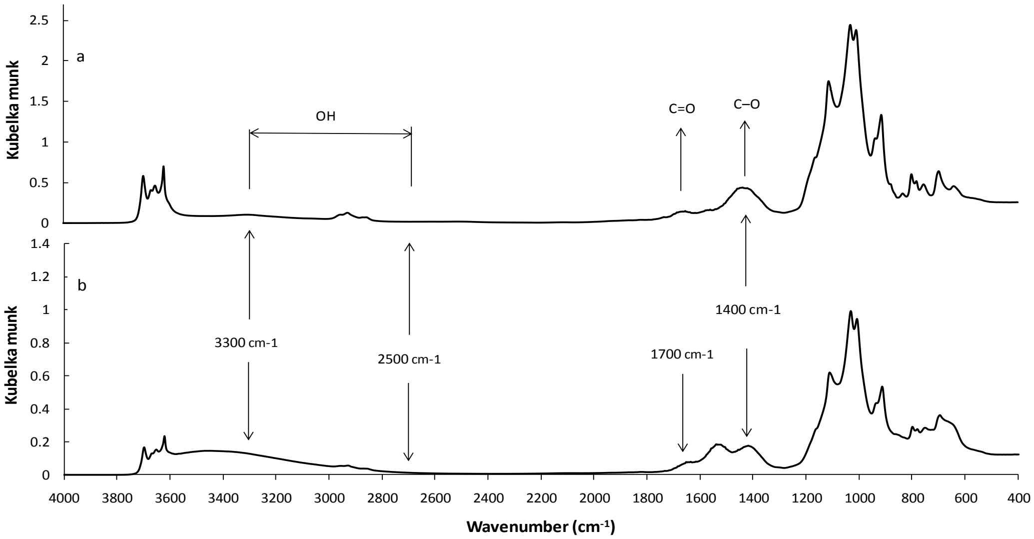

Figure 2.4. Infra-red spectra of the flocs using (a) Dried OSPW, (b) flocs formed after CFS treatment with 250 mg/L alum.

2.3.5. Toxicity to Invertebrates

Growth and survival of the benthic midge (Class *Insecta*, *Chironomus dilutus)* was assessed by exposing animals to a fresh water control, untreated OSPW, OSPW treated with 250 mg alum/L, and OSPW treated with 250 mg alum/L plus 5 mg polyDADMAC/L. Survivals of *C. dilutus* (Figure 2.5) in fresh water and OSPW were not significantly different ($p=0.05$) [47] and were 97.5% and 100%, respectively. Survival of *C. dilutus* exposed to OSPW treated with alum was 75%, but this was not significantly different ($p=0.05$) from the survival in the freshwater control or OSPW. However, survival of *C. dilutus* exposed to OSPW treated with alum plus cationic polymer was 42.5 %, which is significantly less than survival in the freshwater control and OSPW. In addition to effects on survival, decreased growth of *C. dilutus* relative to the control was observed following exposure to each of the OSPW samples (Figure 2.6). There was no statistically significant difference in growth of animals exposed to OSPW compared to alum-treated OSPW. Due to the decrease in the concentration of the organic compounds after alum treatment, the similar growth rate of the animals as compared to OSPW could be related to the presence of the other contaminants in OSPW, such as inorganic ions and metals, to induce toxicity. However, growth of *C. dilutus* exposed to OSPW treated with alum plus polymer was significantly less than the growth of midges in all other treatment groups. These results indicated that the addition of the cationic polymer significantly increased the toxicity of treated OSPW. OSPW was also proved to be toxic to *Daphnia magna* based on a 48 h acute lethality test [48]. Cationic polymers with quaternary amines including polyDADMAC were shown to be toxic to the aquatic organisms such as rainbow trout (*Oncorhynchus mykiss*), *Daphnia pulex*, and fathead minnow (*Pimephales promelas*) [49-51]; there may be a synergistic effect of the cationic polymer or monomer present in the polymer, NAs compounds, and other inorganic contaminants which induced more toxicity [25]. Therefore, based on the relatively slight increase in the contaminant removal from the OSPW by addition of the polymer compared to the coagulant alone, it is recommended to apply only the metallic salt coagulant.

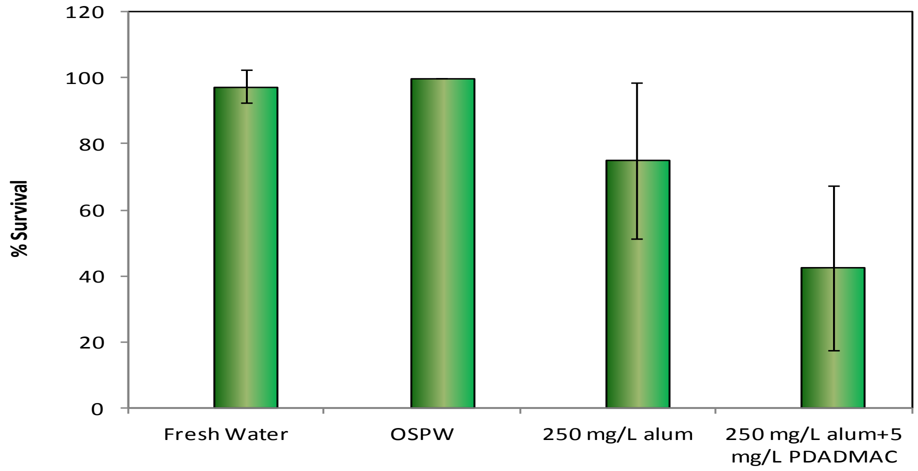

Figure 2.5. Effects of full-strength OSPW, OSPW treated by 250 mg/L alum, and 250 mg/L alum+ 5 mg/L cationic polymer on the survival of *C.dilutus* relative to a freshwater control. Data represent mean ± st dev of 4 independent replicates. (1- way ANOVA with Tukey's post hoc test, $p < 0.05$).

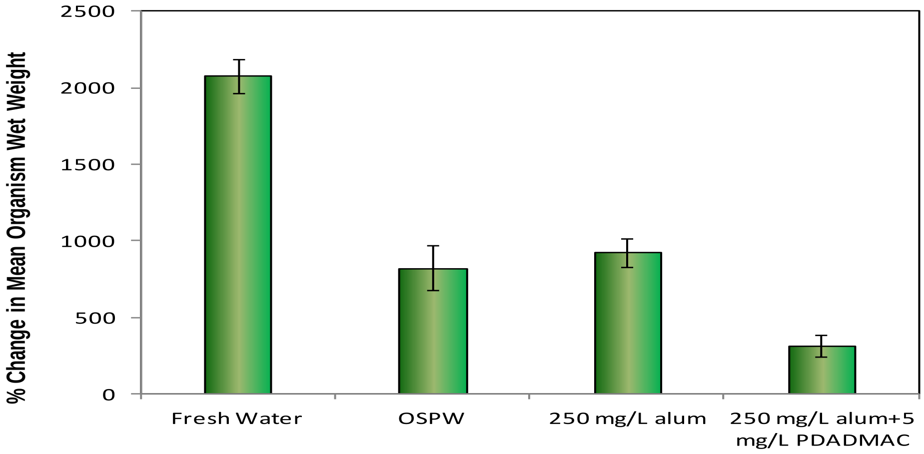

Figure 2.6. Effects of full-strength OSPW, OSPW treated by 250 mg/L alum, and 250 mg/L alum+ 5 mg/L cationic polymer on the growth of *C.dilutus* relative to a freshwater control. Data represent mean ± st dev of 4 independent replicates. (1-way ANOVA with Tukey's post hoc test, $p < 0.05$).

2.4. Conclusions

The results of the current study demonstrate that CFS is a reliable pre-treatment process and could reduce the impact that OSPW has on the environment. This treatment could be combined with other secondary and tertiary treatment processes to enhance the performance and reduce the overall process time of the system. In addition to complete turbidity reduction, organic compounds were efficiently reduced. Moreover, application of alum over the ferric salt coagulants is preferred in regards that it was shown to not only enhance the treatment efficiency, but also to decrease the concentrations of dissolved aluminum ions in the treated waters eliminating any possible link with Alzheimer's disease. Morphology of the flocs indicated that metallic salt coagulants generated compact flocs. Toxicity is a major indicator for the usability of a selected process for the remediation of OSPW. The toxicity approach using an aquatic invertebrate showed that the pre-treatment does not significantly increase the toxicity of the treated water. However, when the cationic polymer polyDADMAC was added over the metallic salt coagulant greater toxicity was observed. Therefore, this combination is not recommended in order to reduce the environmental impact of this pre-treatment.

2.5. References

1. Jarvis, P.; Jefferson, B.; Parsons, S. A., Characterising natural organic matter flocs. *Natural Organic Material Research: Innovations and Applications for Drinking Water* 2004, *4,* (4), 79-87.

2. Jarvis, P.; Jefferson, B.; Parsons, S. A., How the natural organic matter to coagulant ratio impacts on floc structural properties. *Environmental Science & Technology* 2005, *39*, (22), 8919-8924.

3. Duan, J. M.; Gregory, J., Coagulation by hydrolysing metal salts. *Advances in Colloid and Interface Science* 2003, *100*, 475-502.

4. Legrini, O.; Oliveros, E.; Braun, A. M., Photochemical Processes for Water-Treatment. *Chemical Reviews* 1993, *93*, (2), 671-698.

5. Allen, E. W., Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. *Journal of Environmental Engineering and Science* 2008, *7*, (2), 123-138.

6. Peng, H.; Volchek, K.; MacKinnon, M.; Wong, W. P.; Brown, C. E., Application of nanofiltration to water management options for oil sands operations. *Desalination* 2004, *170*, (2), 137-150.

7. Han, X. M.; MacKinnon, M. D.; Martin, J. W., Estimating the in situ biodegradation of naphthenic acids in oil sands process waters by HPLC/HRMS. *Chemosphere* 2009, *76*, (1), 63-70.

8. Holowenko, F. M.; MacKinnon, M. D.; Fedorak, P. M., Characterization of naphthenic acids in oil sands wastewaters by gas chromatography-mass spectrometry. *Water Research* 2002, *36*, (11), 2843-2855.

9. Headley, J. V.; McMartin, D. W., A review of the occurrence and fate of naphthenic acids in aquatic environments. *Journal of Environmental Science and*

Health Part a-Toxic/Hazardous Substances & Environmental Engineering 2004, *39*, (8), 1989-2010.

10. Martin, J. W.; Barri, T.; Han, X.; Fedorak, P. M.; El-Din, M. G.; Perez, L.; Scott, A. C.; Jiang, J. T., Ozonation of oil sands process-affected water accelerates microbial bioremediation. *Environmental Science & Technology* 2010, *44*, (21), 8350-8356.

11. Han, X. M.; Scott, A. C.; Fedorak, P. M.; Bataineh, M.; Martin, J. W., Influence of molecular structure on the biodegradability of naphthenic acids. *Environmental Science & Technology* 2008, *42*, (4), 1290-1295.

12. He, Y. H.; Wiseman, S. B.; Zhang, X. W.; Hecker, M.; Jones, P. D.; El-Din, M. G.; Martin, J. W.; Giesy, J. P., Ozonation attenuates the steroidogenic disruptive effects of sediment free oil sands process water in the H295R cell line. *Chemosphere* 2010, *80*, (5), 578-584.

13. Scott, A. C.; Zubot, W.; MacKinnon, M. D.; Smith, D. W.; Fedorak, P. M., Ozonation of oil sands process water removes naphthenic acids and toxicity. *Chemosphere* 2008, *71*, (1), 156-160.

14. Smith, B. E.; Lewis, C. A.; Belt, S. T.; Whitby, C.; Rowland, S. J., Effects of alkyl chain branching on the biotransformation of naphthenic acids. *Environmental Science & Technology* 2008, *42*, (24), 9323-9328.

15. Whitby, C., Microbial naphthenic acid degradation. In *Advances in Applied Microbiology, Vol 70*, 2010; Vol. 70, pp 93-125.

16. He, Y. H.; Wiseman, S. B.; Zhang, X. W.; Hecker, M.; Jones, P. D.; El-Din, M. G.; Martin, J. W.; Giesy, J. P., Ozonation attenuates the steroidogenic disruptive effects of sediment free oil sands process water in the H295R cell line. *Chemosphere 80*, (5), 578-584.

17. Drzewicz, P.; Afzal, A.; El-Din, M. G.; Martin, J. W., Degradation of a model naphthenic acid, cyclohexanoic acid, by vacuum UV (172 nm) and UV (254 nm)/H_2O_2. *Journal of Physical Chemistry A* 2010, *114*, (45), 12067-12074.

18. Letterman, R. D., *Water quality and treatment: A handbook of community water supplies.* 5th ed.; McGraw-Hill, Inc.: New York, 1999.

19. Verrna, S.; Prasad, B.; Mishra, I. M., Pretreatment of petrochemical wastewater by coagulation and flocculation and the sludge characteristics. *Journal of Hazardous Materials* 2010, *178*, (1-3), 1055-1064.

20. Sharp, E. L.; Jarvis, P.; Parsons, S. A.; Jefferson, B., The impact of zeta potential on the physical properties of ferric-NOM flocs. *Environmental Science & Technology* 2006, *40*, (12), 3934-3940.

21. Yukselen, M. A.; Gregory, J., Properties of flocs formed using different coagulants. *3rd World Water Congress: Drinking Water Treatment* 2002, *2*, (5-6), 95-101.

22. Eddy, M., *Wastewater engineering-treatment, disposal, reuse* 2nd ed.; McGraw-Hill: New York, 1979.

23. Greenberg, A. E., *Standard methods for the examination of water and wastewater* 18th ed.; Amercian Public Health Association Washington, DC 1992.

24. Sun, Y. F.; Pignatello, J. J., Chemical treatment of pesticide wastes - evaluation of Fe(Iii) chelates for catalytic hydrogen-peroxide oxidation of 2,4-D at circumneutral pH. *Journal of Agricultural and Food Chemistry* 1992, *40*, (2), 322-327.

25. Bolto, B.; Gregory, J., Organic polyelectrolytes in water treatment. *Water Research* 2007, *41*, (11), 2301-2324.

26. Wiley, J.; Buckley, C. A.; Jacobs, E. P.; Sanderson, R. D. *Structure and properties of polyDADMAC for water purification*; 2002.

27. Yukselen, M. A.; Gregory, J., Breakage and re-formation of alum flocs. *Environmental Engineering Science* 2002, *19*, (4), 229-236.

28. Yukselen, M. A.; Gregory, J., The reversibility of floc breakage. *International Journal of Mineral Processing* 2004, *73*, (2-4), 251-259.

29. Bina, B.; Mehdinejad, M. H.; Nikaeen, M.; Attar, H. M., Effectiveness of chitosan as natural coagulant aid in treating turbid waters. *Iranian Journal of Environmental Health Science & Engineering* 2009, *6*, (4), 247-252.

30. Gregory, J.; Duan, J. M., Hydrolyzing metal salts as coagulants. *Pure and Applied Chemistry* 2001, *73*, (12), 2017-2026.

31. Crittenden, J. C.; Trussell, R. R.; Hand, D. W.; Howe, K. J.; Tchobanoglous, G., *Water Treatment - Principles and Design* 2nd ed.; John Wiley & Sons 2005; p 687-688.

32. Gregory, J., Fundamentals of flocculation. *Critical Reviews in Environmental Control* 1989, *19*, (3), 185-230.

33. Liang, Z.; Wang, Y. X.; Zhou, Y.; Liu, H.; Wu, Z. B., Variables affecting melanoidins removal from molasses wastewater by coagulation/flocculation. *Separation and Purification Technology* 2009, *68*, (3), 382-389.

34. Yu, J. F.; Wang, D. S.; Ge, X. P.; Yan, M. Q.; Yang, M., Flocculation of kaolin particles by two typical polyelectrolytes: A comparative study on the kinetics and floc structures. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 2006, *290*, (1-3), 288-294.

35. Pang, F.; Teng, S.; Teng, T.; Omar, A. K. M., Heavy metals removal by hydroxide precipitation and coagulation-flocculation methods from aqueous solutions. *Water Quality Research Journal of Canada* 2009, *44*, (2), 174-182.

36. Beltran-Heredia, J.; Sanchez-Martin, J., Removal of sodium lauryl sulphate by coagulation/flocculation with Moringa oleifera seed extract. *Journal of Hazardous Materials* 2009, *164*, (2-3), 713-719.

37. Dupreez, A. C.; Preston, J. S., Solvent-extraction of rare-earth-metals by carboxylic-acids. In *Solvent Extraction 1990, Pts a and B*, Sekine, T., Ed. 1992; Vol. 7, pp 1081-1086.

38. Stuart, B. H., *Infrared spectroscopy: fundamentals and applications*. John Wiley: 2004.

39. Gomes, J. A. G.; Daida, P.; Kesmez, M.; Weir, M.; Moreno, H.; Parga, J. R.; Irwin, G.; McWhinney, H.; Grady, T.; Peterson, E.; Cocke, D. L., Arsenic removal by electrocoagulation using combined Al-Fe electrode system and characterization of products. *Journal of Hazardous Materials* 2007, *139*, (2), 220-231.

40. Taylor, J. A., The Characterization of aluminum-silicon-oxygen compounds by XPS. *Abstracts of Papers of the American Chemical Society* 1982, *184*, (SEP), 25-GEOC.

41. Shen, W.; Li, Z.; Liu, Y., Surface chemical functional groups modification of porous carbon. *Recent Patents on Chemical Engineering* 2008, *1*, 27-40.

42. Beamson G., B. D., *High resolut ion XPS of organic polymers, The Scienta ESCA300 Database*. John Wiley & Sons: New York, 1992.

43. Buchwalter, L. P.; Silverman, B. D.; Witt, L.; Rossi, A. R., X-Ray photoelectron-spectroscopy analysis of hexafluorodianhydride-oxydianiline polyimide-substantiation for substituent effects on aromatic carbon 1s binding-energies. *Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films* 1987, *5*, (2), 226-230.

44. Chan, H. S. O.; Hor, T. S. A.; Sim, M. M.; Tan, K. L.; Tan, B. T. G., X-Ray photoelectron spectroscopic studies of polyquinazolones - an assessment of the degree of cyclization. *Polymer Journal* 1990, *22*, (10), 883-892.

45. Desimoni, E.; Casella, G. I.; Salvi, A. M.; Cataldi, T. R. I.; Morone, A., XPS investigation of ultra-high-vacuum storage effects on carbon-fiber surfaces. *Carbon* 1992, *30*, (4), 527-531.

46. Wagener, K.; Batich, C.; Kirsch, B.; Wanigatunga, S., Chain propagation step propagation polymerization .3. an XPS investigation of poly(oxyethylene)-B-poly(pivalolactone) telechelomer. *Journal of Polymer Science Part a-Polymer Chemistry* 1989, *27*, (8), 2625-2631.

47. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates *U.S. Environmental Protection Agency. EPA 600/R-99/064. Washington DC* 2000.

48. Frank, R. A.; Fischer, K.; Kavanagh, R.; Burnison, B. K.; Arsenault, G.; Headley, J. V.; Peru, K. M.; Van der Kraak, G.; Solomon, K. R., Effect of carboxylic acid content on the acute toxicity of oil sands naphthenic acids. *Environmental Science & Technology* 2009, *43*, (2), 266-271.

49. de Rosemond, S. J. C.; Liber, K., Wastewater treatment polymers identified as the toxic component of a diamond mine effluent. *Environmental Toxicology and Chemistry* 2004, *23*, (9), 2234-2242.

50. Goodrich, M. S.; Dulak, L. H.; Friedman, M. A.; Lech, J. J., Acute and long-term toxicity of water-soluble cationic polymers to rainbow-trout (oncorhynchus-mykiss) and the modification of toxicity by humic-acid. *Environmental Toxicology and Chemistry* 1991, *10*, (4), 509-515.

51. Hall, W. S.; Mirenda, R. J., Acute toxicity of waste-water treatment polymers to daphnia-pulex and the fathead minnow (pimephales-promelas) and

the effects of humic-acid on polymer toxicity. *Research Journal of the Water Pollution Control Federation* 1991, *63*, (6), 895-899.

CHAPTER 3. IMPACT OF PETROELUM COKE CHARACTERISTICS ON THE ADSORPTION OF THE ORGANIC FRACTIONS FROM OIL SANDS PROCESS-AFFECTED WATER[1]

3.1. Introduction

With a recoverable 170.4 billion barrels of bitumen, Athabasca oil sands in Alberta, Canada, constitutes the third largest oil deposit in the world after Venezuela and Saudi Arabia [1-3]. The increasing worldwide demand in crude oil leads to a steady increase in the amount of waste by-products generated by the petroleum industry including coke, fly ash, and water tailings [4-7]. Petroleum coke (PC) is generated in large quantities during the oil refinery process when the ratio of H:C has to be upgraded [8]. With a 20 kg of PC typically produced per barrel of synthetic crude oil [9], the PC inventory in Alberta has reached 68 million tonnes in 2010 [10]. The presence of low combustible volatiles and relatively inactive carbon forms [11, 12] makes PC ineffective in heat generation as compared to coal. The high sulfur and heavy metals content raises significant environmental concern over its potential use as an alternative energy source. PC has been investigated as a precursor of activated carbon for the removal of organic contaminants and heavy metals from aqueous solutions [13-15]. However, it has been reported that the activation of PC significantly increased the vanadium concentration in the treated water as compared to water treated with the

---

[1] A version of this chapter has been submitted for publication. Pourrezaei et al. *International Journal of Environmental Science and Technology* (August 2012).

fresh PC [9]. Therefore, the continuing accumulation and stockpiling of large quantities of PC require development of innovative strategies for the effective utilization of this carbon-rich material on an industrial scale.

Another environmental concern in petroleum industry is the process-affected water. One of the examples of such water is the oil sands process-affected water (OSPW), generated after Clark hot water extraction of bitumen from oil sands operations. OSPW is a complex alkaline mixture of inorganic and organic compounds [5, 6]. OSPW is retained on site and a part of it is recycled back to the extraction process to reduce the freshwater consumption. As a result, it becomes corrosive and highly toxic due to high concentrations of salts and refractory organic compounds such as naphthenic acids (NAs) [16]. The storage of OSPW has raised several environmental concerns, including the presence of trace concentrations of NAs in surface waters around the oil sands operation facilities due to their leaching from tailings ponds [5].

Adsorption is viewed as an effective process to remove persistent organic chemicals from wastewaters [17]. Given the complexity of environmental problems and continuous accumulation of different by-products, that the petroleum industry is facing, the process shortcomings can be turned into benefits by applying one waste to treat another waste product. In this approach, PC can be used as an *in-situ* adsorbent for the treatment of OSPW. Since PC is a residual of oil refining, it is available virtually free of charge and does not require any transportation costs. As such, the investment cost associated with the development of any other technology for OSPW treatment could be significantly reduced. Currently, at Syncrude Canada Ltd. production site in Alberta, Canada, PC, produced after fluid coking process, is mixed with OSPW at approximately 22%wt. before its transport to the tailings ponds for a long-time storage [9]. The operating pipeline acts as a "plug-flow" carbon adsorption reactor that reduces the concentration of organic fraction in OSPW during the transfer process. Water quality analyses have shown that chemical oxygen demand (COD), concentration of extractable organic fraction (EOF) and NAs decreased after adsorption [9, 18]. The PC-treated OSPW required less ozone doses to remove the remaining organics and the resulted water was more biodegradable [18]. Majid et al. [4] showed that PC reduced the concentration of total dissolved carbon from 300–600 mg/L to less than 50 mg/L during the removal of free phase bitumen from a wastewater, produced in oil sands surface mining, by agglomeration.

Leaching of vanadium from PC and its environmental impact has been investigated in several publications [17, 19-21]. Vanadium, released from PC, was accounted as a primary cause of leachate toxicity to a freshwater invertebrate *Ceriodaphnia dubia* in a hard reconstituted water [22]. In a follow-up study, Puttaswany and Liber [20] showed that the concentrations of nickel and vanadium released into water, which mimic anion content of OSPW, was above the chronic *C. dubia* half maximal inhibitory concentration (IC_{50}) or median lethal dose (LC_{50}). However, OSPW treated with PC, did not show any toxicity towards *Vibrio fischeri* and rainbow trout as compared to fresh OSPW [17].

The promising results with respect to the removal of organic compounds and reduced toxicity of OSPW after PC treatment require further evaluation of the PC for the removal of organic compounds in terms of adsorption mechanism, adsorbent properties and vanadium speciation. The objectives of the present study were to: (1) investigate the effect of the contact time and PC concentration on the removals of EOF and NAs from OSPW without any pre-treatment; (2) determine the mechanisms of NAs adsorption on PC; (3) study the effect of physico-chemical properties of PC on the adsorption of NAs; and (4) investigate the vanadium leaching from PC and its speciation during the adsorption process. To achieve these objectives, adsorption studies were performed by mixing the PC and OSPW in various proportions and for different contact times. The experimental data were fitted to different adsorption isotherms to determine the adsorption capacity and elucidate the mechanism of NAs adsorption. The physical and chemical characteristics of the adsorbent were evaluated by using Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), thermo gravimetric analysis (TGA), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) surface area analysis.

3.2. Materials and Methods

3.2.1. Sampling

OSPW was collected in January 2010 from the west in-pit (WIP) recycle tailings pond at Syncrude Canada Ltd., Alberta, Canada. The barrels were transported to the University of Alberta, Edmonton, Canada, and stored at 4°C.

OSPW characteristics are shown in Table 3.1. OSPW was used as-received without any pre-treatment and all adsorption experiments were conducted at room temperature (20–23 °C).

Table 3.1. Characterization of as-received OSPW (average of n = 3 replicates).

Parameter	Value
pH	8.4 ± 0.2
Alkalinity (mg/L as $CaCO_3$)	694 ± 19
COD (mg/L)	233 ± 12
NAs (mg/L)	60.3 ± 3
EOF (mg/L)	81 ± 7
Vanadium (µg/L)	13.1 ± 0.7

3.2.2. Adsorbents

PC was also provided by Syncrude Canada Ltd. The samples were sieved by a No. 40 (0.422 mm) mesh to separate the larger sized clumps. Granular activated carbon (GAC, JA04) was supplied by Jacobi Carbons (Jacobi Carbons Inc., Columbus, OH, USA), and powdered activated carbon (PAC, WPX-Z) was purchased from Calgon Carbon (Calgon Carbon Corporation, Pittsburgh, PA, USA).

3.2.3. Preliminary Adsorption Experiments

This set of experiments was aimed at evaluating the effects of adsorbent concentrations and contact times on the overall adsorption of organic compounds from OSPW. Adsorption studies were performed in a batch mode in 500 mL stoppered conical flasks. Specific pre-weighed amounts of PC, GAC or PAC were mixed with OSPW to result in 50, 100, 200, 300, and 400 g/L concentrations. The control samples were prepared without the addition of adsorbents. The flasks were placed on an incubator shaker (New Brunswick Scientific, Enfield, CT, USA) and shaken at 270 rpm. After pre-determined contact times (1, 3, 6 and 12 h), the mixtures were filtered through 0.45 µm Nylon filters (SUPELCO, Bellefonte, PA, USA). Untreated and treated OSPWs were analyzed in terms of EOF concentration, COD, pH, and alkalinity. The two-tailed t-test at 95% confidence interval was used to determine the statistically significance of the results.

3.2.4. Equilibrium Time Experiments for PC

The aim of this set of experiments was to determine the contact time needed for the concentration of EOF in the liquid phase to reach equilibrium with the PC. Based on the COD and EOF removals during the preliminary adsorption experiments with PC (discussed in details in section 3.3.2), and because of the dense slurry formed upon mixing 300 and 400 g/L of PC with OSPW, 200 g/L concentration of PC was chosen to perform the equilibrium time experiments. The experiments were conducted for the contact times of 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, and 40 h by following the same procedure described in section 3.2.3. Untreated and treated OSPWs were analyzed in terms of EOF removal.

3.2.5. Adsorption Isotherms

In this set of experiments, the specific pre-weighed amounts of PC, GAC or PAC were added to OSPW to result in a series of mixtures with the adsorbent concentrations in the range of 0–200 g/L for PC and 0–20 g/L for PAC or GAC. The isotherms of adsorption experiments were conducted in the same manner described in section 3.2.3 for 16 h and 12 h for PC and GAC/PAC, respectively. The experimental data were fitted to the *Langmuir*, *Freundlich*, and *Dubinin-Radushkevich* isotherm equations as explained in detail in Appendix A.

3.2.6. End-points for NAs Analysis and Physico-Chemical Characterization of Adsorbents

Because of the high cost and complexity associated with the NAs analysis, the NAs removal was measured for 200 g/L of PC after 16 h of treatment and for 50 g/L of PAC/GAC after 12 h of treatment. These conditions were also used for the physico-chemical characterization of adsorbents.

3.2.7. Vanadium Leaching and Speciation Experiments with PC

In adsorption experiments aimed at evaluating vanadium speciation in the treated OSPW, 2.5 mM ethylenediaminetetraacetic acid disodium salt dehydrate (Na_2EDTA) (Sigma-Aldrich, Oakville, Ontario, Canada) was added first to untreated OSPW or Milli-Q water (Millipore, Molsheim, France) to form a stable complex with vanadium (IV) and (V) to prevent speciation change [23]. The adsorption experiments were performed in a similar manner as described in section 3.2.3. The filtrate was diluted using a 2.5 mM Na_2EDTA to a concentration that fell within the calibration range. Vanadium speciation was performed by using a PerkinElmer high performance liquid chromatography-inductively coupled plasma mass spectrometer (HPLC-ICP-MS) instrument

(HPLC, PE Instruments, Shelton, CT, USA and ICP-MS, PE Sciex, Concord, ON, Canada) by following the method described by Li et al. [23]. A Tukey test in combination with ANOVA at 95% confidence interval was used for the analysis of the obtained data. Vanadium speciation analysis was performed in department of chemistry, University of Alberta, Edmonton, Alberta, Canada, under the supervision of Dr. X. Chris Le following the methodology developed for vanadium speciation.

3.2.8. Water Quality Analysis

COD, pH, and alkalinity were determined according to the standard methods [24]. A solid addition method was used to determine the pH of the zero surface charge (PZC) of the adsorbent. The detailed methodologies for the analysis of surface functional groups, BET surface area, TGA, SEM, PZC, and XPS could be found in Appendix A. The EOF concentrations in OSPW before and after adsorption were measured following the methodology explained in details elsewhere [25, 26]. The complete methodology for the NAs analysis is explained in Appendix A. Milli-Q water from Synergy® UV instrument (Millipore, Molsheim, France) was used throughout the study for the preparation of the standard solutions for the analysis.

3.2.9. Equipment

A FT-IR instrument (PerkinElmer Spectrum, 100 FT-IR Spectrometer, Waltham, USA) was used for the quantification of EOF compounds in liquid samples. A Bio-rad diffuse reflectance FT-IR spectrophotometer (FTS 6000, Philadelphia, PA, USA) was used for the identification of surface functional groups on the surface of adsorbents. SEM was performed using a HITACHI S-2500 instrument (Tokyo, Japan). XPS was performed using an AXIS 165 spectrometer (Kratos Analytical, Manchester, UK). TGA was performed by a thermal analyser system (DSC 1, Mettler Toledo, Mississauga, ON, Canada). BET surface area analysis was performed using a surface analyser (IQ2MP, Quantachrome, FL, USA).

3.3. Results and Discussion

3.3.1. pH and Total Alkalinity

The adsorbents used in this study showed different effects on the pH and alkalinity of the samples after adsorptive treatments (Table 3.2). The PC did not significantly change the pH of the treated OSPW, but it caused alkalinity to decrease by 1–27%. The latter could be related to the dissolution of metal oxides present in the PC and their subsequent reaction with bicarbonate ions present in OSPW [9]. Increasing the concentration of PAC did not change the pH and alkalinity of the treated OSPW, whereas increasing the GAC concentration resulted in increments in pH and alkalinity after treatment. This is likely due to the higher amount of OH groups present on the GAC surface (discussed later in XPS analysis section 3.3.7). The effect of contact time on the pH and alkalinity was negligible for PC, PAC and GAC.

Table 3.2. pH and alkalinity of OSPW before and after 12 h of adsorption.

Concentration (g/L)	pH			Alkalinity (mg/L as $CaCO_3$)		
	PC	GAC	PAC	PC	GAC	PAC
0	8.4±0.1	8.5±0.1	8.6±0.1	704±4	704±4	704±4
50	8.5±0.1	9.6±0.1	8.8±0.1	688±4	818±5	696±4
100	8.5±0.1	9.9±0.1	9.1±0.1	664±6	912±5	692±11
200	8.5±0.1	10.4±0.1	8.9±0.1	637±4	1004±6	-
300	8.4±0.1	10.4±0.1	9.0±0.1	595±1	1042±5	717±24
400	8.6±0.1	10.4±0.1	8.9±0.1	544±3	1092±5	720±4

3.3.2. COD and EOF Concentrations

An increase in PC concentration resulted in an increase in COD removal from OSPW (Figure 3.1). No statistically significant difference in the COD removal was observed at 1, 3 and 6 h of contact time; however, when contact time approached 12 h, the COD removal increased for all the studied PC concentrations. The COD removal at 12 h contact time for 200 g/L PC was significantly higher as compared to 50 and 100 g/L, but no statistically significant difference was observed between 200 with 300 g/L, and between 300 with 400 g/L PC at 12 h. At PC concentrations above 200 g/L, very dense slurries were formed resulting in improper contact between the PC and OSPW. This may explain no statistically significant difference in the COD removal for the PC concentrations above 200 g/L. EOF removal followed the same trend as the COD removal, reaching 60% reduction at 200 g/L PC after 12 h of contact (Figure 3.2).

The higher COD and EOF removals at higher PC concentrations are likely arisen from the higher available surface area at higher PC concentrations [27, 28]. Based on the COD and EOF results, 200 g/L of PC was chosen in further equilibrium time studies.

The application of GAC and PAC to OSPW treatment led to COD and EOF removals of >93%, regardless of the contact times and adsorbent concentrations. Higher removal in the case of activated carbons is likely arisen from the significantly higher surface area of the commercial activated carbons as compared to PC (discussed later in section 3.3.8). Therefore, the lowest concentrations of 50 g/L of GAC and PAC at 12 h contact time were chosen for physico-chemical analysis of adsorbents and NAs analysis.

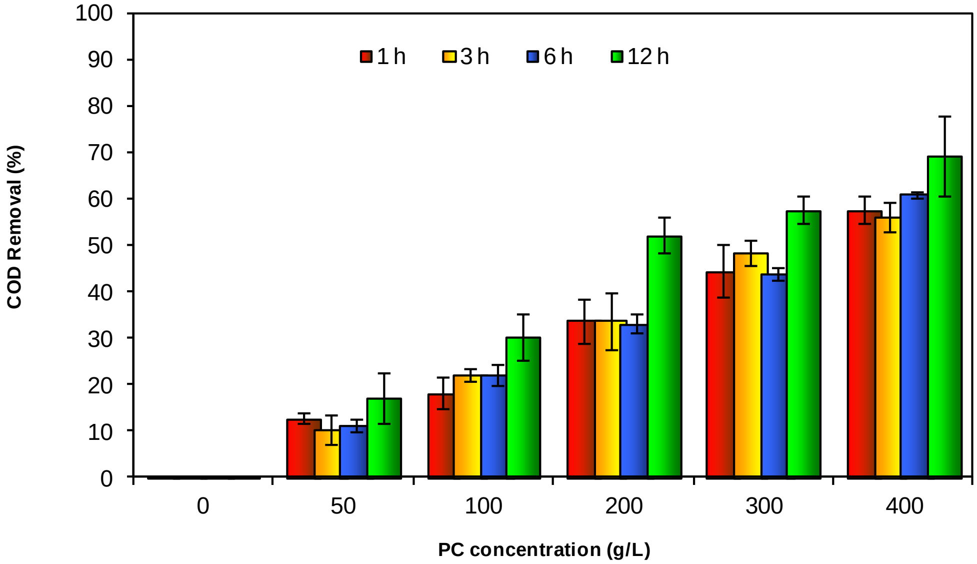

Figure 3.1. COD removal as a function of PC concentration and contact time.

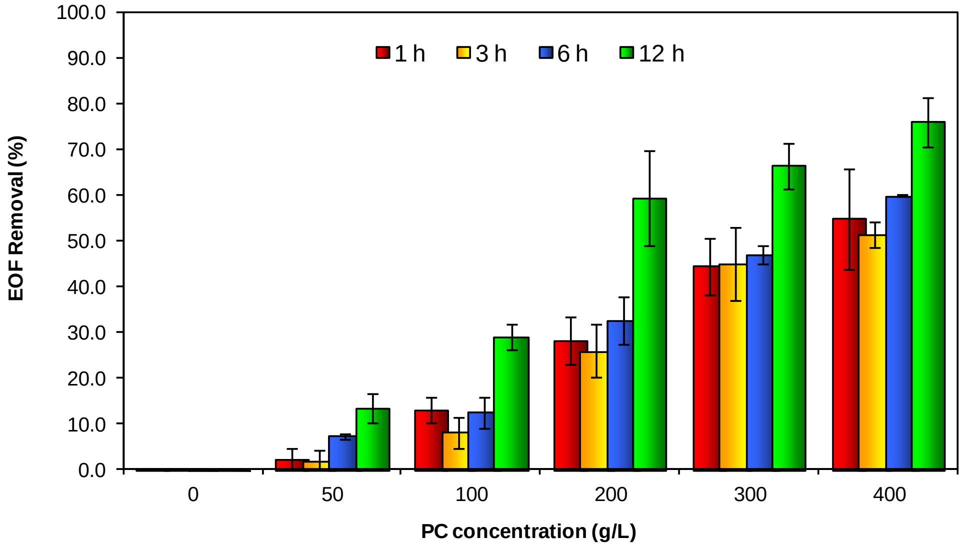

Figure 3.2. EOF removal as a function of PC concentration and contact time.

3.3.3. Equilibrium Time Studies

EOF removal (Figure 3.3) increased gradually from 2 to 16 h and reached a plateau after 16 h of contact. The linear and plateau portions of the curve corresponded to the diffusion of EOF to surface layers and pores, respectively [29]. The observed effect was indicative of the rapid adsorption of EOF on the easily accessible adsorption sites at the beginning of experiment, followed by limited diffusion of the adsorbate molecules into the mesopores [30]. Based on the results, 16 h was chosen as the equilibrium contact time for further physico-chemical analysis of PC and NAs analysis.

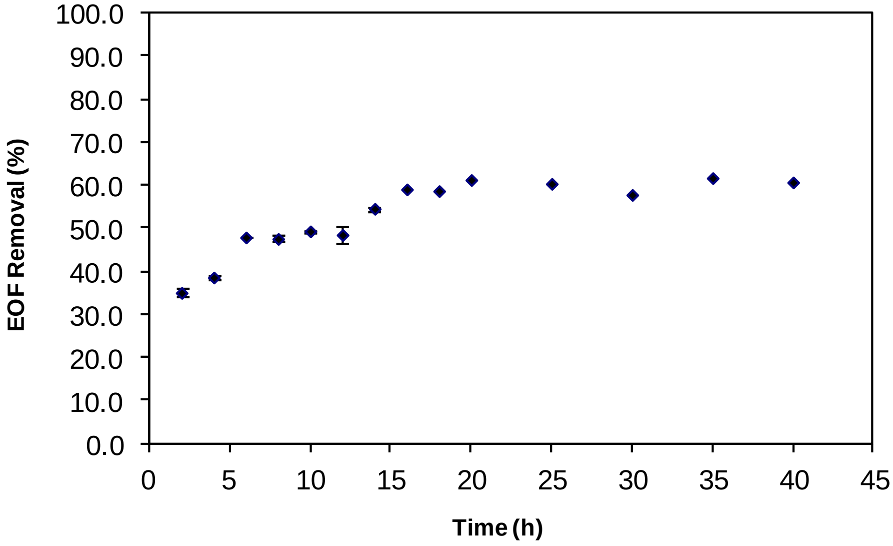

Figure 3.3. EOF removal as a function of contact time at 200 g/L PC.

3.3.4. Adsorption Isotherms

The calculated parameters for the *Langmuir*, *Freundlich*, and *Dubinin-Radushkevich* isotherms for EOF adsorption are shown in Table 3.3. A complete description of the isotherms along with the equations is presented in Appendix A. Plots of the isotherms can be found in Appendix B (Figure B6). Both *Langmuir* and *Freundlich* isotherms showed high correlation coefficients for PC and GAC. For PAC, *Freundlich* isotherm showed higher correlation coefficient as compared to that obtained using the *Langmuir* isotherm. The maximum adsorption capacity (q_m) for the PC to adsorb EOF from OSPW was calculated as 1.0 mg/g by fitting the experimental data to the *Langmuir* isotherm. This value, compared to 51 and 71 mg/g for GAC and PAC, respectively, indicated that larger mass of PC is required for the removal of the EOF from OSPW. The adsorption capacity also decreased with the increase in PC concentration, suggesting that some of the available sites remained unsaturated [27, 31]. The separation factor (R_L) values in the range of 0–1 suggested the favorable adsorption of EOF from OSPW. In addition, the calculated mean free energy of adsorption (E < 8 kJ/mol) suggested that the EOF were physically adsorbed to the surface of the adsorbents.

Table 3.3. Calculated isotherm parameters for EOF adsorption.

Parameters	PC	GAC	PAC
Langmuir			
q_m (mg/g)	1.02	50.5	71.0
K_{ads} (L/mg)	0.01	0.02	0.02
R_L	0.67	0.39	0.52
r^2	0.95	0.98	0.84
Freundlich			
K (mg/g)(L/mg)$^{1/n}$	0.01	1.01	0.23
n	1.22	1.21	1.85
r^2	0.95	0.96	0.92
Dubinin-Radushkevich			
q_m (mg/g)	0.28	12.43	107
β (mol^2/J^2)	7×10^{-5}	5×10^{-6}	3×10^{-5}
E (kJ/mol)	0.01	0.35	0.13
r^2	0.85	0.83	0.97

3.3.5. Removal of NAs

Figure 3.4 shows the distribution of the NAs compounds present in OSPW as a function of the carbon number (n) and the number of the rings ($-Z/2$) before and after treatments with PC, GAC and PAC. The total NAs removals following PC, GAC, and PAC treatment were 75%, 97%, and 95%, respectively. The results of the control samples showed that there was no change in the concentration of the NAs as a result of experimental procedure. The NAs found in OSPW were in the carbon range of 8–22 within 1–6 numbers of rings, indicating that there were no acyclic NAs compounds present. Consistently with previous results [16, 32], monocyclic NAs were the least predominant species among all the Z groups; whereas, bicyclic and tricyclic acids within the carbon range of 12–16 were the most abundant compounds. For the PC (Figure 3.4b), the NAs were predominantly removed in the carbon range of 14–17 (81–100%), 15–20 (86–100%), 15–19 (93–100%), 15–21 (94–100%), and 17–22 (96–100%) for the $-Z$ = 4, 6, 8, 10, and 12 group of compounds, respectively. This implies that the adsorption of NAs onto PC increased with the increase in both n and $-Z$ numbers, with n having greater effect on the adsorption as compared to $-Z$. The NAs removal followed a similar trend for GAC and PAC (Figure 3.4c and d). For the GAC and PAC treatments, the NAs removals exceeded 88% for all individual NAs.

Increase in the molecular mass of NAs renders the compounds less soluble and more hydrophobic, which, in turn, increase their affinity for the adsorption on the surface of the adsorbents [33]. Octanol/water partition coefficient (expressed as log K_{ow}) for the NAs is shown in Figure 3.5 as a function of n and $-Z$. Increasing n within each $-Z$ group of compounds resulted in the increase in the log K_{ow}, which is consistent with the increase in the removal efficiency of the individual NAs by n. This confirms the higher tendency of NAs with the higher number of the carbons to adsorb onto the surface of the adsorbents [34].

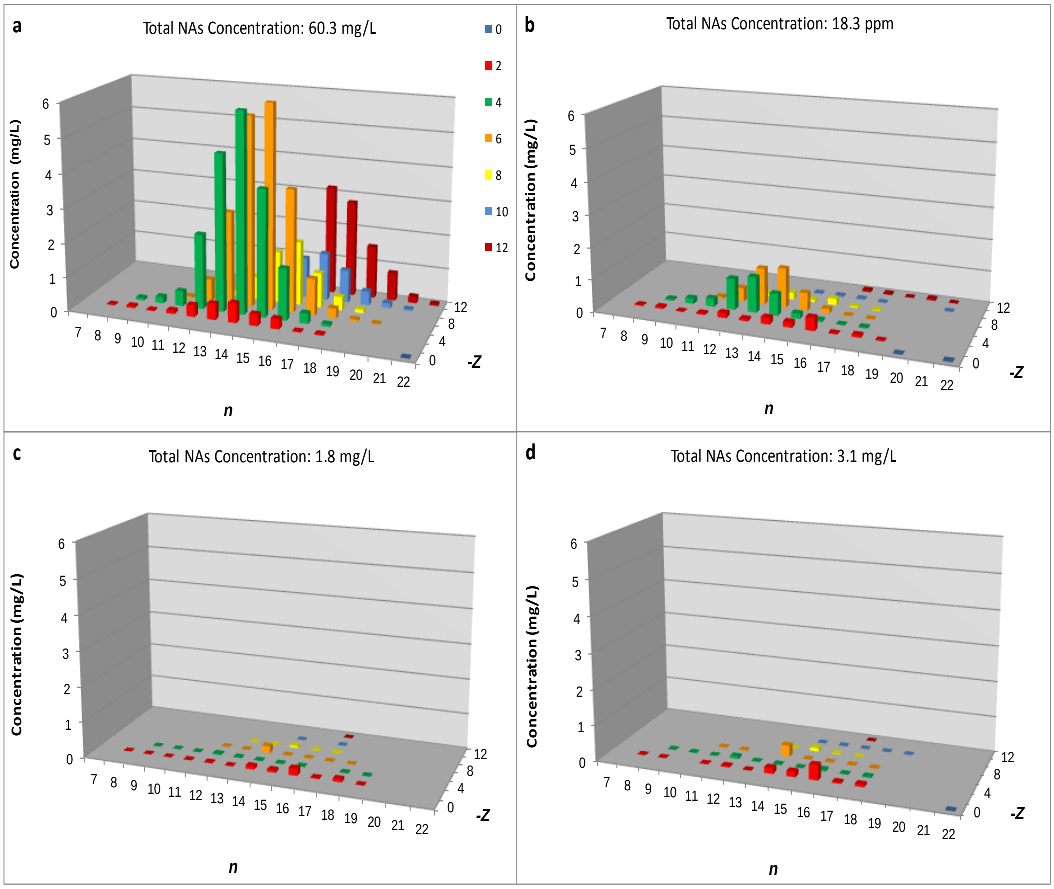

Figure 3.4. Distribution of the NAs compounds for (a) fresh OSPW, (b) OSPW treated with PC at 200 g/L for 16 h, (c) OSPW treated with GAC at 50 g/L for 12 h, and (d) OSPW treated with PAC at 50 g/L for 12 h.

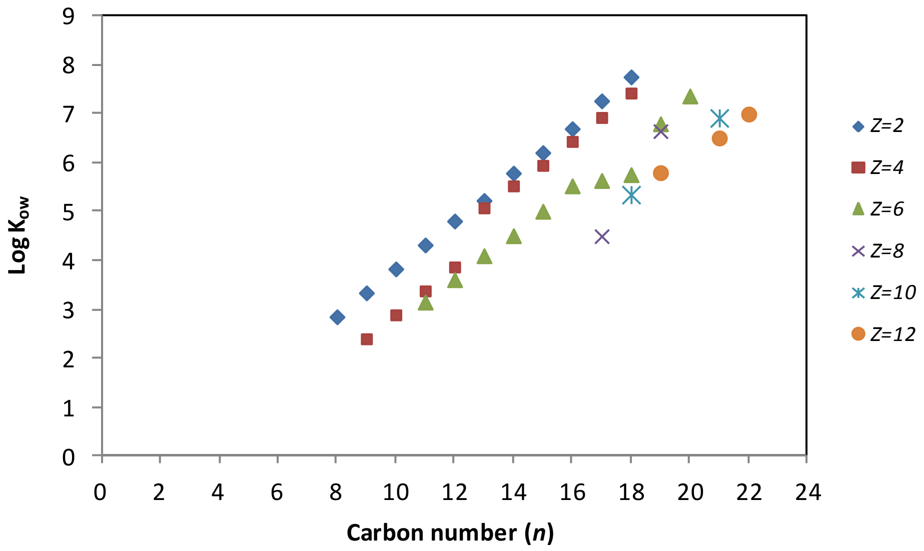

Figure 3.5. Log K_{ow} values for individual NAs as a function of carbon number (*n*) and number of the rings (-*Z/2*). Log K_{ow} values were obtained from ChemSpider chemical database.

3.3.6. Identification of Surface Functional Groups by FT-IR

FT-IR analysis is an important characterization method for the investigation of the changes in the surface properties of the adsorbents [35-37]. The FT-IR absorption spectra of the fresh and saturated PC at 200 g/L and 16 h contact time are shown in Figure 3.6a. The absorption peaks at 1680 cm^{-1}, 1583 cm^{-1}, and 874 cm^{-1} were characteristics of carbonyl stretching vibrations, N–H bending vibration of primary amines, and C-H bending vibrations of benzenes, respectively [35, 38, 39]. The broad absorption band in the region of 3400–2500 cm^{-1} was related to the stretching vibration of O–H groups [38, 40, 41]. The FT-IR spectra of GAC and PAC (Figure 3.6b) also showed the presence of the carbonyl (1682 cm^{-1}), C=C bond of aromatic rings (1477 cm^{-1}), and hydroxyl functional group (2400–2700 cm^{-1}), respectively [38, 40, 41].

Spectra of the fresh and saturated adsorbents showed peaks with similar positions for each identified functional groups, indicating that there was no change in the chemical bonding before and after adsorption. This observation suggests physisorption of organic compounds on the surface of adsorbents [34, 40, 42].

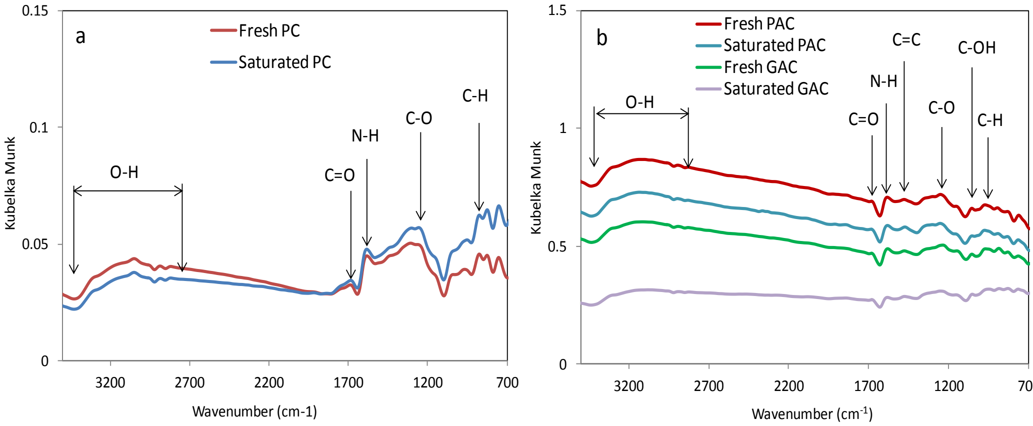

Figure 3.6. FT-IR spectra of the (a) fresh and saturated PC, (b) fresh and saturated GAC and PAC.

3.3.7. XPS Analysis

XPS analysis was performed in order to identify and quantify the functional groups on the surface of the fresh PC, GAC, and PAC. As shown in Table 3.4, carbon comprised the highest atomic concentration (89.08, 89.43, and 93.63% for PC, GAC, and PAC, respectively) in all tested adsorbents. The atomic concentration of oxygen was 6.6, 8.0, and 4.6% for PC, GAC, and PAC, respectively. The N and S contents of the GAC and PAC were lower as compared to those found in PC. The Na, Fe, Ca, Si, Cl, and Al were also detected on the surface of the adsorbent in atomic concentrations of less than 0.5%.

Table 3.4. Elemental composition of fresh PC, GAC, and PAC according to XPS analysis.

Element	Atomic concentration (%)		
	PC	GAC	PAC
C	89.08	89.43	93.63
O	6.63	8.00	4.65
N	1.33	0.03	0.66
S	2.08	0.02	0.14
Ca	0.01	0.23	0.09
Na	0.00	0.00	0.09
Si	0.70	0.37	0.41
Al	0.14	1.11	0.27
Fe	0.03	0.42	0.04
Cl	0.00	0.04	0.00

The results of the peak deconvolution of C_{1s}, O_{1s}, N_{1s}, and S_{2p} could be found in the Appendix B. Peak deconvolution of C_{1s} resulted in three components (Figure B7). The C_{1s} peak with the E_b range of 284.3–284.8 eV was characteristic of graphitic underivatized C–C bonds [39, 43-45]. E_b in the range of 286.0–286.4 eV was attributed to the carbon in C–OH groups [39, 44]. The C_{1s} peak with the E_b range of 287.1–287.9 eV corresponded to the C=O of carbonyl groups [39, 43-45].

Deconvolution of the O_{1s} spectrum showed oxygen peaks with two different E_b (Figure B8). E_b in the range of 531.1–532.2eV was characteristic of carbonyl functional groups [39, 46]. The O_{1s} peak with the E_b in the range of 532.7–533.7eV was attributed to OH groups [46].

Peak deconvolution of N_{1s} (Figure B9a) resulted in two peaks at 398.3 and 399.9 eV, which corresponded to the N–C and N–H functional groups on the surface of the PC, respectively [39]. The S_{2p} peaks with the Eb at 163.7 eV and 164.8 eV were assigned to S^{2-} and S^0, respectively (Figure B9b) [47-49].

The percentage of the oxygen-containing functional groups of PC, GAC, and PAC estimated from the area of the deconvoluted C_{1s} and O_{1s} peaks is shown in Table 3.5. Fraction of hydroxyl functional groups on GAC is higher than that of PC and PAC, which is consistent with the basic surface characteristic of the GAC (pH_{pzc} = 11.9). This may account for the pH increase in the treated OSPW upon its contact with GAC. PC contained higher percentage of carbonyl functional groups as compared to GAC and PAC.

Table 3.5. Concentration of oxygen-containing functional groups as determined by XPS analysis.

Functional group	Oxygen functional groups (%)		
	PC	GAC	PAC
C-OH	1.1	3.2	1.9
C=O	4.4	3.7	2.1

3.3.8. Surface Area Analysis and SEM Images

Surface area is an important factor that affects the adsorption capacity of the adsorbents. BET surface area of PC was calculated as 7.7 m^2/g. The low surface area of PC as compared to 912 and 800 m^2/g for GAC and PAC, respectively, implies that PC has lower porosity as compared to the highly porous structure of the GAC and PAC [37, 50-53]. The pore size distribution curves of PC, GAC, and PAC are shown in Figure 3.7. Size distribution of the pores in PC was in the mesoporous range (2.3–36 nm) with the highest peaks centred at 2.8 and 3.2 nm (Figure 3.7a). No micropores (< 2.0 nm) or macropores (> 50 nm) were detected on the surface of the PC, suggesting that mesopores play a significant role in the adsorption of organic compounds from OSPW. Size distribution of the pores for GAC and PAC (Figure 3.7b and c) was in the range of 0.5–36 nm, with the highest peaks centred in the range of 0.6–1.4 nm among the micropores. SEM images of the PC (Figure 3.8) also showed the spherical non-porous structure of adsorbent; whereas, PAC and GAC showed highly porous structures, which contributed to high surface area and adsorption capacity of these adsorbents.

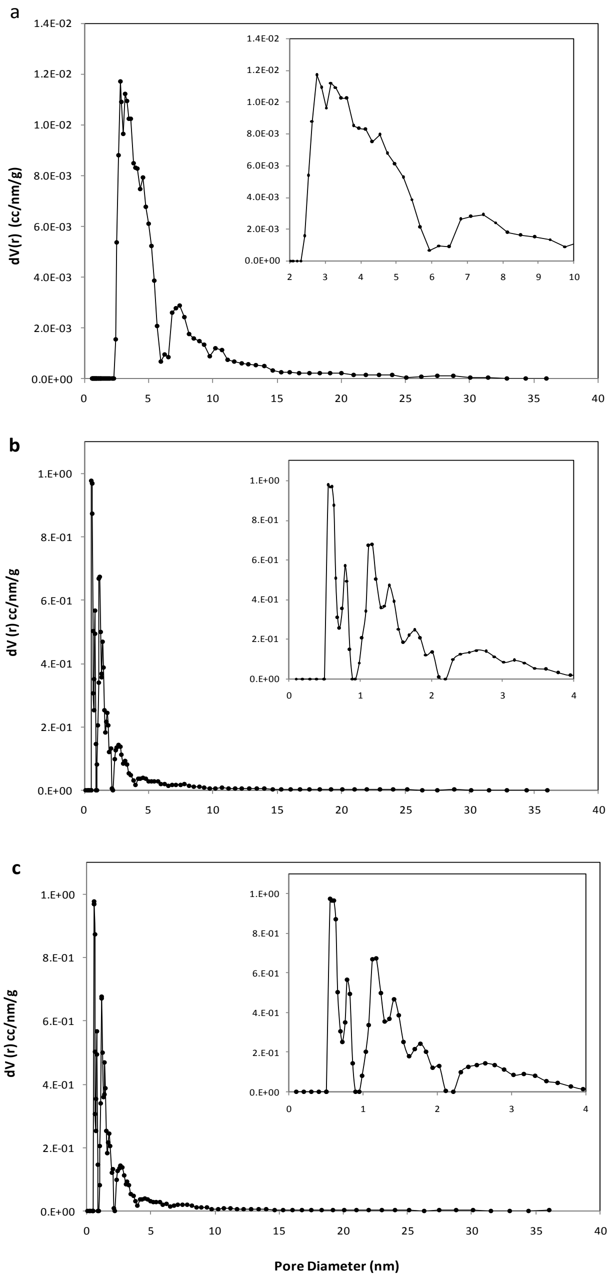

Figure 3.7. Pore size distribution analysis for (a) PC, (b) GAC, and (c) PAC.

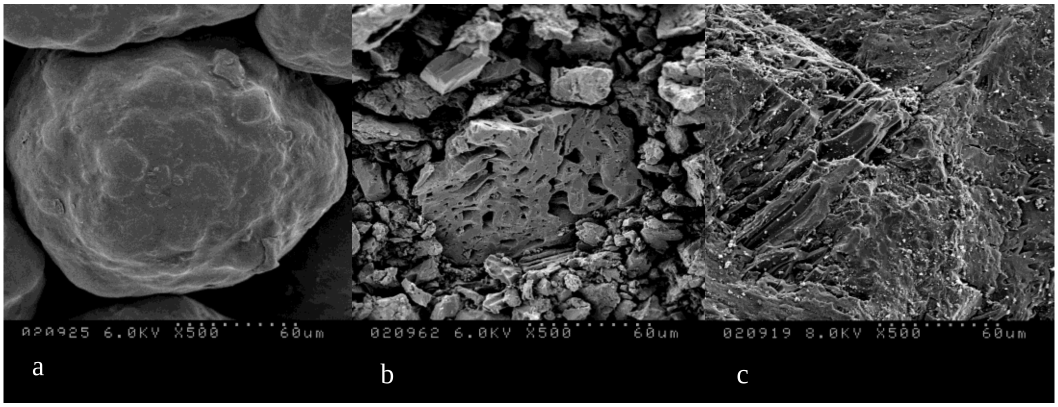

Figure 3.8. SEM images of (a) PC, (b) PAC, and (c) GAC.

3.3.9. Thermal Gravimetric Analysis

TGA analysis was performed on fresh and saturated adsorbents in order to investigate their thermal stability and adsorption mechanism. All TGA curves (Figure 3.9) showed drops at 120 and 400°C, related to the desorption of water and carboxylic acids from the samples [54]. The thermal desorption profile of the samples before and after treatment followed similar trend, suggesting the physisorption of organic compounds on the surface of adsorbents. The PC, GAC and PAC showed higher thermal stability (decomposition temperature of ~1000°C) as compared to other carbonaceous materials such as carbon nanotubes (decomposition temperature of 530°C) [55]. The total weight loss of the adsorbents before the thermal decomposition was 8.4-9.6, 3.0-5.8, and 3.2-3.9% for fresh and saturated PC, GAC and PAC, respectively. The higher weight loss of PC is related to the higher content of the volatile compounds as a result of partial combustion of PC during the coking process [9].

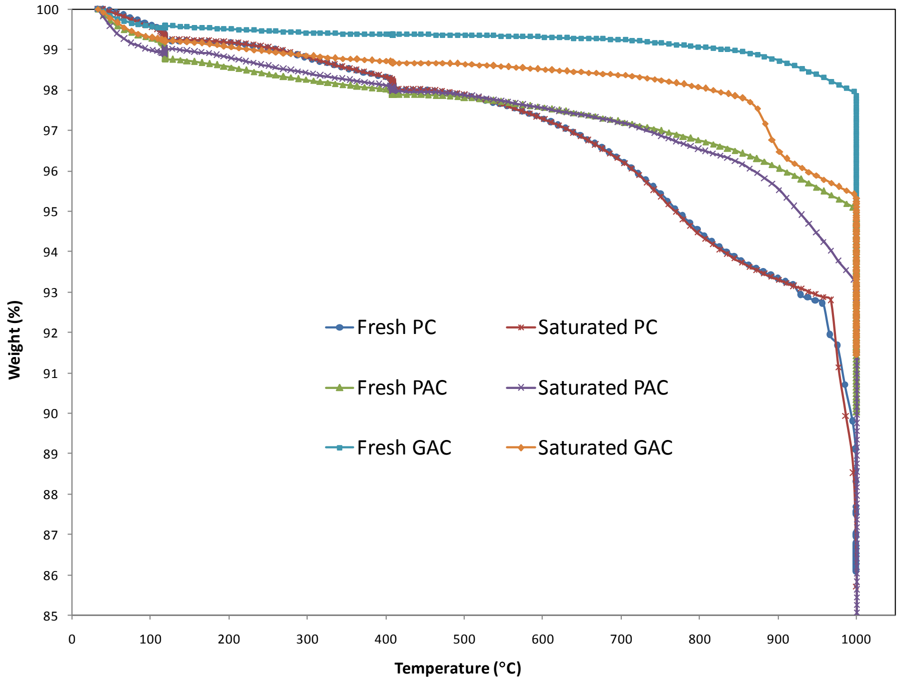

Figure 3.9. TGA analysis of fresh and saturated PC, GAC, and PAC.

3.3.10. Adsorption Mechanism

Organic compounds with high molecular weights and molecular sizes similar to the pore diameters may block the pores and reduce the available adsorption sites [56-61]. However, NAs with low molecular weights (160-500 g/mol) would easily diffuse into the micro and mesopores [30, 61] and there would be no limitation for their diffusion into the pores based on their size.

The pH_{pzc} for the PC was found to be 6.5 ± 0.3 (Figure 3.10a). NAs have a pK_a in the range of 5–6 [62], which implies that over the operating pH of this study (~8.4), they exist in the dissociated form. As a result, the surfaces of the PC and NAs are both negatively charged. Therefore, electrostatic repulsion forces may reduce the adsorption capacity of PC for NAs [63, 64]. On the other hand, the metal ions present in OSPW may neutralize the negative charge of NAs, and thus decrease the repulsion between the NAs and PC [65]. Additionally, based on XPS results, N–H functional groups on the surface of the PC may facilitate formation of hydrogen bonds between the PC and hydroxyl groups of NAs. However, low nitrogen content of the PC suggests that H-bonding does not significantly contribute to the adsorption. NAs with higher molecular weights may contain aromatic rings or double bonds which may increase the adsorption affinity of these compounds through the π-π interactions to the graphite-like surface of the adsorbents [32, 66-68]. Given that NAs are highly hydrophobic compounds, the hydrophobic interactions between the NAs and the surface of PC is suggested as a dominant adsorption mechanism.

At the operating pH of this study, surface of the GAC (pH_{pzc} = 11.9) and PAC (pH_{pzc} = 9.3) (Figure 3.10b and c) are positively charged, which is favourable for the adsorption of NAs through the electrostatic attractive forces [63]. Besides, the high surface area and microporosity of these adsorbents suggests that the adsorption occurred through the micropore filling mechanism. In addition, no change in the peak positions in the FT-IR spectra and desorption profile of the samples in TGA analysis of PC before and after adsorption suggests that the physisorption of the organic compounds mainly depends on the porosity of the adsorbent rather than the surface functionality [40, 42]. This is in accordance with the high adsorption capacity of GAC and PAC and low adsorption capacity of PC.

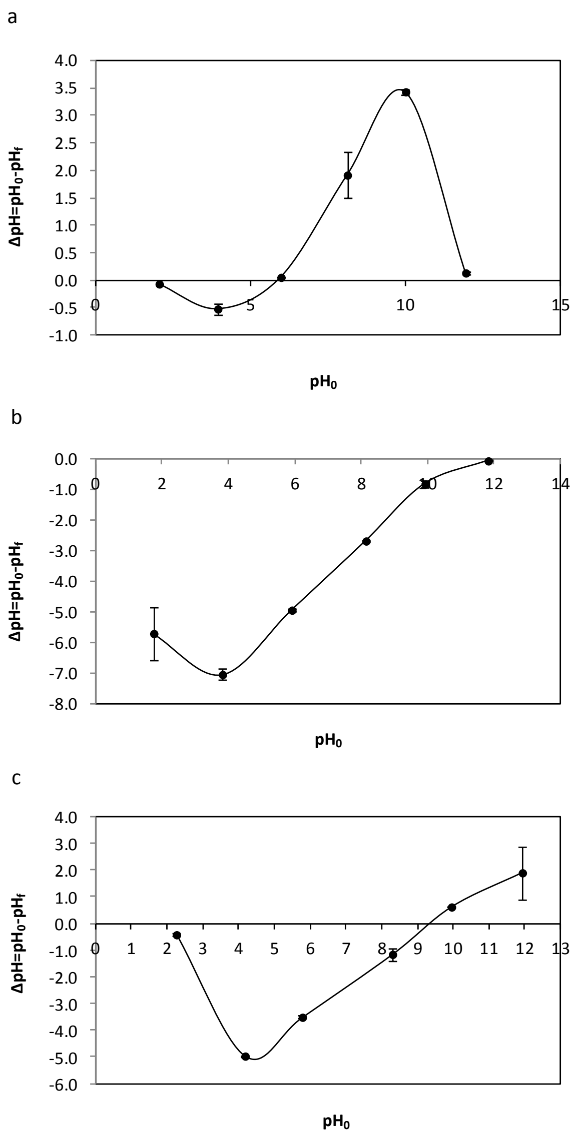

Figure 3.10. Point of zero charge for (a) PC, (b) GAC, and (c) PAC.

3.3.11. Vanadium Leaching

Leaching of vanadium from PC is a complex process, which is expected to depend on water matrix. As shown in Figure 3.11, the amount of vanadium leached from PC increased with the increase in PC concentration from 50 to 400 g/L for both OSPW and Milli-Q water. This is consistent with Galvin et al. [69], who observed the increase in the concentration of a range of metals leached from different recycled aggregates with the increase in the amount of the added material. While studying the leaching of copper, zinc and lead from the cement-based wasted materials, Li et al. [70] showed that metal concentrations increased with increasing solid to liquid ratio, reached equilibrium, and remained constant afterwards. Under the experimental conditions applied in this study, the equilibrium between the solid-phase and liquid-phase vanadium was not achieved, suggesting that more leaching could occur if higher PC concentration is used for the removal of organic compounds from OSPW.

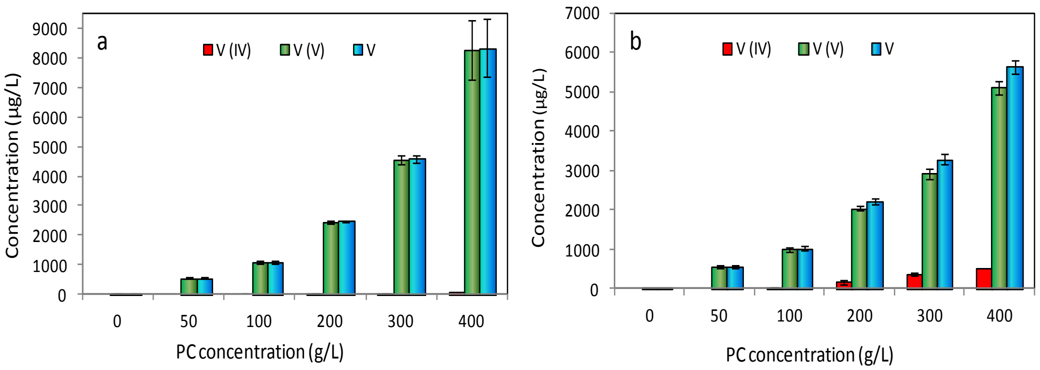

Figure 3.11. Concentration of vanadium (IV), vanadium (V), and vanadium leached from PC into (a) OSPW, and (b) Milli-Q water after 12 h of contact.

Depending on the PC concentration, the percentage of leached vanadium was in the range of 8.7–17.0% and 9.1–11.5% for OSPW and Milli-Q water, respectively (Table 3.6). The leaching of vanadium (V) increases with increasing pH [71]. Puttaswamy and Liber [22] showed that as pH increased, more vanadium leached from PC into hard reconstituted water (688 µg/L at pH 5.5 and 2205 µg/L at pH 9.5 for a PC to water v/v ratio of 1:4). Therefore, the increase in vanadium mobility with the pH increase may account for the higher amount of vanadium leached from OSPW at pH 8.4 ± 0.2 as compared to that leached from Milli-Q water at pH 4.6 ± 0.2. While studying the effect of inorganic anions on vanadium leaching from PC in water which contained sulfur, chloride and bicarbonate ions, Puttaswamy and Liber [20] showed that bicarbonate ions increased the release of vanadium from PC. Since the concentration of bicarbonate ions in OSPW is very high (775–950 mg/L) [5], this may also promote leaching of vanadium from PC upon its contact with OSPW. In addition, the organic fraction of OSPW contains large variety of compounds which could stabilize vanadium in the aqueous phase and increase its equilibrium concentration as compared to Milli-Q water. Although the percentage of the released vanadium did not exceed 20% of the vanadium content present in the typical PC for all studied PC concentrations, its concentrations exceeded the background vanadium concentrations reported for natural waters (0.5 to 300 μg/L) [23, 72] in both OSPW and Milli-Q water.

Table 3.6. Percentage of vanadium leached from PC.

[a]PC, g/L	% of vanadium leached	
	OSPW	Milli-Q water
50	8.7	9.1
100	8.8	8.4
200	10.1	9.1
300	12.5	8.9
400	17.0	11.5

[a]The total vanadium content of PC is 1226 mg/kg PC [9].

The vanadium leached from PC was predominantly vanadium (V) for both OSPW and Milli-Q water, although vanadium (IV) was also detected (Figure 3.11). However, given that vanadium (IV) is unstable at circumneutral pH, it is expected that it would be oxidized into vanadium (V) upon its release into OSPW. Consistently with the vanadium speciation as a function of pH, the fraction of vanadium (IV) was larger in Milli-Q water as compared to OSPW at all studied PC concentrations.

3.4. Conclusions

The results of this study demonstrated that two waste by-products generated by petroleum industry, PC and process-affected water, can be successfully coupled together in the adsorption process in order to remove persistent organic contaminants from liquid stream. This, in turn, could reduce the adverse impacts of the petroleum industry on the environment. A significant advantage of this process is that while the concentration of toxic compounds is reduced, the amount of dry waste does not increase. A huge amount of PC is continuously produced worldwide. Currently, PC is stockpiled in huge quantities on-site of the refinery plants. PC is virtually cheap and its direct application as an adsorbent does not require large investments. The ability of PC to adsorb organic contaminants, in conjunction with the manner petroleum industry produce, transport and store the PC, present a unique opportunity to treat generated process-affected waters for large scale applications. PC also has a potential in commercial wastewater applications provided that the activation process is optimized with respect to increasing surface area and minimizing leaching of trace metals.

3.5. References

1. Watkins, E., PDVSA, Eni initiate heavy oil, refinery projects in Venezuela. *Oil & Gas Journal* 2010, *108,* (46), 41-42.

2. Board, E. R. C., ST98–2009: Alberta’s energy reserves 2008 and supply/demand outlook 2009–2018;. In Alberta, G. o., Ed. Calgary, AB, Canada, 2008; p 220.

3. Gray, M.; Xu, Z. H.; Masliyah, J., Physics in the oil sands of Alberta. *Physics Today* 2009, *62*, (3), 31-35.

4. Majid, A.; L. Kotlyar, B. D. S., Potential applications of oil sands industry wastes. *Journal of Canadian Petroleum Technology* 1999, *38*, (11), 29-33.

5. Allen, E. W., Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. *Journal of Environmental Engineering and Science* 2008, *7*, (2), 123-138.

6. Allen, E. W., Process water treatment in Canada's oil sands industry: II. A review of emerging technologies. *Journal of Environmental Engineering and Science* 2008, *7*, (5), 499-524.

7. Malekshahian, M.; Hill, J. M., Effect of pyrolysis and CO(2) gasification pressure on the surface area and pore size distribution of petroleum coke. *Energy & Fuels* 2011, *25*, (11), 5250-5256.

8. Speight, J. G., The chemistry and physics of coking. *Korean Journal of Chemical Engineering* 1998, *15,* (1), 1-8.

9. Zubot, W. A. Removal of naphthenic acids from oil sands process water using petroleum coke. M.Sc. Dissertation. University of Alberta, Edmonton, Alberta, Canada;, 2010.

10. Board, E. R. C., ST98- 2011: Alberta's Energy Reserves 2010 and Supply/Demand Outlook 2011- 2020. In Alberta, G. o., Ed. Calgary, AB, Canada, 2011; p 74.

11. Parmar, B. S.; Tollefson, E. L., Desulfurization of oil sands coke. *Canadian Journal of Chemical Engineering* 1977, *55*, (2), 185-191.

12. Friedrich, F. D.; Lee, G. K.; Desai, D. L., Fluidized-bed combustion of petroleum coke. *Mechanical Engineering* 1983, *105*, (1), 81-81.

13. Zamora, R. M.; A. Durán Pilotzi; Mora, R. D.; Moreno, A. D., Removal of detergents by activated petroleum coke from a clarified wastewater treated for reuse. *Water Science and Technology* 2004, *50*, (2), 91–98.

14. Zamora, R. M. R.; R Schouwenaars, A. D. M. a. G. B., Production of activated carbon from petroleum coke and its application in water treatment for the removal of metals and phenol. *Water Science & Technology* 2000, *42*, (5-6), 119–126.

15. Yuan, M.; Tong, S.; Zhao, S.; Jia, C. Q., Adsorption of polycyclic aromatic hydrocarbons from water using petroleum coke-derived porous carbon. *Journal of Hazardous Materials* 2010, *181*, (1–3), 1115-1120.

16. Jones, D.; Scarlett, A. G.; E., W. C.; J., R. S., Toxicity of individual naphthenic acids to vibrio fischeri. *Environmental Science & Technolog* 2011, *45*, (22), 9776–9782.

17. Zubot, W.; MacKinnon, M. D.; Chelme-Ayala, P.; Smith, D. W.; El-Din, M. G., Petroleum coke adsorption as a water management option for oil sands process-affected water. *Science of the Total Environment* 2012, *427*, 364-372.

18. El-Din, M. G.; Fu, H. J.; Wang, N.; Chelme-Ayala, P.; Perez-Estrada, L.; Drzewicz, P.; Martin, J. W.; Zubot, W.; Smith, D. W., Naphthenic acids speciation and removal during petroleum-coke adsorption and ozonation of oil

sands process-affected water. *Science of the Total Environment* 2011, *409,* (23), 5119-5125.

19. Small, C. C.; Hashisho, Z.; Ulrich, A. C., Preparation and characterization of activated carbon from oil sands coke. *Fuel* 2012, *92*, (1), 69-76.

20. Puttaswamy, N.; Liber, K., Influence of inorganic anions on metals release from oil sands coke and on toxicity of nickel and vanadium to Ceriodaphnia dubia *Chemosphere* 2012, *86*, (5), 521-529.

21. Puttaswamy, N.; Turcotte, D.; Liber, K., Variation in toxicity response of Ceriodaphnia dubia to Athabasca oil sands coke leachates. *Chemosphere* 2010, *80*, (5), 489-497.

22. Puttaswamy, N.; Liber, K., Identifying the causes of oil sands coke leachate toxicity to aquatic invertebrates. *Environmental Toxicology and Chemistry* 2011, *30*, (11), 2576-2585.

23. Li, X. S.; Glasauer, S.; Le, X. C., Speciation of vanadium in oil sand coke and bacterial culture by high performance liquid chromatography inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* 2009, *648*, (1), 128-128.

24. Greenberg, A. E., *Standard methods for the examination of water and wastewater* 18th ed.; Amercian Public Health Association Washington, DC 1992.

25. Pourrezaei, P.; Drzewicz, P.; Wang, Y. N.; El-Din, M. G.; Perez-Estrada, L. A.; Martin, J. W.; Anderson, J.; Wiseman, S.; Liber, K.; Giesy, J. P., The impact of metallic coagulants on the removal of organic compounds from oil sands process-affected water. *Environmental Science & Technology* 2011, *45*, (19), 8452-8459.

26. Jivraj, M. N.; MacKinnon, M.; Fung, B. Naphthenic acid extraction and quantitative analysis with FT-IR spectroscopy; Syncrude Canada Ltd. Internal Report: Edmonton: Syncrude Canada Ltd., 1996.

27. Khan, M. A.; Lee, S. H.; Kang, S.; Paeng, K. J.; Lee, G.; Oh, S. E.; Jeon, B. H., Adsorption studies for the removal of methyl tert-butyl ether on various commercially available GACs from an aqueous medium. *Separation Science and Technology* 2011, *46*, (7), 1121-1130.

28. Sharma, Y. C.; Uma; Upadhyay, S. N., An economically viable removal of methylene blue by adsorption on activated carbon prepared from rice husk. *Canadian Journal of Chemical Engineering* 2011, *89*, (2), 377-383.

29. Goel, J.; Kadirvelu, K.; Rajagopal, C.; Garg, V. K., Investigation of adsorption of lead, mercury and nickel from aqueous solutions onto carbon aerogel. *Journal of Chemical Technology and Biotechnology* 2005, *80*, (4), 469-476.

30. Yuan, M. J.; Tong, S. T.; Zhao, S. Q.; Jia, C. Q., Adsorption of polycyclic aromatic hydrocarbons from water using petroleum coke-derived porous carbon. *Journal of Hazardous Materials* 2010, *181*, (1-3), 1115-1120.

31. Sharma, D. C.; Forster, C. F., Removal of hexavalent chromium using sphagnum moss peat. *Water Research* 1993, *27*, (7), 1201-1208.

32. Rowland, S. J.; West, C. E.; Jones, D.; Scarlett, A. G.; Frank, R. A.; Hewitt, L. M., Steroidal aromatic 'naphthenic acids' in oil sands process-affected water: structural comparisons with environmental estrogens. *Environmental Science & Technology* 2011, *45*, (22), 9806-9815.

33. Bansal, R. C.; Goyal, M., Activated carbon adsorption. In CRC Press Taylor & Francis Group: Boca Raton, FL, 2005; pp 193-194.

34. Gotovac, S.; Song, L.; Kanoh, H.; Kaneko, K., Assembly structure control of single wall carbon nanotubes with liquid phase naphthalene adsorption. *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 2007, *300*, (1-2), 117-121.

35. Juan, Y.; Ke-Qiang, Q., Preparation of activated carbon by chemical activation under vacuum. *Environmental Science & Technology* 2009, *43*, (9), 3385-3390.

36. Rennert, T.; Kaufhold, S.; Mansfeldt, T., Identification of iron-cyanide complexes in contaminated soils and wastes by Fourier transform infrared spectroscopy. *Environmental Science & Technology* 2007, *41*, (15), 5266-5270.

37. Alhamed, Y. A.; Bamufleh, H. S., Sulfur removal from model diesel fuel using granular activated carbon from dates' stones activated by ZnCl(2). *Fuel* 2009, *88*, (1), 87-94.

38. Pradhan, B. K.; Sandle, N. K., Effect of different oxidizing agent treatments on the surface properties of activated carbons. *Carbon* 1999, *37*, (8), 1323-1332.

39. Shen, W.; Li, Z.; Liu, Y., Surface chemical functional groups modification of porous carbon. *Recent Patents on Chemical Engineering* 2008, *1*, 27-40.

40. Njoku, V. O.; Hameed, B. H., Preparation and characterization of activated carbon from corncob by chemical activation with H(3)PO(4) for 2,4-dichlorophenoxyacetic acid adsorption. *Chemical Engineering Journal* 2011, *173*, (2), 391-399.

41. Jiang, B. C.; Zhang, Y. C.; Zhou, J. X.; Zhang, K.; Chen, S. Y., Effects of chemical modification of petroleum cokes on the properties of the resulting activated carbon. *Fuel* 2008, *87*, (10-11), 1844-1848.

42. Leng, C. C.; Pinto, N. G., Effects of surface properties of activated carbons on adsorption on behavior of selected aromatics. *Carbon* 1997, *35*, (9), 1375-1385.

43. Clark, D. T.; Thomas, H. R., Applications of esca to polymer chemistry .17. Systematic investigation of core levels of simple homopolymers. *Journal of Polymer Science Part a-Polymer Chemistry* 1978, *16*, (4), 791-820.

44. Rey, A.; Zazo, J. A.; Casas, J. A.; Bahamonde, A.; Rodriguez, J. J., Influence of the structural and surface characteristics of activated carbon on the catalytic decomposition of hydrogen peroxide. *Applied Catalysis a-General* 2011, *402*, (1-2), 146-155.

45. Zaror, C.; Soto, G.; Valdes, H.; Mansilla, H., Ozonation of 1,2-dihydroxybenzene in the presence of activated carbon. *Water Science and Technology* 2001, *44*, (5), 125-130.

46. Briggs, D.; Beamson, G., XPS studies of the oxygen-1s and oxygen-2s levels in a wide-range of functional polymers. *Analytical Chemistry* 1993, *65*, (11), 1517-1523.

47. Cai, J. H.; Morris, E.; Jia, C. Q., Sulfur speciation in fluid coke and its activation products using K-edge X-ray absorption near edge structure spectroscopy. *Journal of Sulfur Chemistry* 2009, *30*, (6), 555-569.

48. Thomas, J. M.; Adams, I.; Williams, R. H.; Barber, M., Valence band structures and core-electron energy levels in the monochalcogenides of gallium. Photoelectron spectroscopic study. *Journal of the Chemical Society, Faraday Transactions 2* 1972, *68*, 755-764.

49. Zhao, S. Q.; Sparks, B. D.; Kotlyar, L. S.; Chung, K. H., Reactivity of sulphur species in bitumen pitch and residua during fluid coking and hydrocracking. *Petroleum Science and Technology* 2002, *20*, (9-10), 1071-1085.

50. Lu, Q. L.; Sorial, G. A., The role of adsorbent pore size distribution in multicomponent adsorption on activated carbon. *Carbon* 2004, *42*, (15), 3133-3142.

51. Carter, E. M.; Katz, L. E.; Speitel, G. E.; Ramirez, D., Gas-phase formaldehyde adsorption isotherm studies on activated carbon: correlations of adsorption capacity to surface functional group density. *Environmental Science & Technology* 2011, *45*, (15), 6498-6503.

52. Ahn, S.; Werner, D.; Karapanagioti, H. K.; McGlothlin, D. R.; Zare, R. N.; Luthy, R. G., Phenanthrene and pyrene sorption and intraparticle diffusion in polyoxymethylene, coke, and activated carbon. *Environmental Science & Technology* 2005, *39*, (17), 6516-6526.

53. Ding, L.; Snoeyink, V. L.; Marinas, B. J.; Yue, Z. R.; Economy, J., Effects of powdered activated carbon pore size distribution on the competitive adsorption of aqueous atrazine and natural organic matter. *Environmental Science & Technology* 2008, *42*, (4), 1227-1231.

54. Terzyk, A. P., Adsorption of biologically active compounds from aqueous solutions on to commercial unmodified activated carbons. Part V. The mechanism of the physical and chemical adsorption of phenol. *Adsorption Science & Technology* 2003, *21*, (6), 539-585.

55. Salam, M. A.; Makki, M. S. I.; Abdelaal, M. Y. A., Preparation and characterization of multi-walled carbon nanotubes/chitosan nanocomposite and its application for the removal of heavy metals from aqueous solution. *Journal of Alloys and Compounds* 2011, *509*, (5), 2582-2587.

56. de Ridder, D. J.; Verliefde, A. R. D.; Heijman, S. G. J.; Verberk, J.; Rietveld, L. C.; van der Aa, L. T. J.; Amy, G. L.; van Dijk, J. C., Influence of natural organic matter on equilibrium adsorption of neutral and charged pharmaceuticals onto activated carbon. *Water Science and Technology* 2011, *63*, (3), 416-423.

57. Newcombe, G.; Drikas, M., Adsorption of NOM onto activated carbon: Electrostatic and non-electrostatic effects. *Carbon* 1997, *35*, (9), 1239-1250.

58. Kilduff, J. E.; Karanfil, T.; Weber, W. J., Competitive effects of nondisplaceable organic compounds on trichloroethylene uptake by activated carbon. II. Model verification and applicability to natural organic matter. *Journal of Colloid and Interface Science* 1998, *205*, (2), 280-289.

59. Pelekani, C.; Snoeyink, V. L., Competitive adsorption in natural water: Role of activated carbon pore size. *Water Research* 1999, *33*, (5), 1209-1219.

60. Matsui, Y.; Knappe, D. R. U.; Takagi, R., Pesticide adsorption by granular activated carbon adsorbers. 1. Effect of natural organic matter preloading on removal rates and model simplification. *Environmental Science & Technology* 2002, *36*, (15), 3426-3431.

61. Moore, B. C.; Wang, Y. J.; Cannon, F. S.; Metz, D. H.; Westrick, J., Relationships between adsorption mechanisms and pore structure for adsorption of natural organic matter by virgin and reactivated granular activated carbons during water treatment. *Environmental Engineering Science* 2010, *27*, (2), 187-198.

62. Perez-Estrada, L. A.; Han, X. M.; Drzewicz, P.; El-Din, M. G.; Fedorak, P. M.; Martin, J. W., Structure-reactivity of naphthenic acids in the ozonation process. *Environmental Science & Technology* 2011, *45*, (17), 7431-7437.

63. Ayranci, E.; Hoda, N.; Bayram, E., Adsorption of benzoic acid onto high specific area activated carbon cloth. *Journal of Colloid and Interface Science* 2005, *284*, (1), 83-88.

64. Faria, P. C. C.; Orfao, J. J. M.; Pereira, M. F. R., Activated carbon catalytic ozonation of oxamic and oxalic acids. *Applied Catalysis B-Environmental* 2008, *79*, (3), 237-243.

65. Pan, B.; Xing, B., Adsorption mechanisms of organic chemicals on carbon nanotubes. *Environmental Science & Technology* 2008, *42*, (24), 9005-9013.

66. Kavanagh, R. J.; Burnison, B. K.; Frank, R. A.; Solomon, K. R.; Van Der Kraak, G., Detecting oil sands process-affected waters in the Alberta oil sands region using synchronous fluorescence spectroscopy. *Chemosphere* 2009, *76*, (1), 120-126.

67. Lin, D. H.; Xing, B. S., Adsorption of phenolic compounds by carbon nanotubes: Role of aromaticity and substitution of hydroxyl groups. *Environmental Science & Technology* 2008, *42*, (19), 7254-7259.

68. Zhu, D. Q.; Pignatello, J. J., Characterization of aromatic compound sorptive interactions with black carbon (charcoal) assisted by graphite as a model. *Environmental Science & Technology* 2005, *39*, (7), 2033-2041.

69. Galvin, A. P.; Ayuso, J.; Jimenez, J. R.; Agrela, F., Comparison of batch leaching tests and influence of pH on the release of metals from construction and demolition wastes. *Waste Management* 2012, *32*, (1), 88-95.

70. Li, X. D.; Poon, C. S.; Sun, H.; Lo, I. M. C.; Kirk, D. W., Heavy metal speciation and leaching behaviors in cement based solidified/stabilized waste materials. *Journal of Hazardous Materials* 2001, *82*, (3), 215-230.

71. Wehrli, B.; Stumm, W., Vanadyl in natural waters - adsorption and hydrolysis promore oxygenation. *Geochimica Et Cosmochimica Acta* 1989, *53*, (1), 69-77.

72. Crans, D. C.; Amin, S. S.; Keramidas, A. D., *Chemistry of Relevance to Vanadium in the Environment, in Vanadium in The Environment. Part 1: Chemistry and Biochemistry*. John Wiley & Sons: 1998; p 73-95.

CHAPTER 4. REMOVAL OF THE ORGANIC COMPOUNDS FROM OIL SANDS PROCESS-AFFECTED WATER USING ZERO VALENT IRON ENHANCED BY PETROLEUM COKE[1]

4.1. Introduction

The Athabasca oil sands in Alberta, Canada, contain one of the largest oil deposits in the world [1]. During the oil refining process in the petroleum industry, a large amount of waste by-products, including process-affected water and petroleum coke (PC), are generated [1-4]. In Alberta, generated oil sands process-affected water (OSPW) and PC are accumulated on site until suitable treatment technologies are advanced [5]. As a result, storage of these waste by-products has caused environmental problems for the oil sand industry [1].

OSPW, generated during the Clark hot water extraction of bitumen, contains high concentrations of inorganic salts and refractory organic compounds, mainly naphthenic acids (NAs) [1, 3]. Presence of these contaminants makes OSPW corrosive and toxic to a variety of aquatic biota and mammals [6-12]. Slow degradation rate of NAs in OSPW necessitates the development of new advanced methods to accelerate their decomposition and removal [13, 14]. On the other hand, PC cannot serve as an efficient source of energy for the heat generation due to its high sulphur content and low combustible volatiles [15, 16]. In turn, PC, which has shown promising results for the removal of contaminants from OSPW, could be used as an abundant and free of charge adsorbent for OSPW treatment [17, 18]. PC at 300 g/L has shown to remove 60% of dissolved organic carbon, 77% of extractable organic fraction (EOF), and 94% of the NAs from OSPW [17, 18]. However, it has been found that metal ions (e.g., vanadium, molybdenum, and nickel), accumulated in PC during the coking process, could be

---

[1] A version of this chapter has been submitted for publication. Pourrezaei et al. *Environmental Science and Technology* (December 2012).

released into the liquid phase upon contact between PC and water. As such, the release of these metals from PC, which increased the toxicity of treated OSPW [19-25], might be a limiting factor for its application as an adsorbent, which necessitates further research.

Zero valent iron (ZVI) has been shown to be a cost effective and an environmentally friendly reducing agent [26-30]. Recently, the application of ZVI and iron based alloys has drawn significant attention for the remediation of wastewater and ground water [31-45]. Implementation of the iron walls for the ground water remediation was the first successful use of this technology [31, 36, 43, 45]. ZVI has been successfully used for the removal of the refractory organic compounds [46], halogenated compounds [41, 47, 48], nitroaromatics [49, 50], nitramines [51], azo dyes [52, 53], nitrate [54], metals [30, 55, 56], and radionuclides [57, 58].

Although the actual removal mechanisms of the organic compounds by ZVI are a matter of debate [26, 59, 60], depending on water characteristics, possible removal mechanisms in the ZVI/water system include direct or indirect reduction, adsorption, co-precipitation, and oxidation of organic compounds in the presence of oxygen [26, 27, 31, 34, 36, 52, 60-64]. Most of the studies have investigated the reduction of the organic pollutants in the presence of ZVI and there are only few studies investigating the oxidation of organic contaminants and their removal mechanisms [26]. Benzoic acid was shown to be oxidized to p-hydroxy benzoic acid with the use of nano-particle ZVI in the presence of oxygen [65]. Phenol was also shown to be oxidized by the hydroxyl radicals formed as a result of ZVI oxidation in the presence of oxygen [26]. Depending on the pH of water and oxygen availability, ZVI is quickly oxidized to Fe^{2+} and Fe^{3+} and forms various forms of iron oxy (hydroxides) (FeO, $FeO(OH)$, and Fe_2O_3) [31, 61, 66]. Surface corrosion of ZVI in the presence of oxygen was also suggested to produce Fe^{2+} and H_2O_2, with the subsequent reactions of these two reagents in a Fenton-type process to generate highly reactive hydroxyl radicals [27, 67].

The carbonaceous materials such as PC have been known to possess electron conducting characteristics, which enable them to act as both electron conductor and adsorption sites [68-70]. The reduction of 2,4-dinitrotoluene by ZVI [45] and hydrolysis of lindane and 1,1,2,2-tetrachloroethane [71, 72] were reported to significantly increase in the presence of graphite and activated carbon. The oxidation of terephthalic acid, which is a dicarboxylic acid, was shown to be effectively enhanced in the presence of phosphotungstic acid as an electron conductor [44].

In the present study, we investigated the hypothesis that PC could be applied as an electron conductor to provide a simultaneous adsorption and oxidation sites to enhance the removal of the organic compounds from OSPW using ZVI as a source of electrons. The application of ZVI in combination with PC has not been reported previously and it is the first time this process has been studied with respect to removal of organic pollutants from OSPW. The objectives of the present study were to investigate the impact of the contact time and ZVI loading on the removal of organic compounds from OSPW; to understand the potential role of PC in the improvement of the organic compounds removal; and to determine the removal mechanisms of the organic compounds. To achieve these, ZVI alone and in combination with PC was mixed with OSPW at different contact times and concentrations. The effect of OSPW oxygen content on the removal of the organic compounds was also investigated. The change in the concentration of the organic compounds before and after treatments was analyzed and the removal mechanisms were investigated.

4.2. Materials and Methods

4.2.1. Sampling

OSPW was collected from the active west in-pit (WIP) tailings pond at Syncrude Canada Ltd., Alberta, Canada. Two batches of OSPW, received in January 2011 and September 2012, were used for the experiments. OSPW was stored at 4°C and brought to the room temperature (20-23°C) before conducting the experiments. Typical OSPW characteristics are shown in Table 4.1.

Table 4.1. Characterization of the as-received OSPW.

Parameter	Value
pH	8.5 ± 0.5
EOF (mg/L)	61.0 ± 2.0
NAs (mg/L)	26.2 ± 3.6
Oxidized NAs (mg/L)	12.6 ± 1.5
COD (mg/L)	204.0 ± 10.0
TOC (mg/L)	39.5 ± 4.0
Alkalinity (mg/L as $CaCO_3$)	650.0 ± 20.0

4.2.2. Adsorbents

PC, produced during fluid coking process in Syncrude Canada Ltd., was used as an adsorbent. Two different batches of PC, received in January 2010 and June 2011, were used to conduct the experiments. High-purity ZVI powder (<100 mesh, >99%) was purchased from Fisher Scientific (Ottawa, ON, Canada). The ZVI was used as-received without any pretreatment.

4.2.3. Adsorption/Oxidation Experiments

The batch adsorption/oxidation experiments were aimed at investigating the impact of the ZVI alone (ZVI), PC alone (PC), and combination of the PC and ZVI (CZVI) on the removal of organic compounds (fluorophore organic compounds, EOF, and NAs) and metals from OSPW. The first set of experiments was aimed at evaluating the effect of the contact time on the overall adsorption/oxidation of the flurophore organic compounds and metals from OSPW. Before conducting the experiments, 2.5 g of ZVI alone, 25 g of PC alone, or ZVI+PC were transferred to the 250 mL conical flasks. A 100 mL of OSPW was added to each flask. Control samples contained OSPW without any PC or ZVI. The flasks were left open to the atmosphere and shaken vigorously at 270 rpm using an orbital shaker (New Brunswick Scientific, Enfield, CT, USA), to maintain required oxygen supply. After pre-determined contact times (4, 8, 16, 32, 56, 80, 104 and 208 h), the samples were centrifuged (Eppendorf, Ontario, Canada) at 10,000 rpm for 5 min to settle the ZVI and/or PC. Supernatants were withdrawn from the vials and analyzed for any changes in the concentration of the fluorophore organic compounds. The supernatant was then filtered using 0.45 µm Nylon filters (SUPELCO, Bellefonte, PA, USA) and analyzed for metals content. Each adsorption experiment was run in duplicates.

After finding the required contact time for the adsorption/oxidation, the effect of ZVI concentration on the removal of the organic compounds and metals was investigated. The experiments were conducted in the same way as described above except that the ZVI concentrations of 1.25, 2.5, and 5 g in 100 mL of OSPW were used to result in the 12.5 g/L, 25 g/L, and 50 g/L of ZVI. The mass of PC was 25 g in CZVI samples. Fluorophore organic compounds, EOF, NAs, metals, and toxicity to *Vibrio fisheri* bacteria were analyzed for these samples.

Another set of experiments was performed to investigate the effect of the dissolved oxygen on the removal/oxidation of the fluorophore organic compounds, EOF, and NAs. The OSPW was purged with pure nitrogen until the oxygen level reached 0.51±0.05 mg/L. ZVI at 25 g/L was used to perform the experiments at 56 h of contact time in stoppered Winkler bottles. The headspace of the flasks was purged with nitrogen and sealed before conducting the experiments. The two-tailed t-test at 95% confidence interval was used to determine if the difference in water quality characteristics before and after treatments was statistically significant.

4.2.4. Equipment

An ultra performance liquid chromatograph (UPLC, Waters, MA, USA) with a Phenyl BEH column (150×1 mm, 1.7 µm) (Waters, Milford, MA, USA) was used for the chromatographic separation and analysis of NAs before and after treatments. The chromatographic conditions were the same as those described by Perez-Estrada *et al.* [73]. A Fourier transform infrared (FT-IR) instrument (PerkinElmer Spectrum, 100 FT-IR Spectrometer, Waltham, USA) was used to measure the EOF concentrations in OSPW according to the method described by Jivraj et al. [74]. The fluorophore organic compounds in OSPW were analyzed using Fluorescence Spectrophotometer (Varian Cary Eclipse, Ontario, Canada). A model 500 Microtox® analyzer (Strategic Diagnostic Inc., Delaware, USA) was used to measure the light emitted by the *Vibrio fischeri* bacteria as a result of their normal metabolic processes for the toxicity of the samples before and after treatments as described in Appendix A [75-77]. The X-ray photoelectron spectroscopy (XPS) was performed using an AXIS 165 spectrometer (Kratos Analytical, Manchester, UK). An Elan 6000 ICP Mass Spectrometer (PerkinElmer, MA, USA) was used to quantify the concentration of the trace metals. Ultrapure water (18 MΩ cm), prepared by a Synergy® UV instrument (Millipore, Molsheim, France), was used in the entire set of experiments. The detailed methodology for these analyses could be found in Appendix A.

4.3. Results and Discussion

4.3.1. Effect of the Contact Time on SFS

The synchronous fluorescence spectroscopy (SFS) analysis of OSPW samples showed a number of peaks at 270-274 nm, 308-310 nm, 324-326 nm, and 406-415 nm. The position of each peak is pointed by arrows in Figure 4.1 to Figure 4.4. To simplify the further discussion, these peaks are herein called as (I), (II), (III), and (IV), respectively. The peaks (I), and [(II), (III)] represent one and two member ring compounds, respectively, and peak (IV) was related to above four member rings in the structure of the aromatic acids compounds [2, 79]. OSPW control samples (Figure 4.1) showed the highest intensity of the peaks followed by ZVI, PC, and CZVI treatments, respectively, indicating the highest removal of the related compounds by CZVI treatment. There was no change in the intensity of the peaks (I), (II), and (III) for OSPW control samples except the peak (IV), for which intensity decreased with time. One possible explanation for the observed trend is that these compounds could be removed from OSPW due to their higher hydrophobicity. For PC (Figure 4.2), the removal of compounds in groups (II) and (III) was higher than that of (I). The observed effect is consistent with the previous work on the removal of NAs by PC, where greater removal was achieved for NAs with higher molecular weights due to their higher hydrophobicity [78]. The decrease in the intensity of peak (IV) followed the same trend as OSPW control with the complete removal at >100 h contact time. The compounds related to these peaks were removed completely by ZVI and CZVI at all the contact times (Figure 4.3 and Figure 4.4). The removal of compounds corresponded to peak (I) using PC was less than that of ZVI; whereas, the removal of the compounds in groups (II) and (III) were higher as compared to ZVI. The compounds in group (I) are more soluble; therefore they have less affinity to be adsorbed on the PC than compounds in groups (II) and (III).

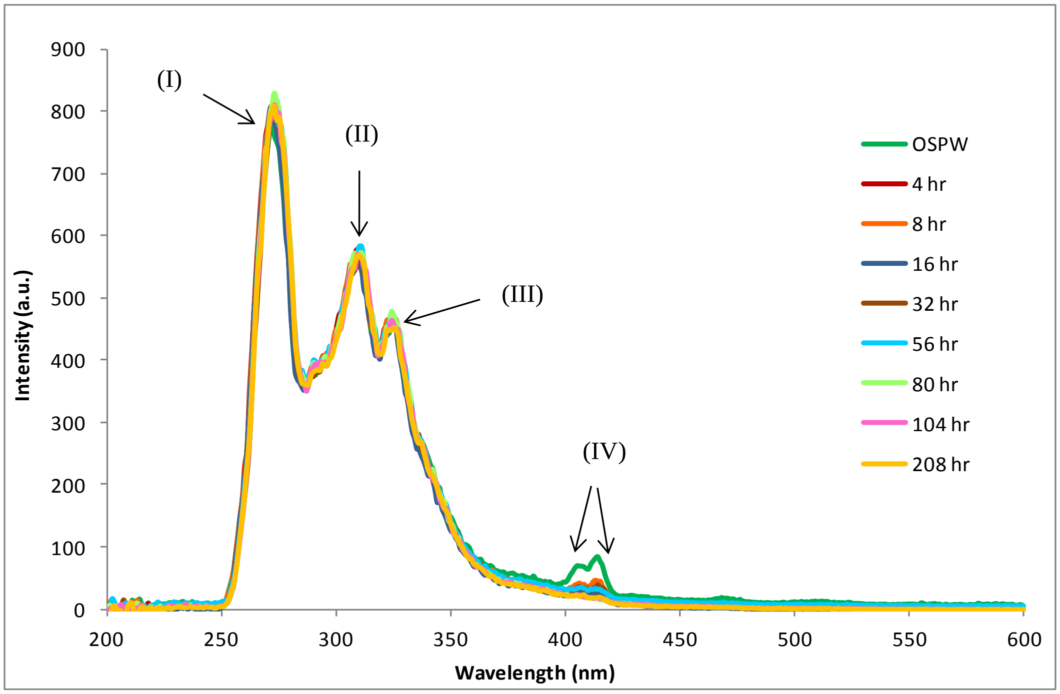

Figure 4.1. SFS spectra of OSPW control as a function of contact time.

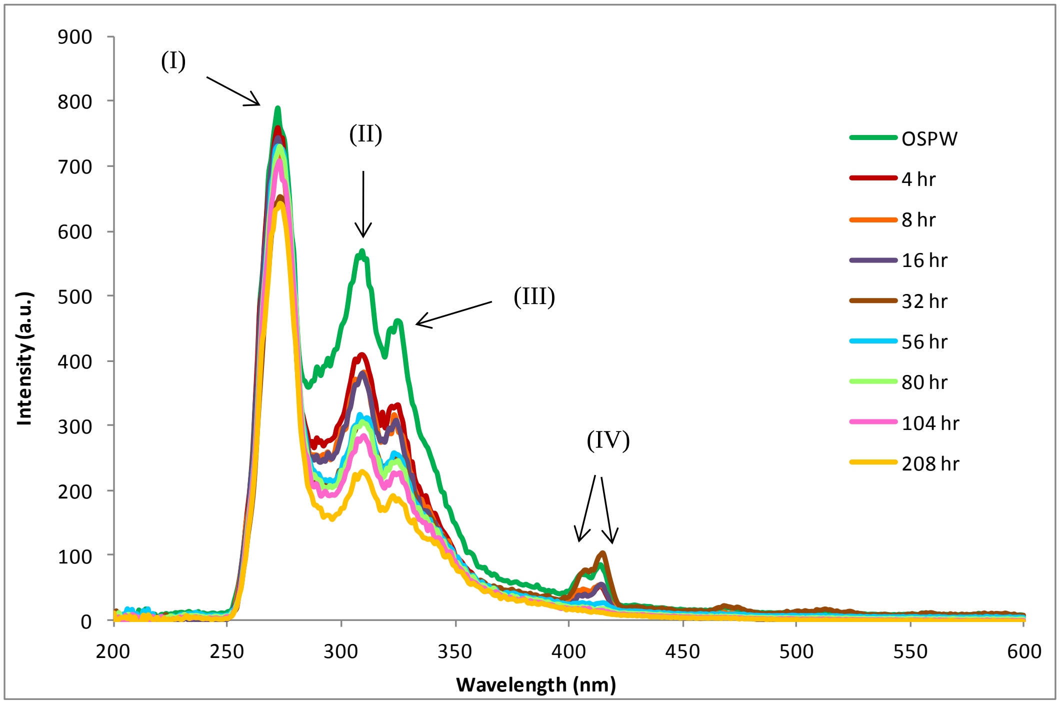

Figure 4.2. SFS spectra of PC-treated OSPW at 200 g/L as a function of contact time.

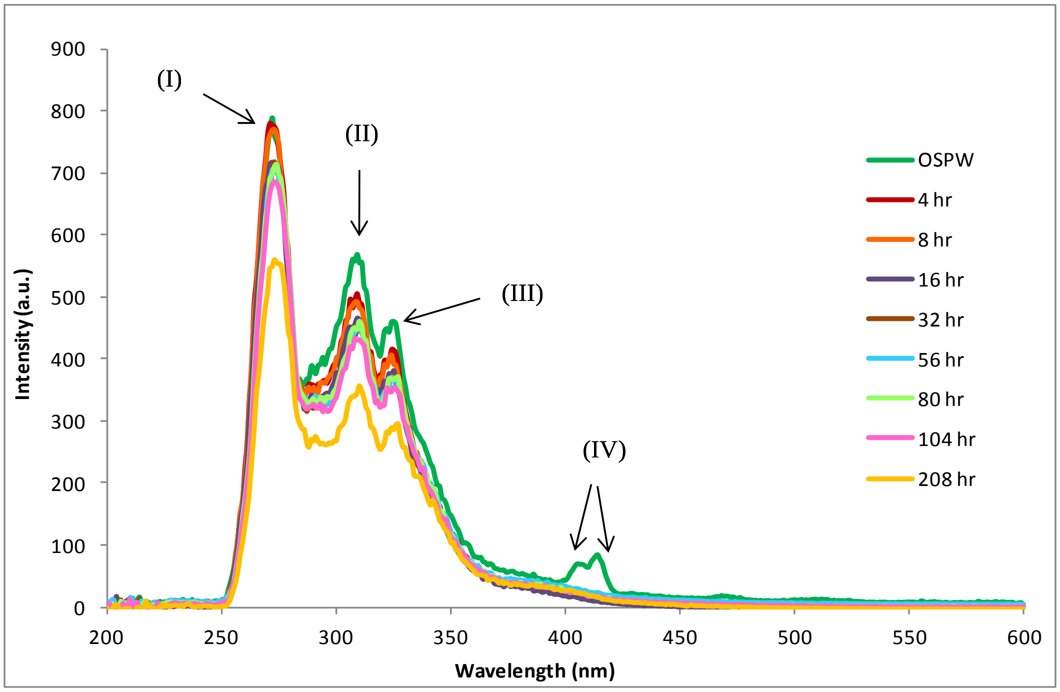

Figure 4.3. SFS spectra of ZVI-treated OSPW at 25 g/L as a function of contact time.

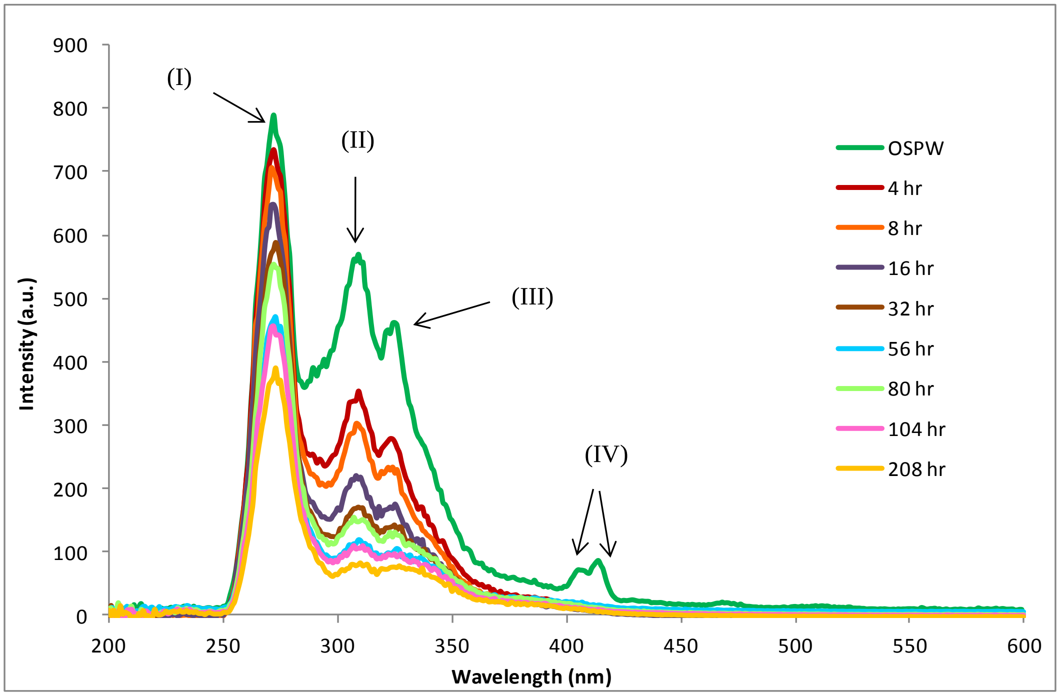

Figure 4.4. SFS spectra of CZVI-treated OSPW at 25 g/L as a function of contact time.

Removal of compounds corresponded to peaks (I), (II), and (III) using ZVI alone after 208 h contact time indicated the oxidative/adsorptive ability of ZVI. The ability of ZVI to reduce concentration of organic compounds was also reported by other studies [44, 65]. The intensities of the peaks (I), (II), and (III) were plotted versus the contact time for the OSPW control, PC, ZVI, and CZVI treated OSPW samples. As shown in Figure 4.5, the reaction proceeded faster during the initial hours of experiments using CZVI treatment up to 56 h followed by a slower rate. The reduction in the peaks intensity exhibited biphasic kinetics with a rapid removal of the compounds in the first 56 h followed by a slower removal. Rasheed et al. [80] also showed that the degradation of the organic compounds from a wastewater using nanoscale ZVI followed a similar trend during the reaction time. Based on this observation, 56 h contact time was chosen for further experiments. Upon addition of ZVI to the samples, they turned orange due to oxidation of iron. The lower removal rate may indicate the presence and build up of the oxide products on the surface of ZVI [65], resulting in the lower available reactive surfaces. Vigorous mixing and the presence of the PC in CZVI samples may facilitate the removal of the oxide products from the ZVI surface resulting in an increase in the number of sites available for reaction. The XPS spectroscopy (Figure B10) revealed a peak at 724.3 eV indicating the presence of the FeO(OH) on the surface of ZVI [81]. This is consistent with previous studies [64, 66], which also reported formation of FeO(OH) on the surface of ZVI during the degradation of azo-dyes and pharmaceuticals at pH>5.

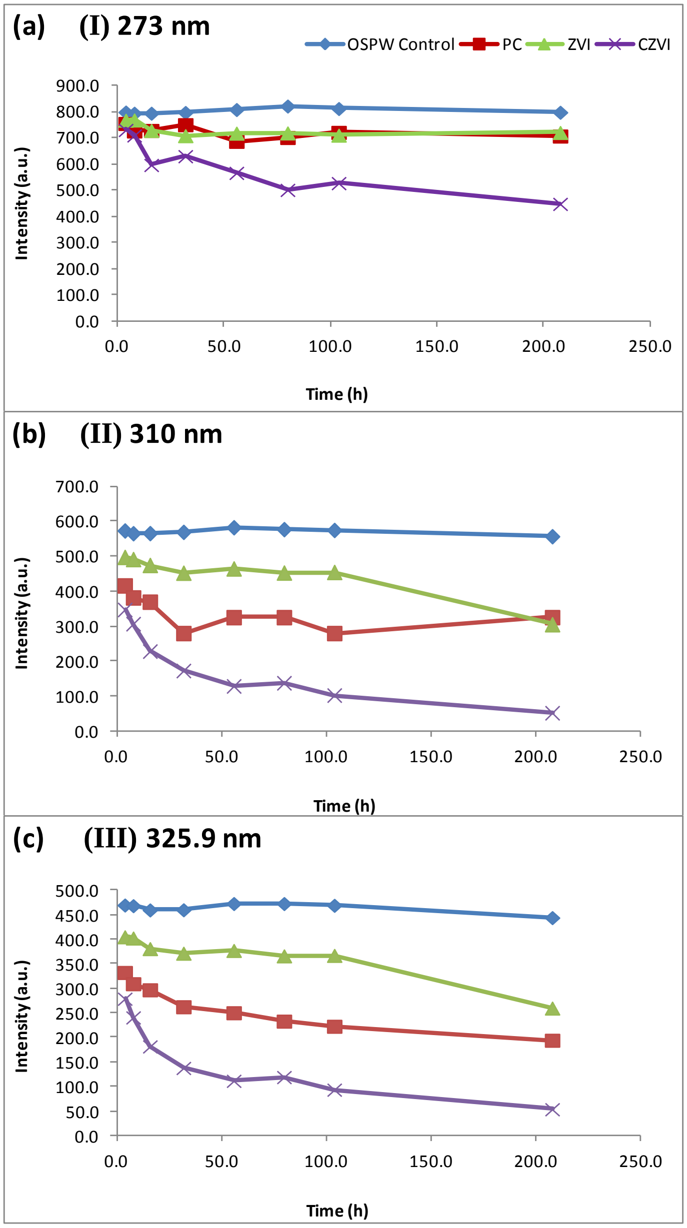

Figure 4.5. The effect of the contact time on the intensity of the peaks of fluorophore organic compounds in untreated and treated OSPW at (a) (I) 273 nm, (b) (II) 310 nm, and (c) (III) 325.9 nm. The concentration of ZVI and PC were 25 g/L and 200 g/L, respectively.

4.3.2. Effect of the Contact Time on Metals Removal

As Figure 4.6 show, V, Mn, Ni, and Mo were released from the PC upon contact with OSPW. The concentration of released V increased with increasing contact time, while no significant changes in the concentration of Mn, Ni, and Mo were observed. When ZVI was added to OSPW, concentration of V, Mn, Ni, and Mo decreased below their original concentration in OSPW in both ZVI and CZVI treated OSPW samples. After 208 h, the reduction in ZVI and CZVI treatments was 24±6% and 87±2%, 81±25% and 98±1%, 76±1% and 78±3%, 96±0% and 93±8% for V, Mn, Ni, and Mo, respectively. As ICP-MS results indicated, no leaching from PC was observed for As, Cd, Co, Sb, Sr, and U (Figure 4.7). The concentration of these elements also decreased during ZVI and CZVI treatments below their concentration in untreated OSPW. The removal of the As, Cr, and Zn from ground water using ZVI was also reported by several studies [55, 82-84]. The authors attributed the observed effect to the adsorption of the metals onto the iron hydroxides and co-precipitation. The results of this study indicate that although addition of PC resulted in the release of some toxic metals into aqueous phase, its consequences could be successfully eliminated by ZVI addition.

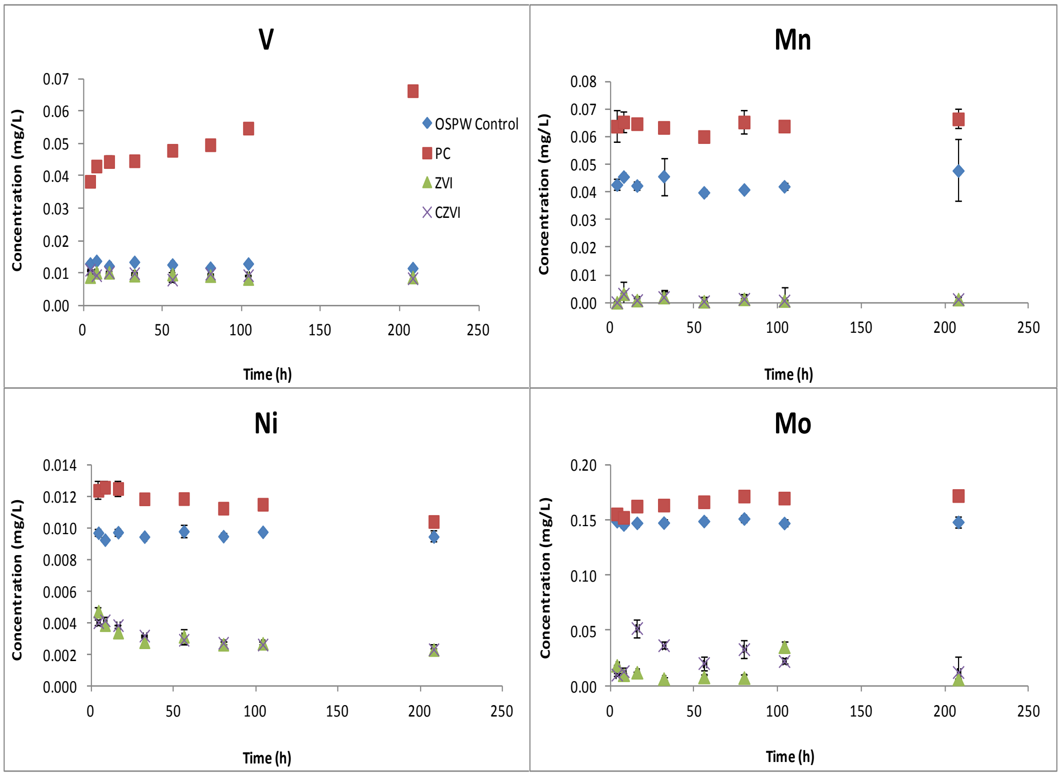

Figure 4.6. The effect of the contact time on the concentration of metals leached from PC into PC, ZVI, and CZVI-treated OSPW. The concentration of ZVI was 25g/L.

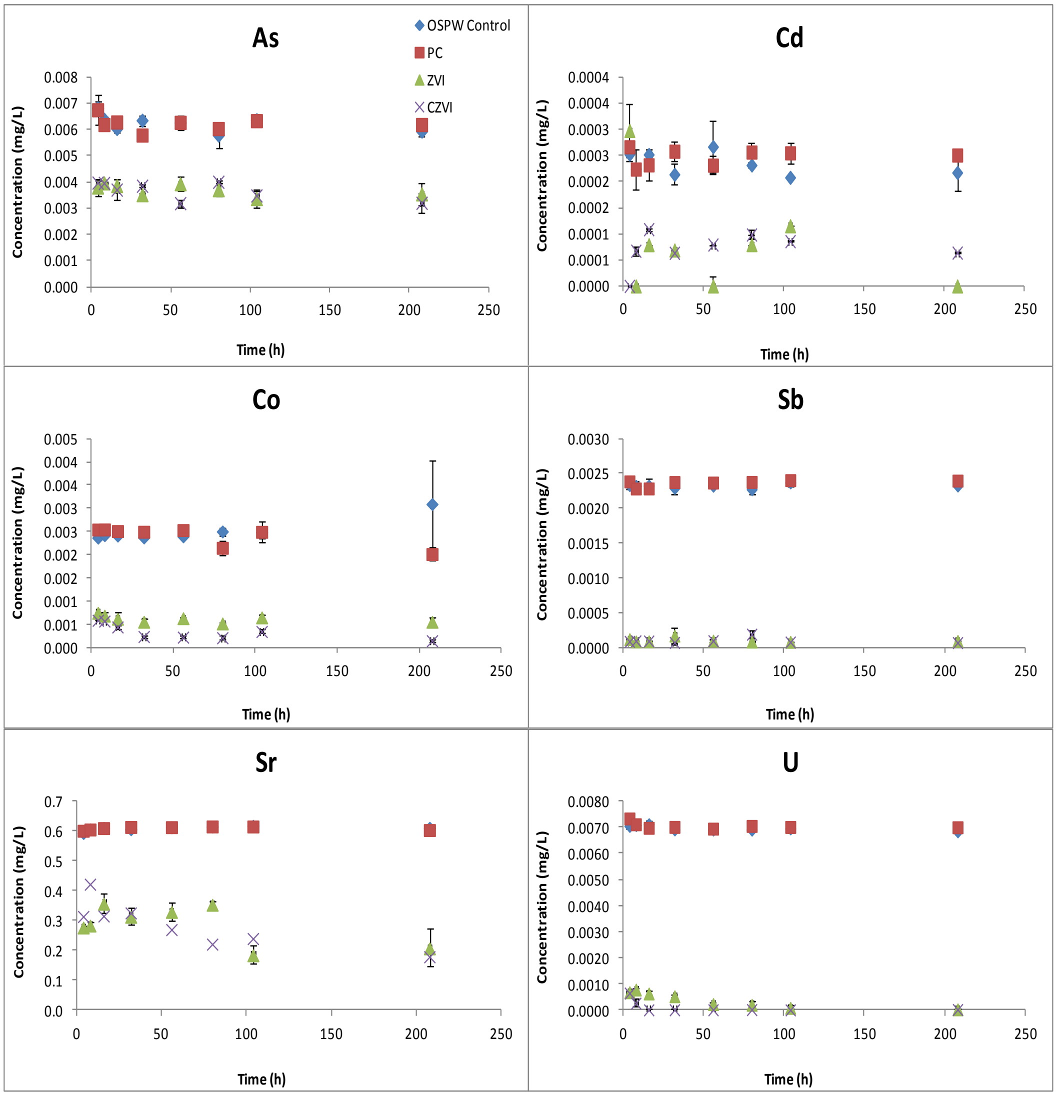

Figure 4.7. The effect of the contact time on the concentration of the metals in OSPW control, PC, ZVI, and CZVI-treated OSPW. The concentration of ZVI was 25g/L.

4.3.3. Effect of ZVI Concentration on SFS, EOF, NAs, and Metal Removal

Figure 4.8 shows the effect of the ZVI concentration on the SFS spectra. Intensity of peaks (I), (II), and (III) decreased with increasing ZVI concentration in both ZVI and CZVI treated OSPW. Larger decrease in the intensity of the peaks was observed at 50 g ZVI/L in ZVI and CZVI treated OSPW samples. In addition, CZVI treatment resulted in the lower peak intensity as compared to samples containing ZVI for all three ZVI concentrations. The reduction in the intensity of the peaks (II) and (III) was higher than that of peak (I) for both 12.5 g/L and 25 g/L ZVI in both ZVI and CZVI treated OSPW, showing higher removal of the compounds with two rings. However, this phenomenon was not observed at 50 g/L ZVI. The observed peaks with the higher intensity in the region of 380-406 nm at 50 g/L of ZVI could be due to the shift in the positions of the peaks caused by the presence of high concentration of hydroxides or the formation of unknown by-products.

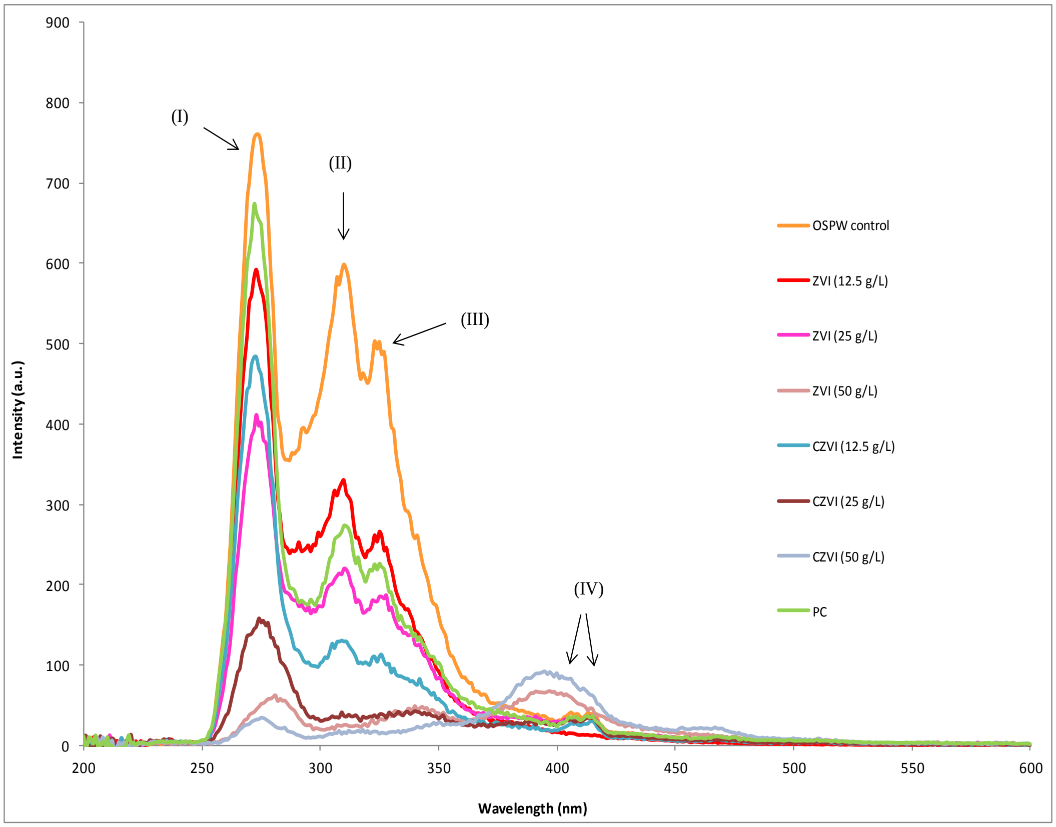

Figure 4.8. The effect of the ZVI concentration on the SFS spectra for ZVI, CZVI, and PC-treated OSPW at 56 h contact time.

The results of the EOF and NAs removal for the ZVI and CZVI treated OSPW with increasing the ZVI concentrations are shown in Table 4.2. The difference between the addition of 12.5 g/L and 25 g/L ZVI to OSPW was not statistically significant at 95% confidence interval in the ZVI treated OSPW samples; whereas, addition of 50 g/L ZVI resulted in significant increase in the EOF removal. In the CZVI treated OSPW samples, the increase in ZVI concentration from 12.5 g/L to 25 g/L resulted in more than twice increase in the removal of EOF (from 34.9% to 74.4%). When ZVI concentration was further increased to 50 g/L, it did not results in a significant improvement in EOF removal efficiency (*p*=0.04). The observed trend is consistent with the results on the removal of fluorophore organic compounds by CZVI treatment. Kavanagh et al. [79] observed a linear correlation between the concentration of fluorophore organic compounds and EOF in OSPW. The authors suggested that the aromatic acids, with similar chemical properties to NAs could co-isolate with NAs and be accounted in the SFS analysis as contaminants. This may explain the similarities in the removal of fluorophore organic compounds, NAs, and EOF compounds.

Table 4.2. EOF and NAs removal of the treated OSPW samples with increasing the ZVI concentration at 56 h contact time.

Treatment type	EOF Removal (%)	NAs Removal (%)
ZVI (12.5 g/L)	22.6 ± 3.1	37.7 ± 6.0
ZVI (25 g/L)	28.8 ± 2.2	58.4 ± 0.9
ZVI (50 g/L)	68.9 ± 5.9	97.7 ± 0.4
CZVI(12.5 g/L)	34.9 ± 0.2	62.1 ± 5.5
CZVI (25 g/L)	74.4 ± 0.8	90.9 ± 0.5
CZVI (50 g/L)	83.4 ± 6.2	98.9 ± 0.0
PC (200 g/L)	13.9 ± 0.0	16.3 ± 8.8

Figure 4.9 and Figure 4.10 show the effect of the ZVI concentration on metals removal. For all applied ZVI concentrations, the removal of the leached V, Mn, Ni, and Mo from PC was 97.7±0.08%, 98.2±1.2%, 93.4±6.2%, and 97.6±1.6%, respectively (Figure 4.9). The removal of As, Cd, Co, Sb, Se, and Sr was 69.0±1.7%, 100.0±0.0%, 91.1±6.3%, 96.2±2.7%, 62.6±3.2%, and 98.8±0.5%, respectively (Figure 4.10). The removal of the metals in ZVI treated OSPW samples was similar to the CZVI treated OSPW samples. Although increasing the ZVI concentration did not enhance the metal removal; their concentration effectively decreased at all ZVI concentrations. In addition, there was no significant change in the concentrations of the metals between the ZVI and CZVI treatments.

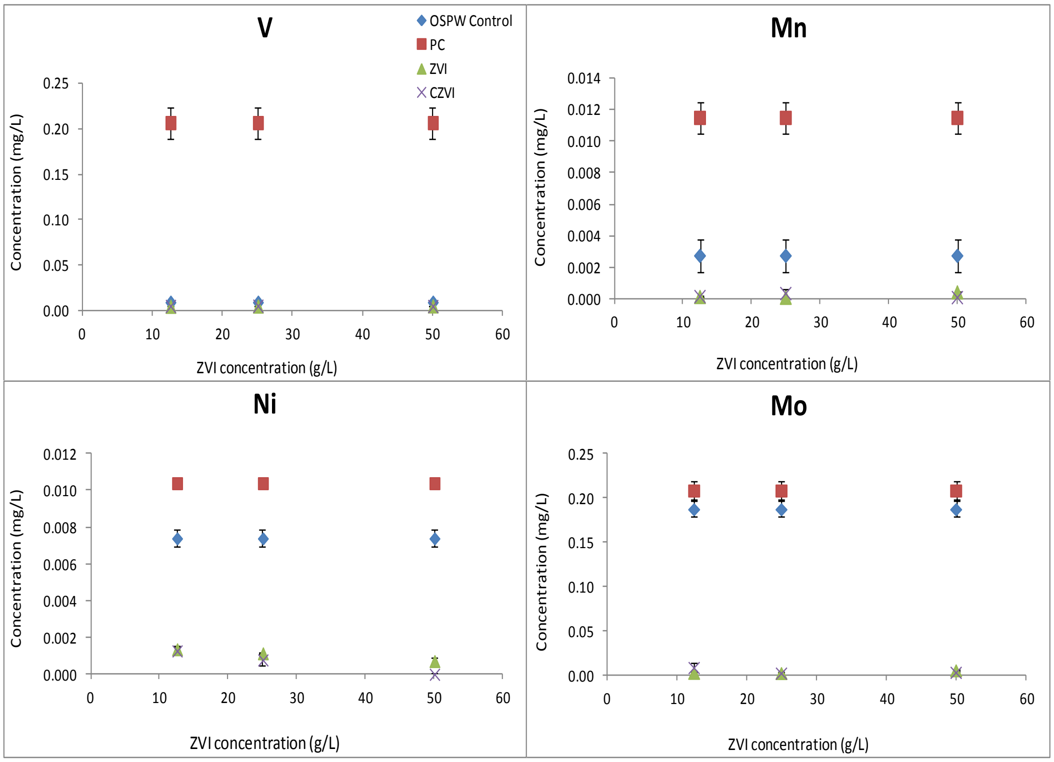

Figure 4.9. The effect of the ZVI concentration on the concentration of the leached metals from PC into PC, ZVI, and CZVI-treated OSPW.

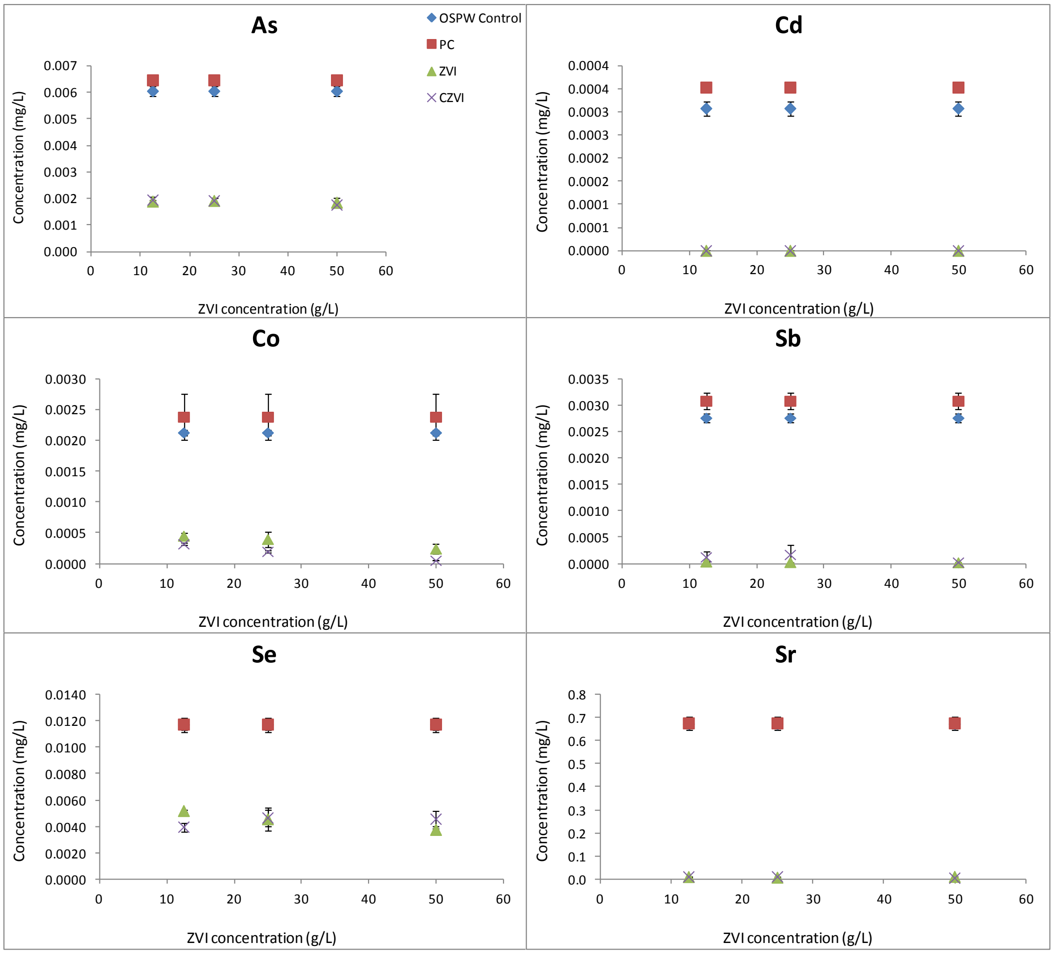

Figure 4.10. The effect of the ZVI concentration on the concentration of the metals in PC, ZVI, and CZVI-treated OSPW.

4.3.4. Toxicity to *Vibrio fischeri*

Microtox® bioassay, used in this study to evaluate the toxicity of the treated OSPW, is an accepted toxicity test by Environment Canada for the measurement and control the release of the harmful substances to aquatic biota. Figure 4.11 shows the effect of the ZVI concentration on the toxicity of the samples to *Vibrio fischeri* bacteria using Microtox® bioassay. The untreated OSPW was found to be toxic to the luminescent bacteria with 58.9±1% inhibition. All the treated OSPW with ZVI, CZVI, and PC showed lower inhibition effects as compared to the untreated OSPW. The inhibition decreased to less than 10% by the addition of the ZVI to PC, as compared to the ZVI alone and PC treated OSPW samples. This shows the synergistic effect of the ZVI and PC on the decrease in the toxicity of the treated OSPW. Due to the small change in the concentration of the metals between the ZVI and CZVI treated samples, the decrease in the toxicity could be related to the higher removal of the organic compounds by the addition of the ZVI into PC samples. The inhibition concentration (IC) of OSPW and ZVI at 25 g/L after 15 min of exposure was also calculated. The IC_{20} and IC_{50} for OSPW were found to be 27.8±1% (v v^{-1}) and 69.5±3% (v v^{-1}), respectively. For ZVI, the IC_{20} and IC_{50} were found to be 51.2±3% (v v^{-1}) and >100% (v v^{-1}), respectively, showing the reduction in the toxicity of the OSPW after ZVI treatment.

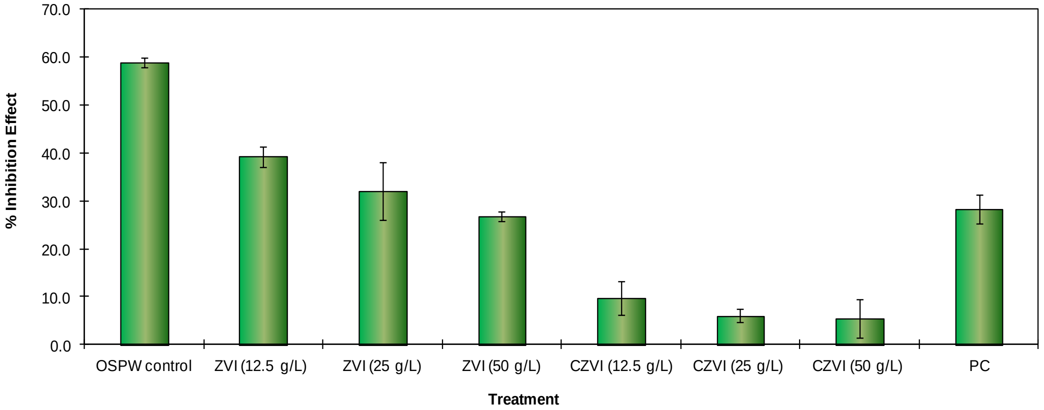

Figure 4.11. Effect of the ZVI concentration on the toxicity of untreated and treated OSPW to *Vibrio fischeri* bacteria.

4.3.5. NAs Removal

The distribution of the NAs species present in OSPW before and after treatments with ZVI, PC, and CZVI (at 25 g ZVI/L) is shown in Figure 4.12 as a function of the carbon number (*n*) and cyclicity (-*Z*). The removal of the total NAs was 58.4% in ZVI treated OSPW sample; whereas, 90.1% removal was achieved in CZVI treated OSPW sample. In ZVI treatment (Figure 4.12b), the removal of the NA species were in the range of 35-100% (-*Z*=2, n=10-16), 39-

100% (-*Z*=4, *n*=10-18), 25-67% (-*Z*=6, *n*=11-18), 21-100% (-*Z*=8, *n*=13-19), 51-100% (-*Z*=10, *n*=15-20), and 57-67% (-*Z*=12, *n*=17-21), respectively. The removals of the individual NAs species were higher in CZVI treatment (Figure 4.12c) as compared to ZVI treatment. NAs removal in CZVI treated OSPW were in the range of 84-100% (-*Z*=2, *n*=10-16), 50-100% (-*Z*=4, *n*=10-18), 41-100% (-*Z*=6, *n*=11-18), 35-100% (-*Z*=8, *n*=13-19), 82-100% (-*Z*=10, *n*=15-20), and 94-100% (-*Z*=12, *n*=17-21). The concentration of the individual NA species before and after treatment is shown in Appendix C (Tables C1 to C4). The removal of the NA species increased with the increase in *n* for each -*Z* group of compounds due to increase in their hydrophobicity [14, 78]. This, in turn, enhances the adsorption of NAs on the surface of ZVI/PC, and facilitates their further oxidation. Concentration of the total oxidized NAs increased by 34% after treatment using ZVI due to the oxidation of NAs by ZVI. As opposite, the concentration of the oxidized NAs decreased by 44% as compared to untreated OSPW upon addition of PC in CZVI treated OSPW sample. There was no general trend observed for the change in the concentration of the oxidized NA species in ZVI and CZVI treatments with respect to *n* and -*Z* (Table C6 and C7 in Appendix C). However, increase in the concentration of the oxidized NAs with two (-*Z*=4) and three (-*Z*=6) rings was slightly higher than the other species. The previous studies showed that concentration of NAs with two or three rings was generally higher as compared to other species [7, 14, 85]. Therefore, it can be expected that oxidized NAs would also contain higher number of these species.

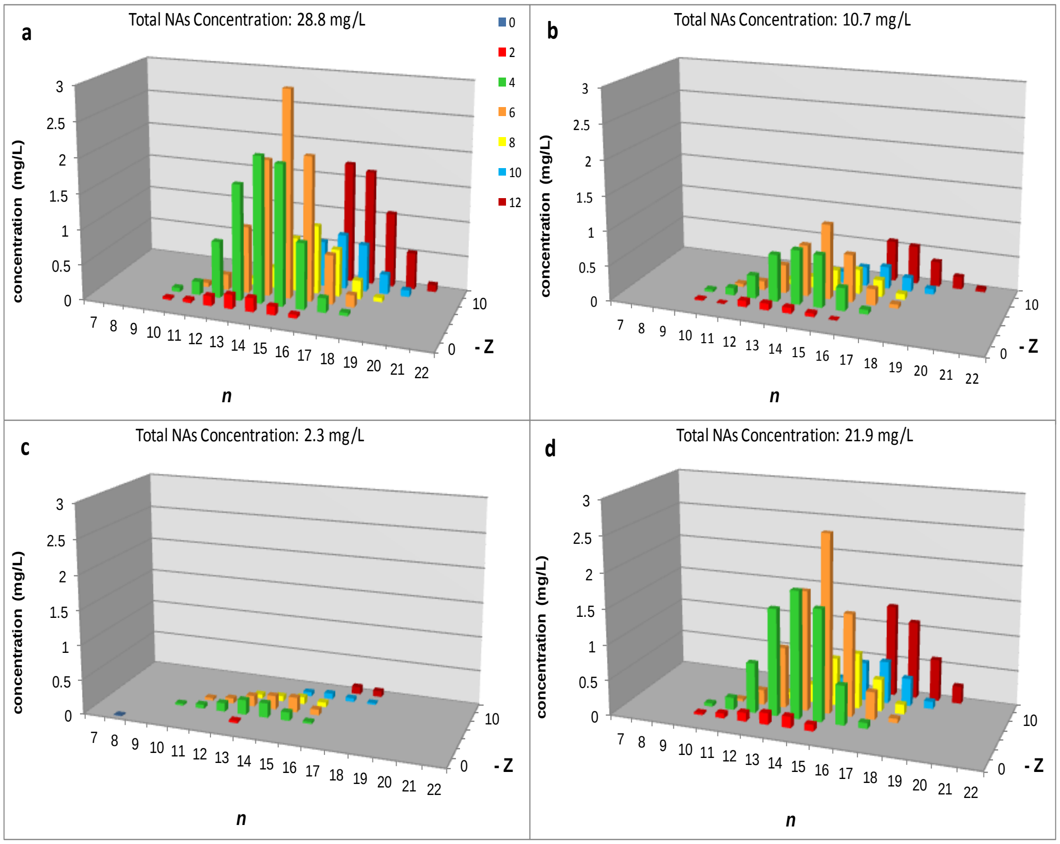

Figure 4.12. Changes in the distribution of the NAs species for (a) OSPW control, (b) OSPW treated with ZVI at 25 g/L, (c) OSPW treated with CZVI at 25 g/L of ZVI, and (d) OSPW treated with PC at 200 g/L. The contact time was 56 h.

4.3.6. The Effect of Oxygen on NAs and EOF Removal

NAs and EOF removals in ZVI and CZVI treated OSPW for the de-oxygenated OSPW are shown in Table 4.3. When the OSPW was de-oxygenated to 0.51 mg O_2/L, the efficiency of EOF removal significantly decreased to 3.1 and 23.2% in ZVI and CZVI treated OSPW samples, respectively. In the OSPW with the oxygen level of 7.8±0.2 mg/L, EOF removal was 28.8 and 74.4% for ZVI and CZVI treatments, respectively. Figure 4.13 shows the effect of the de-oxygenation on the SFS spectra of the treated samples. Similar to EOF, the dissolved oxygen in samples had a strong effect on the efficiency of the removal of fluophore organic compounds from OSPW during the applied treatments. At the same applied treatment, the intensity of the peaks corresponded to de-oxygenated samples was higher as compared to non-oxygenated samples. Lower NAs removals of 17.5% and 65.4% were also obtained for ZVI and CZVI treated-OSPW in de-oxygenated samples (Table 4.3).

The removal of the NA species did not change with the increase in *n* and -*Z* for ZVI treatment (Table C9 in Appendix C); whereas, in CZVI treatment, increasing the *n* resulted in the increase in the removal of NA species in each -*Z* group (Table C10 in Appendix C). These results clearly indicated that oxygen enhanced the removal of organic compounds likely because of the formation of the hydroxyl radicals [82]. According to Joo et al. [62], the removal of molinate using nanoscale ZVI in the absence of oxygen was negligible; whereas, 70% removal was achieved in the aerated or vigorously shaken samples. The turbulence created by aeration or shaking can facilitate the continuous removal of the passivating layer on the ZVI, resulting in the more effective electron transfer from ZVI to the contaminants/oxygen. In addition, vigorous mixing may facilitate the oxygen uptake and increase the oxygen transfer to the ZVI surface for the formation of hydroxyl radicals. As Table 4.3 shows, there was no increase in oxidized NAs concentration in de-oxygenated samples indicating that the NAs did not oxidize when the sample was purged.

Table 4.3. EOF, NAs, and oxidized NAs removal in de-oxygenated samples at 56 h contact time.

Treatment type	EOF Removal (%)	NAs Removal (%)	Oxidized NAs Removal (%)
ZVI (25 g/L) (de-oxygenated)	3.1 ± 1.5	17.5 ± 0.4	16.3 ± 0.8
CZVI (25 g/L) (de-oxygenated)	23.2 ± 4.5	65.4 ± 4.5	40.8 ± 0.8
PC (200 g/L) (de-oxygenated)	16.1 ± 1.0	64.7 ± 4.7	58.0 ± 3.3

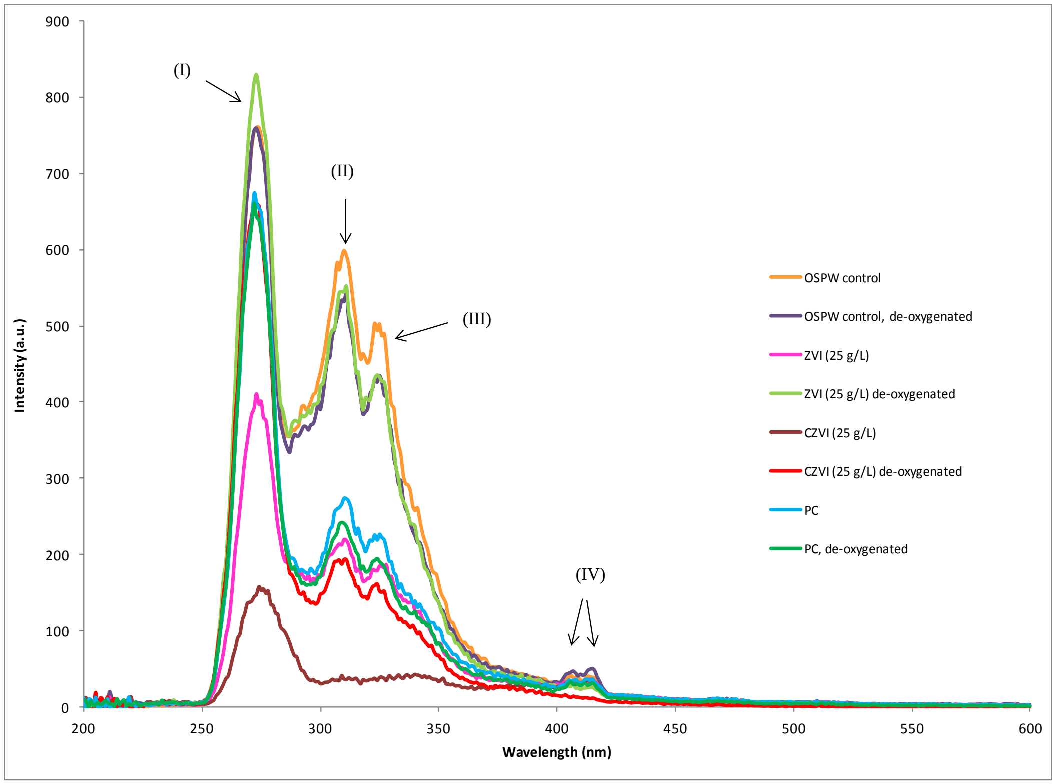

Figure 4.13. The effect of the oxygen on the SFS spectra for OSPW control, ZVI, CZVI, and PC-treated OSPW at 56 h of contact time.

4.3.7. Removal Mechanisms

In aqueous solutions, ZVI is quickly oxidized to form Fe^{2+} and Fe^{3+} products [44, 65]. Positively charged iron oxy/hydroxide precipitates, formed at pH>5 [31, 61], are the predominant species generated in ZVI/water system [30, 31, 55, 89]. The presence of these species was confirmed by the XPS analysis of ZVI. The deconvolution of the Fe_{2p} (Figure B10) showed peaks at 710.8, 713.4, and 724.3 eV indicating the presence of the Fe^{3+}, Fe^{2+}, and $FeO(OH)/Fe_2O_3$ compounds on the surface of ZVI, respectively [14, 27, 81, 90, 91]. The peak indicating the presence of the Fe^0 on the surface of the ZVI was not observed [27, 86, 90]. These iron oxy/hydroxide products could contribute to the adsorption/co-precipitation of the organic compounds [45], resulting in their removal from OSPW. Adsorption of organic compounds on the surface of iron oxy/hydroxides at pH>5 has been reported by several studies [26, 30, 31, 34, 40, 46, 92]. In addition, carboxylic functional groups of the NAs may form complexes with the dissolved Fe^{2+} [2, 14, 30], resulting in the increased hydrophobicity of the NAs and enhanced adsorption onto the surface of PC or ZVI [14]. Increased concentration of the iron complexes (such as Fe-NAs), on the other hand, may facilitate their aggregation [30, 93]. These aggregates could further attach to the surface of the precipitates to form complex oxide products containing iron and NAs. Organic and inorganic contaminants could also be trapped in the matrix of the forming iron hydroxide precipitates [31]. As long as the hydroxides are not dissolved (high pH values), the contaminants are immobilized and removed together with the precipitates [31].

The removal mechanisms of the metals from ground waters were also reported to be based on the adsorption of the metals on the surface of ZVI and co-precipitation with the iron oxy/hydroxides during the oxidation of ZVI [30, 56, 82, 94, 95]. Karthikeyan et al. [98] showed that freshly formed iron hydroxides have the binding sites for Cu adsorption. Cr (III), Ni, and Zn [96, 97], Cr (III) [98], As (V) [99], and were shown to be removed by co-precipitation using iron oxy/hydroxides. The observed effect for the removal of these elements was attributed to the higher available surface area of the iron oxy/hydroxides, which in turn, contain higher binding sites for the adsorption. Metal ions could be also incorporated into the hydroxide lattice to form mixed-crystals resulting in their co-precipitation [31, 96, 97, 100, 101].

Besides the adsorption/co-precipitation of the organic compounds, oxidation is another removal mechanism in the presence of high concentration of oxygen in the solutions. Reactions (1) and (2) below show the possible pathways in the presence of oxygen and ZVI as suggested in a number of studies [14, 26, 44, 62, 64, 65, 81]. The generated electrons from the oxidation of ZVI could be transferred to oxygen, which results in the production of H_2O_2 (eq. 2).

$Fe^0 + O_2 \rightarrow Fe^{2+} + H_2O_2 + 2OH^-$ (1)

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\circ OH + OH^-$ (2)

The highly reactive hydroxyl radicals could be formed during reaction (2) [62, 64, 65]. High concentration of oxygen in OSPW (7.8±0.2 mg/L) and formation of the reactive radicals as a result of the ZVI corrosion suggests the possibility of NAs oxidation [64]. As shown by Drzewicz et al. [14], the application of ZVI at pH 9 resulted in the oxidation of cyclohexanoic acid (CHA), a simple model NAs, to form oxidized CHA by generated hydroxyl radicals. The reaction of hydroxyl radicals with CHA and OSPW NAs, using UV/H_2O_2 and vacuum UV processes, was also shown to form oxo and hydroxy-CHA and NAs [87]. Simultaneous increase in concentration of the oxidized NA and decrease in the concentration of the NAs after ZVI treatment suggested the oxidation pathway of NAs similar to the observed studies.

The oxidation reactions are assumed to occur on or adjacent to ZVI surface [62, 65]. Therefore, organic compounds (such as NAs) with greater affinity for surface adsorption would have high possibility to be oxidized [65]. Adsorption of trichloroethylene on the activated carbon-ZVI composite surface was also shown to increase its degradation by ZVI [88]. NAs with greater molecular weights and higher hydrophobicity tend to adsorb more on the surface of PC and ZVI [14, 78]. This, in turn, could increase their oxidation and removal compared to less hydrophobic species [14], as shown in NAs Removal Section. The NAs removal in the presence of ZVI alone was significantly lower than that of CZVI treatment suggesting that ZVI in contact with PC enhanced removal/oxidation of the NAs. Since electron transfer is responsible for all of the reactions, the application of PC, as an electron conductor, could accelerate the electron transfer to oxygen to enhance the process efficiency [44]. Graphite and granular activated carbon were also shown to be good conductors for electrons from the ZVI surface to the adsorbed organic compounds to be reduced [45, 68]. The significantly lower NAs and EOF removals and the higher peak intensity of

SFS spectra in the de-oxygenated samples also highlighted the important role of oxygen in removal of the organic compounds.

The iron hydroxide precipitates formed on the ZVI surface upon its contact with water [26, 59, 65] may decrease the electron transfer to the ZVI surface and the decomposition rate of the contaminant [26]. However, it was shown that the effective mixing can result in the removal of the precipitates from the ZVI surface revealing fresh reactive iron surface [26, 86]. As the reaction proceeds, the thickness of the passivating layer would increase, which explains the decrease in the removal efficiency of the organic compounds with time (Figure 4.5). Availability of ZVI and oxygen, and continuous oxidation of ZVI to generate Fe^{2+} and H_2O_2 could enhance the formation of hydroxyl radicals [62], which translated into high removal of the organic compounds. Although the degradation of the organic compounds was a slow process, its effectiveness at high pH suggests the possibility of the ZVI application for *in situ* OSPW remediation without any pH adjustment.

4.4. Conclusions

The results of the present study clearly indicated that the presence of PC enhanced the removal of the organic compounds in OSPW by facilitating the electron transfer from ZVI to the reactants. ZVI/PC could be successfully applied for the removal of the organic compounds, including NAs, EOF, and fluorophore organic compounds, from OSPW. PC could serve as a simultaneous adsorption and oxidation site for the organic compounds. This is the advantage of the PC as an electron conductor over the non-conductive adsorbents such as polymers for OSPW remediation. Furthermore, treated OSPW using ZVI/PC treatment showed decreased toxicity towards *Vibrio fischeri* bacteria as compared to untreated OSPW. The promising results obtained in this study can imply that the proposed treatment has a potential to be used as an *in situ* process on an industrial scale to treat the large volumes of generated OSPW. In addition, it will utilize the PC, which is free of charge and stockpiled on the oil production sites.

4.5. References

1. Allen, E. W., Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. *Journal of Environmental Engineering and Science* 2008, *7*, (2), 123-138.

2. Kannel, P. R.; Gan, T. Y., Naphthenic acids degradation and toxicity mitigation in tailings wastewater systems and aquatic environments: A review. *Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering* 2012, *47*, (1), 1-21.

3. Allen, E. W., Process water treatment in Canada's oil sands industry: II. A review of emerging technologies. *Journal of Environmental Engineering and Science* 2008, *7*, (5), 499-524.

4. Malekshahian, M.; Hill, J. M., Effect of pyrolysis and CO(2) gasification pressure on the surface area and pore size distribution of petroleum coke. *Energy & Fuels* 2011, *25*, (11), 5250-5256.

5. Board, E. R. C., ST98- 2011: Alberta’s Energy Reserves 2010 and Supply/Demand Outlook 2011- 2020. In Alberta, G. o., Ed. Calgary, AB, Canada, 2011; p 74.

6. Pourrezaei, P.; Drzewicz, P.; Wang, Y. N.; El-Din, M. G.; Perez-Estrada, L. A.; Martin, J. W.; Anderson, J.; Wiseman, S.; Liber, K.; Giesy, J. P., The impact of metallic coagulants on the removal of organic compounds from oil sands process-affected water. *Environmental Science & Technology* 2011, *45*, (19), 8452-8459.

7. Jones, D.; Scarlett, A. G.; E., W. C.; J., R. S., Toxicity of individual naphthenic acids to vibrio fischeri. *Environmental Science & Technology* 2011, *45,* (22), 9776–9782.

8. Frank, R. A.; Fischer, K.; Kavanagh, R.; Burnison, B. K.; Arsenault, G.; Headley, J. V.; Peru, K. M.; Van der Kraak, G.; Solomon, K. R., Effect of

carboxylic acid content on the acute toxicity of oil sands naphthenic acids. *Environmental Science & Technology* 2009, *43*, (2), 266-271.

9. Garcia-Garcia, E.; Pun, J.; Perez-Estrada, L. A.; Din, M. G. E.; Smith, D. W.; Martin, J. W.; Belosevic, M., Commercial naphthenic acids and the organic fraction of oil sands process water downregulate pro-inflammatory gene expression and macrophage antimicrobial responses. *Toxicology Letters* 2011, *203*, (1), 62-73.

10. Warith, M. A.; Yong, R. N., Toxicity assessment of sludge fluid associated with tar sand tailings. *Environmental Technology* 1994, *15*, (4), 381-387.

11. Frank, R. A.; Kavanagh, R.; Burnison, B. K.; Arsenault, G.; Headley, J. V.; Peru, K. M.; Van Der Kraak, G.; Solomon, K. R., Toxicity assessment of collected fractions from an extracted naphthenic acid mixture. *Chemosphere* 2008, *72*, (9), 1309-1314.

12. Dokholyan, V. K.; Magomedov, A. K., Effect of sodium naphthenate on survival and some physiological–biochemical parameters of some fishes. *J. Ichthyol.* 1983, *23*, 125 –132.

13. Han, X. M.; MacKinnon, M. D.; Martin, J. W., Estimating the in situ biodegradation of naphthenic acids in oil sands process waters by HPLC/HRMS. *Chemosphere* 2009, *76*, (1), 63-70.

14. Drzewicz, P.; Perez-Estrada, L.; Alpatova, A.; Martin, J. W.; Gamal El-Din, M., Impact of peroxydisulfate in the presence of zero valent iron on the oxidation of cyclohexanoic acid and naphthenic acids from oil sands process-affected water. *Environmental Science & Technology*

2012, *46*, (16), 8984-8991.

15. Friedrich, F. D.; Lee, G. K.; Desai, D. L., Fluidized-bed combustion of petroleum coke. *Mechanical Engineering* 1983, *105*, (1), 81-81.

16. Parmar, B. S.; Tollefson, E. L., Desulfurization of oil sands coke. *Canadian Journal of Chemical Engineering* 1977, *55*, (2), 185-191.

17. Small, C. C., Ulrich, A.C., Hashisho, Z., Adsorption of acid extractable oil sands tailings organics onto raw and activated oil sands coke. *Journal of Environmental Engineering and Science* 2012.

18. Zubot, W.; MacKinnon, M. D.; Chelme-Ayala, P.; Smith, D. W.; El-Din, M. G., Petroleum coke adsorption as a water management option for oil sands process-affected water. *Science of the Total Environment* 2012, *427*, 364-372.

19. Fedorak, P. M.; Coy, D. L., Oil sands cokes affect microbial activities. *Fuel* 2006, *85*, (12-13), 1642-1651.

20. Puttaswamy, N.; Turcotte, D.; Liber, K., Variation in toxicity response of Ceriodaphnia dubia to Athabasca oil sands coke leachates. *Chemosphere* 2010, *80*, (5), 489-497.

21. Squires, A. J. Ecotoxicological assessment of using coke in aquatic reclamation strategies at the Alberta oil sands. University of Saskatchewan, Saskatoon, Saskatchewan, Canada, 2005.

22. Puttaswamy, N.; Liber, K., Identifying the causes of oil sands coke leachate toxicity to aquatic invertebrates. *Environmental Toxicology and Chemistry* 2011, *30*, (11), 2576-2585.

23. Kessler, S.; Hendry, M. J. *Geochemistry and Leaching of Coke from Syncrude and Suncor Sites*; Report submitted to Syncrude Canada Ltd. and Suncor Energy Inc.: 2006.

24. Li, X. S.; Glasauer, S.; Le, X. C., Speciation of vanadium in oil sand coke and bacterial culture by high performance liquid chromatography inductively

coupled plasma mass spectrometry (vol 602, pg 17, 2007). *Analytica Chimica Acta* 2009, *648*, (1), 128-128.

25. Puttaswamy, N.; Liber, K., Influence of inorganic anions on metals release from oil sands coke and on toxicity of nickel and vanadium to Ceriodaphnia dubia *Chemosphere* 2012, *86*, (5), 521-529.

26. Shimizu, A.; Tokumura, M.; Nakajima, K.; Kawase, Y., Phenol removal using zero-valent iron powder in the presence of dissolved oxygen: Roles of decomposition by the Fenton reaction and adsorption/precipitation. *Journal of Hazardous Materials* 2012, *201*, 60-67.

27. Li, X. Q.; Elliott, D. W.; Zhang, W. X., Zero-valent iron nanoparticles for abatement of environmental pollutants: Materials and engineering aspects. *Critical Reviews in Solid State and Materials Sciences* 2006, *31*, (4), 111-122.

28. Noubactep, C., A critical review on the process of contaminant removal in Fe-0-H2O systems. *Environmental Technology* 2008, *29*, (8), 909-920.

29. Higgins, M. R.; Olson, T. M., Life-cycle case study comparison of permeable reactive barrier versus pump-and-treat remediation. *Environmental Science & Technology* 2009, *43*, (24), 9432-9438.

30. Mak, M. S. H.; Lo, I. M. C., Influences of redox transformation, metal complexation and aggregation of fulvic acid and humic acid on Cr(VI) and As(V) removal by zero-valent iron. *Chemosphere* 2011, *84*, (2), 234-240.

31. Noubactep, C., The fundamental mechanism of aqueous contaminant removal by metallic iron. *Water Sa* 2010, *36*, (5), 663-670.

32. Gillham, R. W.; Ohannesin, S. F., Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground Water* 1994, *32*, (6), 958-967.

33. Lipczynskakochany, E.; Harms, S.; Milburn, R.; Sprah, G.; Nadarajah, N., Degradation of carbon-tetrachloride in the presence of iron and sulfur-containing-compounds. *Chemosphere* 1994, *29*, (7), 1477-1489.

34. Matheson, L. J.; Tratnyek, P. G., Reductive dehalogenation of chlorinated methanes by iron metal. *Environmental Science & Technology* 1994, *28*, (12), 2045-2053.

35. Schreier, C. G.; Reinhard, M., Transformation of chlorinated organic compounds by iron and manganese powders in buffered water and in landfill leachate. *Chemosphere* 1994, *29*, (8), 1743-1753.

36. O'Hannesin, S. F.; Gillham, R. W., Long-term performance of an in situ "iron wall" for remediation of VOCs. *Ground Water* 1998, *36*, (1), 164-170.

37. Bigg, T.; Judd, S. J., Zero-valent iron for water treatment. *Environmental Technology* 2000, *21*, (6), 661-670.

38. Scherer, M. M.; Richter, S.; Valentine, R. L.; Alvarez, P. J. J., Chemistry and microbiology of permeable reactive barriers for in situ groundwater clean up. *Critical Reviews in Environmental Science and Technology* 2000, *30*, (3), 363-411.

39. Lee, G.; Rho, S.; Jahng, D., Design considerations for groundwater remediation using reduced metals. *Korean Journal of Chemical Engineering* 2004, *21*, (3), 621-628.

40. Henderson, A. D.; Demond, A. H., Long-term performance of zero-valent iron permeable reactive barriers: A critical review. *Environmental Engineering Science* 2007, *24*, (4), 401-423.

41. Cundy, A. B.; Hopkinson, L.; Whitby, R. L. D., Use of iron-based technologies in contaminated land and groundwater remediation: A review. *Science of the Total Environment* 2008, *400*, (1-3), 42-51.

42. Jeen, S. W.; Blowes, D. W.; Gillham, R. W., Performance evaluation of granular iron for removing hexavalent chromium under different geochemical conditions. *Journal of Contaminant Hydrology* 2008, *95,* (1-2), 76-91.

43. Puls, R. W.; Paul, C. J.; Powell, R. M., The application of in situ permeable reactive (zero-valent iron) barrier technology for the remediation of chromate-contaminated groundwater: a field test. *Applied Geochemistry* 1999, *14*, (8), 989-1000.

44. Lee, J.; Kim, J.; Choi, W., Oxidation on zerovalent iron promoted by polyoxometalate as an electron shuttle. *Environmental Science & Technology* 2007, *41*, (9), 3335-3340.

45. Oh, S. Y.; Cha, D. K.; Chiu, P. C., Graphite-mediated reduction of 2,4-dinitrotoluene with elemental iron. *Environmental Science & Technology* 2002, *36*, (10), 2178-2184.

46. Mantha, R.; Taylor, K. E.; Biswas, N.; Bewtra, J. K., A continuous system for Fe(0) reduction of nitrobenzene in synthetic wastewater. *Environmental Science & Technology* 2001, *35,* (15), 3231-3236.

47. Orth, W. S.; Gillham, R. W., Dechlorination of trichloroethene in aqueous solution using Fe-O. *Environmental Science & Technology* 1996, *30*, (1), 66-71.

48. Eykholt, G. R.; Davenport, D. T., Dechlorination of the chloroacetanilide herbicides alachlor and metolachlor by iron metal. *Environmental Science & Technology* 1998, *32*, (10), 1482-1487.

49. Agrawal, A.; Tratnyek, P. G., Reduction of nitro aromatic compounds by zero-valent iron metal. *Environmental Science & Technology* 1996, *30*, (1), 153-160.

50. Devlin, J. F.; Klausen, J.; Schwarzenbach, R. P., Kinetics of nitroaromatic reduction on granular iron in recirculating batch experiments. *Environmental Science & Technology* 1998, *32*, (13), 1941-1947.

51. Singh, J.; Comfort, S. D.; Shea, P. J., Iron-mediated remediation of RDX-contaminated water and soil under controlled Eh/pH. *Environmental Science & Technology* 1999, *33*, (9), 1488-1494.

52. Weber, E. J., Iron-mediated reductive transformations: Investigation of reaction mechanism. *Environmental Science & Technology* 1996, *30*, (2), 716-719.

53. Nam, S.; Tratnyek, P. G., Reduction of azo dyes with zero-valent iron. *Water Research* 2000, *34*, (6), 1837-1845.

54. Alowitz, M. J.; Scherer, M. M., Kinetics of nitrate, nitrite, and Cr(VI) reduction by iron metal. *Environmental Science & Technology* 2002, *36*, (3), 299-306.

55. Blowes, D. W.; Ptacek, C. J.; Jambor, J. L., In-situ remediation of Cr(VI)-contaminated groundwater using permeable reactive walls: Laboratory studies. *Environmental Science & Technology* 1997, *31*, (12), 3348-3357.

56. Su, C. M.; Puls, R. W., Arsenate and arsenite removal by zerovalent iron: Kinetics, redox transformation, and implications for in situ groundwater remediation. *Environmental Science & Technology* 2001, *35*, (7), 1487-1492.

57. Fiedor, J. N.; Bostick, W. D.; Jarabek, R. J.; Farrell, J., Understanding the mechanism of uranium removal from groundwater by zero-valent iron using X-ray photoelectron spectroscopy. *Environmental Science & Technology* 1998, *32*, (10), 1466-1473.

58. Gu, B.; Liang, L.; Dickey, M. J.; Yin, X.; Dai, S., Reductive precipitation of uranium(VI) by zero-valent iron. *Environmental Science & Technology* 1998, *32*, (21), 3366-3373.

59. Noubactep, C.; Schoner, A., Metallic iron for environmental remediation: Learning from electrocoagulation. *Journal of Hazardous Materials* 2010, *175*, (1-3), 1075-1080.

60. Wang, K. S.; Lin, C. L.; Wei, M. C.; Liang, H. H.; Li, H. C.; Chang, C. H.; Fang, Y. T.; Chang, S. H., Effects of dissolved oxygen on dye removal by zero-valent iron. *Journal of Hazardous Materials* 2010, *182*, (1-3), 886-895.

61. Aleksanyan, A. Y.; Podobaev, A. N.; Reformatskaya, II, Steady-state anodic dissolution of iron in neutral and close-to-neutral media. *Protection of Metals* 2007, *43*, (1), 66-69.

62. Joo, S. H.; Feitz, A. J.; Waite, T. D., Oxidative degradation of the carbothioate herbicide, molinate, using nanoscale zero-valent iron. *Environmental Science & Technology* 2004, *38*, (7), 2242-2247.

63. Katsoyiannis, I. A.; Ruettimann, T.; Hug, S. J., pH dependence of Fenton reagent generation and As(III) oxidation and removal by corrosion of zero valent iron in aerated water. *Environmental Science & Technology* 2008, *42*, (19), 7424-7430.

64. Stieber, M.; Putschew, A.; Jekel, M., Treatment of pharmaceuticals and diagnostic agents using zero-valent iron - kinetic studies and assessment of transformation products assay. *Environmental Science & Technology* 2011, *45*, (11), 4944-4950.

65. Joo, S. H.; Feitz, A. J.; Sedlak, D. L.; Waite, T. D., Quantification of the oxidizing capacity of nanoparticulate zero-valent iron. *Environmental Science & Technology* 2005, *39*, (5), 1263-1268.

66. Mielczarski, J. A.; Atenas, G. M.; Mielczarski, E., Role of iron surface oxidation layers in decomposition of azo-dye water pollutants in weak acidic solutions. *Applied Catalysis B-Environmental* 2005, *56*, (4), 289-303.

67. Shi, Z. Q.; Nurmi, J. T.; Tratnyek, P. G., Effects of nano zero-valent iron on oxidation-reduction potential. *Environmental Science & Technology* 2011, *45*, (4), 1586-1592.

68. Tang, H.; Zhu, D. Q.; Li, T. L.; Kong, H. N.; Chen, W., Reductive dechlorination of activated carbon-adsorbed trichloroethylene by zero-valent Iron: carbon as electron shuttle. *Journal of Environmental Quality* 2011, *40*, (6), 1878-1885.

69. Leon, C.; Radovic, L. R., Interfacial chemistry and electrochemistry of carbon surfaces. *Chemistry and Physics of Carbon, Vol 24* 1994, *24*, 213-310.

70. Ranganathan, S.; Kuo, T. C.; McCreery, R. L., Facile preparation of active glassy carbon electrodes with activated carbon and organic solvents. *Analytical Chemistry* 1999, *71*, (16), 3574-3580.

71. Mackenzie, K.; Battke, J.; Koehler, R.; Kopinke, F. D., Catalytic effects of activated carbon on hydrolysis reactions of chlorinated organic compounds - Part 2. 1,1,2,2-tetrachloroethane. *Applied Catalysis B-Environmental* 2005, *59*, (3-4), 171-179.

72. MacKenzie, K.; Battke, J.; Kopinke, F. D., Catalytic effects of activated carbon on hydrolysis reactions of chlorinated organic compounds - Part 1. gamma-hexachlorocyclohexane. *Catalysis Today* 2005, *102*, 148-153.

73. Perez-Estrada, L. A.; Han, X. M.; Drzewicz, P.; El-Din, M. G.; Fedorak, P. M.; Martin, J. W., Structure-reactivity of naphthenic acids in the ozonation process. *Environmental Science & Technology* 2011, *45*, (17), 7431-7437.

74. Jivraj, M. N.; MacKinnon, M.; Fung, B. *Naphthenic acid extraction and quantitative analysis with FT-IR spectroscopy*; Syncrude Canada Ltd. Internal Report: Edmonton: Syncrude Canada Ltd., 1996.

75. Chelme-Ayala, P.; El-Din, M. G.; Smith, R.; Code, K. R.; Leonard, J., Advanced treatment of liquid swine manure using physico-chemical treatment. *Journal of Hazardous Materials* 2011, *186*, (2-3), 1632-1638.

76. Chelme-Ayala, P.; El-Din, M. G.; Smith, D. W.; Adams, C. D., Oxidation kinetics of two pesticides in natural waters by ozonation and ozone combined with hydrogen peroxide. *Water Research* 2011, *45*, (8), 2517-2526.

77. Scott, A. C.; Zubot, W.; MacKinnon, M. D.; Smith, D. W.; Fedorak, P. M., Ozonation of oil sands process water removes naphthenic acids and toxicity. *Chemosphere* 2008, *71*, (1), 156-160.

78. Pourrezaei, P.; Alpatova, A.; Chelme-Ayala, P.; Perez-Estrada, L. A.; Jensen-Fontaine, M.; Le, X. C.; Gamal El-Din, M., Impact of petroleum coke characteristics on the adsorption of the organic Fractions from oil sands process-affected water. *International Journal of Environmental Science and Technology (submitted)* 2012.

79. Kavanagh, R. J.; Burnison, B. K.; Frank, R. A.; Solomon, K. R.; Van Der Kraak, G., Detecting oil sands process-affected waters in the Alberta oil sands region using synchronous fluorescence spectroscopy. *Chemosphere* 2009, *76*, (1), 120-126.

80. Rasheed, Q. J.; Pandian, K.; Muthukumar, K., Treatment of petroleum refinery wastewater by ultrasound-dispersed nanoscale zero-valent iron particles. *Ultrasonics Sonochemistry* 2011, *18*, (5), 1138-1142.

81. Chen, J. H.; Qiu, X. Q.; Fang, Z. Q.; Yang, M.; Pokeung, T.; Gu, F. L.; Cheng, W.; Lan, B. Y., Removal mechanism of antibiotic metronidazole from

aquatic solutions by using nanoscale zero-valent iron particles. *Chemical Engineering Journal* 2012, *181*, 113-119.

82. Abedin, M. A.; Katsumi, T.; Inui, T.; Kamon, M., Arsenic removal fron contaminated ground water by zero valent iron: a mechanistic and long-term performance study. *Soils and Foundations* 2011, *51*, (3), 369-377.

83. Kishimoto, N.; Iwano, S.; Narazaki, Y., Mechanistic consideration of zinc ion removal by zero-valent iron. *Water Air and Soil Pollution* 2011, *221*, (1-4), 183-189.

84. Mamindy-Pajany, Y.; Hurel, C.; Marmier, N.; Romeo, M., Arsenic (V) adsorption from aqueous solution onto goethite, hematite, magnetite and zero-valent iron: Effects of pH, concentration and reversibility. *Desalination* 2011, *281*, 93-99.

85. Rowland, S. J.; West, C. E.; Jones, D.; Scarlett, A. G.; Frank, R. A.; Hewitt, L. M., Steroidal aromatic 'naphthenic acids' in oil sands process-affected water: structural comparisons with environmental estrogens. *Environmental Science & Technology* 2011, *45*, (22), 9806-9815.

86. Noubactep, C.; Licha, T.; Scott, T. B.; Fall, M.; Sauter, M., Exploring the influence of operational parameters on the reactivity of elemental iron materials. *Journal of Hazardous Materials* 2009, *172*, (2-3), 943-951.

87. Drzewicz, P.; Afzal, A.; El-Din, M. G.; Martin, J. W., Degradation of a model naphthenic acid, cyclohexanoic acid, by vacuum UV (172 nm) and UV (254 nm)/H_2O_2. *Journal of Physical Chemistry A* 2010, *114*, (45), 12067-12074.

88. Tseng, H. H.; Su, J. G.; Liang, C. J., Synthesis of granular activated carbon/zero valent iron composites for simultaneous adsorption/dechlorination of trichloroethylene. *Journal of Hazardous Materials* 2011, *192*, (2), 500-506.

89. Satoh, Y.; Kikuchi, K.; Kinoshita, S.; Sasaki, H., Potential capacity of coprecipitation of dissolved organic carbon (DOC) with iron(III) precipitates. *Limnology* 2006, *7*, (3), 231-235.

90. Nurmi, J. T.; Sarathy, V.; Tratnyek, P. G.; Baer, D. R.; Amonette, J. E.; Karkamkar, A., Recovery of iron/iron oxide nanoparticles from solution: comparison of methods and their effects. *Journal of Nanoparticle Research* 2011, *13*, (5), 1937-1952.

91. Zhang, X.; Lin, S.; Chen, Z. L.; Megharaj, M.; Naidu, R., Kaolinite-supported nanoscale zero-valent iron for removal of Pb(2+) from aqueous solution: Reactivity, characterization and mechanism. *Water Research* 2011, *45*, (11), 3481-3488.

92. Gu, B. H.; Schmitt, J.; Chen, Z. H.; Liang, L. Y.; McCarthy, J. F., Adsorption and desoprtion of natural organic matter on iron-oxide-mechansims and models. *Environmental Science & Technology* 1994, *28*, (1), 38-46.

93. Ghosh, S.; Mashayekhi, H.; Pan, B.; Bhowmik, P.; Xing, B. S., Colloidal behavior of aluminum oxide nanoparticles as affected by pH and natural organic matter. *Langmuir* 2008, *24*, (21), 12385-12391.

94. Lackovic, J. A.; Nikolaidis, N. P.; Dobbs, G. M., Inorganic arsenic removal by zero-valent iron. *Environmental Engineering Science* 2000, *17*, (1), 29-39.

95. Manning, B. A.; Hunt, M. L.; Amrhein, C.; Yarmoff, J. A., Arsenic(III) and Arsenic(V) reactions with zerovalent iron corrosion products. *Environmental Science & Technology* 2002, *36*, (24), 5455-5461.

96. Crawford, R. J.; Harding, I. H.; Mainwaring, D. E., Adsorption and coprecipitation of single heavy-metal ions onto the hydrated oxides of iron and chromium. *Langmuir* 1993, *9*, (11), 3050-3056.

97. Crawford, R. J.; Harding, I. H.; Mainwaring, D. E., Adsorption and coprecipitation of multiple heavy-metal ions onto the hydrated oxides of iron and chromium. *Langmuir* 1993, *9,* (11), 3057-3062.

98. Charlet, L.; Manceau, A., X-ray absorption spectroscopic study of the sorption of Cr (III) at the oxide water interface .2. adsorption, coprecipitation, and surface precipitation on hydrous ferric-oxide *Journal of Colloid and Interface Science* **1992,** *148,* (2), 443-458.

99. Waychunas, G. A.; Rea, B. A.; Fuller, C. C.; Davis, J. A., Surface chemistry of ferrihydrite .1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate *Geochimica Et Cosmochimica Acta* **1993,** *57,* (10), 2251-2269.

100. Karthikeyan, K. G.; Elliott, H. A.; Cannon, F. S., Adsorption and coprecipitation of copper with the hydrous oxides of iron and aluminum. *Environmental Science & Technology* 1997, *31*, (10), 2721-2725.

101. Crane, R. A.; Scott, T. B., Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology. *Journal of Hazardous Materials* 2012, *211*, 112-125.

CHAPTER 5. GENERAL CONCLUSIONS AND RECOMMENDATIONS

5.1. Thesis Overview

OSPW, generated after Clark hot water extraction of bitumen from oil sands operations in Northern Alberta, Canada, is a complex alkaline mixture of inorganic and organic compounds as well as a stable suspension of fine particles. Based on a zero discharge policy, oil sands companies are required to store OSPW in tailings ponds near the mining sites. Storage of OSPW results in several environmental problems, including the presence of the trace concentrations of NAs in surface waters around the oil sands operation facilities due to their leaching from tailings ponds. Because of the continuous recycling to the extraction process, OSPW becomes corrosive and highly toxic due to the presence of high concentrations of salts and refractory organic compounds such as NAs. On the other hand, PC is generated in large quantities during the oil upgrading process as a waste by-product. The production of PC has continuously increased and up to date no significant practical application of PC has been reported. Therefore, continuing accumulation and stockpiling of large quantities of PC requires development of innovative strategies for the effective utilization of this carbon-reach material at an industrial scale.

Various treatment technologies including biological treatment, membrane filtration, adsorption, and advanced oxidation processes have been tested for the removal of the contaminants from OSPW. However, there are still significant knowledge gaps considering the effectiveness and applicability of the proposed treatment technologies for the OSPW remediation at an industrial scale. In order to minimize the fresh water intake from the Athabasca River, the treatment technologies should be optimized to treat the OSPW to a level suitable for the utilities. Furthermore, for the release of OSPW into the nearby rivers, the quality of the treated OSPW should meet the standard guidelines, and the removal of the NAs and other organic and inorganic compounds should be considered as the highest treatment priority. To achieve this, a series of consecutive treatment processes is needed to remove the contaminants. Currently, there is no economical and viable treatment technology to handle huge amounts of generated waste by-products (OSPW and PC).

CFS is a potential pre-treatment option for the removal of the suspended solids and colloidal particles from OSPW. Because of their small size and surface charge, without any pre-treatment, suspended particles are difficult to remove by filtration or sedimentation. Moreover, suspended solids may interfere with ultraviolet light (UV)-based advanced oxidation processes (UV/O_3, UV/H_2O_2) by scattering light, thus reducing the efficiency of these processes. Therefore, removal of the suspended particles may improve the performance of filtration, advanced oxidation, and membrane separation processes. It was expected that the CFS pre-treatment of OSPW would decrease the particle and organic loading on the subsequent treatment processes and enhance the performance of remediation processes.

Given the complexity of environmental problems and continuous accumulation of different by-products, that the oil sands industry is facing, the process shortcomings can be turned into benefits by applying one waste to treat another waste product. Adsorption is viewed as an effective process to remove persistent organic chemicals from OSPW. Considering the abundance of PC in oil sands industry, it could be effectively applied for adsorptive treatment of OSPW. In this approach, PC can be used as an *in-situ* adsorbent for the OSPW treatment. In addition, the carbonaceous materials such as PC have been known to possess electron conducting characteristics, which enable them to act as both adsorption sites and electron mediator. ZVI can serve as a source of electron, which depending on the water characteristics (e.g., pH and oxygen availability), could facilitate the reduction or oxidation of the refractory organic compounds. It was hypothesized that application of PC as an electron conductor in combination with

ZVI could enhance the removal/oxidation of the organic compounds, including NAs, from OSPW.

This work focused on assessing the feasibility and efficacy of CFS, PC adsorption, and PC mediated-ZVI oxidation processes for the removal of different types of contaminants, including suspended solids and dissolved organic compounds, from OSPW. The objectives of this research were achieved through the application of these treatment processes in different phases.

In order to achieve these objectives, the metallic salt coagulants (alum, ferric sulfate, and ferric chloride), and organic polymers (cationic, anionic, and non-ionic) were tested to assess the removal of the suspended particles and dissolved organic compounds (TOC and NAs) in the first phase. Identification of coagulation mechanism and assessment of the properties of the flocs (size and surface functional groups) were performed. In the second phase, adsorption of different fractions of organic contaminants (EOF and NAs) using PC; determination of adsorption mechanisms; studying the effect of physico-chemical properties of PC on the adsorption process; and investigating the speciation of the leached vanadium from PC during the adsorption process were comprehensively investigated. In the third phase, the hypothesis that PC could be applied as an electron conductor to enhance the NAs removal/oxidation using ZVI, as a source of electron generation, was evaluated.

5.2. Conclusions

Based on the experimental results and analysis obtained in this research, the following conclusions were drawn:

1. Based on the TOC removal and turbidity reduction, alum and ferric sulfate showed superior performance compared to ferric chloride. Alum and ferric sulfate resulted in the same removal efficiencies. However, addition of the ferric salts resulted in a reddish color of the treated OSPW with higher color intensity at higher coagulant

concentrations. Since this might require additional treatment for color removal, alum, the most commonly used coagulant, was chosen as the coagulant.

2. The results of the optimization studies indicated that alum at 250 mg/L removed 97% and 12% turbidity and TOC, respectively. In addition, NAs and oxidized NAs were removed by 10-37% and 64-86%, respectively. The optimum rapid and slow mixing conditions were found to be 120 rpm for 30 s followed by 10 min at 30 rpm, respectively. The resulting flocs were allowed to settle for 1 h. While application of nonionic and anionic polymers showed adverse or no effect on the TOC removal, the addition of 5 mg/L cationic polymer polyDADMAC to alum slightly improved the TOC removal to 14%.

3. Positively charged aluminum hydroxide precipitates contributed to the destabilization of the particles. Destabilization occurred by deposition of the hydroxides on the surface of the particles through adsorption and hetero-coagulation. This process resulted in charge neutralization of the particles. Dissolved organic compounds could be also adsorbed and neutralized by the precipitates resulting in their lower solubility and co-precipitation. Measurement of changes in zeta potential with the increase of alum concentration showed that ~1000 mg/L alum should be applied to reach the zero zeta potential point, which corresponds to the complete charge neutralization in the system. Therefore, at the optimum concentration of alum (250 mg/L), charge neutralization through adsorption was proposed as the removal mechanism of the particles and organic compounds.

4. Aluminum concentration decreased up to 96% from its initial concentration in OSPW because of the formation of the aluminum hydroxide precipitates. Concentrations of vanadium and barium decreased by 67–78% and 42–63%, respectively. Removal

mechanisms of vanadium and barium might involve either adsorption of soluble metals to the active sites of the hydroxide or formation of complexes with organic compounds and co-precipitation.

5. FT–IR spectroscopy of the flocs treated at 250 mg alum/L showed the absorption band of the hydroxyl groups which may be related to the presence of trapped water or the oxidized NAs in the flocs. The absorption bands representing the carboxylic acids were also detected on the surface of the flocs confirming the removal of the NAs from OSPW to the formed flocs.

6. Results of the growth and survival of the benthic midge (Class *Insecta, Chironomus dilutus)* by exposing animals to a fresh water control, untreated OSPW, OSPW treated with 250 mg alum/L, and OSPW treated with 250 mg alum/L plus 5 mg polyDADMAC/L indicated that addition of the polyDADMAC increased the toxicity of the treated OSPW towards the animals. The cationic polymer or monomer present in the polymer and NAs together may have a synergistic effect to induce more toxicity.

7. Application of PC at 200 g/L mixed for 16 h resulted in EOF and NAs removal of 60% and 75%, respectively. A q_m for PC to adsorb EOF from OSPW was calculated as 1.0 mg/g (by fitting the experimental data to the *Langmuir* isotherm). This value, compared to 51 and 71 mg/g for GAC and PAC, respectively, indicated that larger mass of PC is required for the removal of the EOF from OSPW. BET surface area of PC (7.7 m^2/g), as compared to 912 and 800 m^2/g for GAC and PAC, respectively, implies that PC has lower porosity comparing to the highly porous structure of the GAC and PAC.

8. Distribution of the NA species in OSPW as a function *n* and -*Z* before and after treatment with PC implied that the adsorption of NAs onto

PC increased with the increase in both *n* and -*Z* numbers. Increasing *n* resulted in greater removal of the species for each -*Z* group, whereas, increase in the -*Z* for each *n* group of NAs did not affect the removal. These results were consistent with the log K_{ow} for NAs as a function of *n* and -*Z*. Increase in the NAs molecular mass renders the compounds less soluble and more hydrophobic, which increases their affinity for the adsorption on the surface of the PC. Given that NAs are highly hydrophobic compounds, the hydrophobic interactions between the NAs and the surface of PC is suggested as a dominant adsorption mechanism.

9. Investigation of the FT-IR spectra of the PC before and after adsorption showed peaks with similar positions for each identified functional groups, suggesting physisorption of organic compounds on the surface of PC. In addition, the calculated mean free energy of adsorption (E < 8 kJ/mol) suggested that the EOF were physically adsorbed on the surface of the PC.

10. The vanadium release occurred when PC was mixed with OSPW. The leached vanadium was predominantly vanadium (V). Although in very low concentration, vanadium (IV) was also detected. However, given that vanadium (IV) is unstable at circumneutral pH, it was expected that it would be oxidized into vanadium (V) upon its release into OSPW. Although the percentage of the released vanadium did not exceed 20% of the vanadium present in PC, its concentrations exceeded the background vanadium concentrations reported for natural waters.

11. Application of ZVI in combination with PC enhanced the removal of the organic compounds, including fluorophore organic compounds, EOF, and NAs, from OSPW as compared to PC or ZVI alone treated OSPW. The investigation of the effect of contact time on the removal

of the fluorophore organic compounds during the CZVI treatment revealed that the reaction proceeded faster during the initial 56 h followed by a slower rate afterwards. The lower removal rate at the end of the exposure may indicate the presence and build up of the oxide products on the surface of ZVI, resulting in the lower rate of electron transfer. The calculated first order rate constants for CZVI treated OSPW samples were higher than those of ZVI or PC alone and show the synergistic effect of the ZVI and PC.

12. Increasing ZVI concentration resulted in the increase in the removal of the fluorophore organic compounds, EOF, and NAs from OSPW in both CZVI and ZVI treated OSPW samples. There was a statistically significant difference in the removal of the EOFs at 25 g/L of ZVI between ZVI alone and CZVI treatments. The removal of EOF increased from 28.8% in ZVI to 74.4% in CZVI treated OSPW samples. NAs removal also increased to 90.1% using CZVI as compared to 58.4% in ZVI alone treatment. V, Mn, Ni, and Mo were shown to be released from PC upon its contact with OSPW. However, addition of ZVI to PC resulted in the 97.6-97.8%, 96.9-99.1%, 87.8-100%, and 95.8-98.8% removals of these metals, respectively. The removal of As, Cd, Co, Sb, Se, and Sr from OSPW were in the range of 67.8-70.9%, 100%, 85.0-97.6%, 93.9-99.1%, 60.3-66.3%, and 98.5-99.3%, respectively.

13. The untreated OSPW was found to be toxic to *Vibrio fischeri* bacteria by 58.9% inhibition. On the contrary, all treated OSPW with ZVI, CZVI, and PC showed lower inhibition effects. The inhibition effect decreased to 6.1% by the addition of the ZVI to PC at 25 g/L, as compared to the ZVI alone (32.0%) and PC alone (28.3%) treated OSPW samples. This shows the synergistic effect of ZVI and PC on the decrease in the toxicity of the treated OSPW. The IC_{20} and IC_{50} for

OSPW were found to be 27.8% (v v^{-1}) and 69.5±3% (v v^{-1}), respectively. For ZVI, the IC_{20} and IC_{50} were found to be 51.2±3% (v v^{-1}) and >100% (v v^{-1}), respectively, showing the reduction in the toxicity of the OSPW after ZVI treatment.

14. In OSPW with the oxygen level of 7.8±0.2 mg/L, EOF removal was 28.8 and 74.4% for ZVI and CZVI treatments, respectively. The efficiency of EOF removal significantly decreased to 3.1 and 23.2% in ZVI and CZVI treated OSPW samples, respectively, when OSPW was purged to remove oxygen to 0.51 mg O_2/L. Lower NAs removals of 17.5% and 65.4% were also obtained for ZVI and CZVI treated-OSPW in de-oxygenated samples as compared to 58.4% and 90.1%, respectively in non de-oxygenated samples. These results clearly indicated that oxygen played an important role in the removal of the organic compounds by increasing the oxidation rate of the iron products and subsequent oxidation of the contaminants. High concentration of oxygen in OSPW (7.8±0.2 mg/L) and formation of the highly reactive hydroxyl radicals as a result of ZVI corrosion suggests the possibility of NAs oxidation. Hydroxyl radicals could react with NAs to form carbon radicals. Further reaction of these radicals with oxygen results in the formation of oxidized NAs. Simultaneous 34% increase in the concentration of the oxidized NAs and decrease in the concentration of the NAs after ZVI treatment also suggested the oxidation of the NAs.

5.3. Recommendations

Based on the obtained results and drawn conclusions, the following recommendations can be addressed for future research:

1. The CFS process could be simulated and optimized using response surface methodology (RSM)/artificial neural network (ANN) using the results obtained from this study. In addition, other coagulants (including poly aluminum chloride (PACl) or poly aluminum sulphate) or natural flocculants (chitosan) could be applied as alternative coagulants following the same methodology to compare the results with the current data and generate more data for the model development. The CFS treatment could be conducted at different temperatures and pH values to provide more information for the simulation.
2. The flocs strength could be examined by increasing the mixing intensity to result in the floc breakage after they have been formed. The mixing intensity could then be decreased to the initial condition to assess the ability of the broken flocs to re-grow.
3. Electro-coagulation, with aluminum or iron electrodes, can be applied for the removal of suspended solids, heavy metals, oil and grease, and dissolved organics. In addition, it can remove the microorganisms. The destabilized contaminants could be removed by either precipitation or flotation. Since no chemical (e.g. alum) is added to the system, there would be no increase in the concentration of the ions associated with the common coagulants (e.g. sulfate) after the treatment.
4. A comparative study regarding the application of other adsorbent, such as carbon nanotubes, exfoliated graphite, and polyurethanes, which are known to have high adsorption capacity, could be performed for OSPW remediation.
5. Functionalization of the PC surface or impregnation of the nano-particles, such as nanoscale ZVI, could enhance the adsorption

capacity of the PC for the selective adsorption of the organic contaminants from OSPW.

6. The adsorption studies could be performed using commercial model NAs to better understand and characterize the removal mechanisms and formation of the oxidation by-products.

APPENDIX A: Experimental Procedures

A.1. Quantification Methods for Water Quality Analysis

pH was measured using an Accumet Research AR20 pH Meter, Fisher Scientific. An Orbeco-Hellige 965 Turbidimeter, Orbeco Analytical Systems Inc. was used to measure the turbidity of the samples based on the light scattering principle. An Apollo 9000 TOC Combustion Analyzer, FOLIO Instruments Inc. was used to analyze TOC content of the samples. Each sample was analyzed in triplicate and the average value with less than 5% standard deviation was considered as the TOC. COD and CBOD5 were measured according to the Standard Methods for the Examination of Water and Wastewater. Total alkalinity of the samples was measured by titration with 0.02 N sulfuric acid. A Thermo Orion Portable 130A Conductivity Meter was used to quantify the conductivity of the samples. Major cations and anions were analyzed using a Dionex 2500 and a 2000 IC system equipped with an AS50 auto-sampler with 25 µL injection loop, GP50 gradient pump, CD25 conductivity detector, NG1, AG14A, AS14A columns, ASRS Ultra Π suppressor, eluent reservoir with 4×2L suitable plastic containers, and nitrogen compressed gas. An Elan 9000 ICP Mass Spectrometer, PerkinElmer SCIEX was used to quantify the concentration of the trace metals. To analyze the total metal contents, samples were digested with concentrated nitric acid for 10 min. Digested samples were filtered through a 0.45 μm filter and diluted before injection into to the ICP-MS.

A.2. X-ray Photoelectron Spectroscopy Analysis Methodology

The XPS measurements were performed on AXIS 165 spectrometer (Kratos Analytical) at the Alberta Centre for Surface Engineering and Science (ACSES), University of Alberta. The base pressure in the analytical chamber was lower than 3 x 10-8 Pa. Monochromatic Al Kα source (hν = 1486.6 eV) was used at a power of 210 W. The analysis spot was 400 x 700 um. The resolution of the instrument is 0.55 eV for Ag 3d and 0.70 eV for Au 4f peaks. The survey scans were collected for binding energy spanning from 1100 eV to 0 with analyzer pass energy of 160 eV and a step of 0.4 eV. For the high-resolution spectra the pass-energy was 20 eV with a step of 0.1 eV. Electron flood gun was used to compensate the sample charging. Vision-2 instrument software was applied to process the data. All spectra were calibrated for C1s binding energy position at 284.8 eV. Compositions were calculated from the survey spectra using the major elemental peaks and sensitivity factors provided by the database.

A.3. Surface Functional Groups Analysis by Fourier Transform Infra Red (FT-IR)

A Bio-rad diffuse reflectance FT-IR spectrophotometer was used to identify the surface functional groups. Dried flocs/adsorbents were mixed with potassium bromide (KBr) (FT-IR grade, Sigma-Aldrich) in a 5% by weight ratio and ground to form a very five powder. The mixture was then analyzed by the infrared spectroscopy. Pure KBr was also used to collect the background spectra. The spectra were recorded with 128 scans and 4 cm^{-1} spectral resolution.

A.4. SEM Analysis Methodology

Dried flocs were used for image analysis. The sample particles were scattered onto the stub pasted with a thin layer of silicon, then the samples were sputter coated with a thin layer of gold before it were examined with Hitachi SEM S-2500 (Tokyo, Japan). The samples' images were examined in the SEM instrument by adjusting various parameters including working distance, beam current, KV, contrast, and brightness to obtain the highest possible quality for images. Photos were taken at 3K, 6K magnification at 8.0KV.

A.5. Thermo Gravimetric Analysis (TGA)

TGA was performed by a thermal analyzer system (TGA/DSC 1, Mettler Toledo, Mississauga, ON, Canada) under the 50 standard cubic centimeters per minute N_2 flow at a heating rate of 10°C/min. The experiments started at 30°C and finished at 1000°C. The temperature was increased to 120°C and 400°C maintaining for 60 min at each temperature to completely remove moisture and NAs, respectively. Afterwards, the temperature was raised to 1000°C.

A.6. BET Surface Area Analysis

The surface area was determined from the nitrogen adsorption/desorption isotherms performed at 350°C using a surface analyzer (IQ2MP, Quantachrome, FL, USA). Prior to analysis, samples were degassed at 300°C for 5 h. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) equation at the relative pressure range of 0.01-0.07. The V–t model was used to calculate the micropore volume. A density functional theory (DFT) model for slit pores was used to obtain the pore size distribution.

A.7. Point of Zero Charge (PZC)

A solid addition method was used to determine the pH of the zero surface charge on the adsorbent. 50 mL solutions of 0.1 N NaCl, adjusted to the desired pH, were transferred to a series of 125 mL stoppered flasks. The initial pH of the solutions was adjusted between 2 and 12 by adding 0.1 N HCl or 0.1 N NaOH and recorded as the initial pH (pH_0) of the solutions. Then 1 g of PC was added to each flask and capped immediately. The suspensions were shaken by the incubator shaker for 48 h to reach equilibrium. After the designated time, the final pH (pH_f) of the supernatant was recorded. The difference between the final and initial pH values ($\Delta pH = pH_f - pH_0$) was plotted against the pH_0. The point of intersection of the curve at which $\Delta pH = 0$ corresponds to the pH_{PZC}.

A.8. Vanadium Speciation

Vanadium speciation was performed on a HPLC-ICP-MS (HPLC, PE Instruments, Shelton, CT, USA and ICP-MS, PE Sciex, Concord, ON, Canada) using the method developed by Li et al. [1]. A Perkin Elmer Series 200 HPLC system equipped with an autosampler was connected to a Perkin Elmer Elan 6100 DRC^{plus} ICP-MS using a 38 cm long piece of Peek tubing (1/16” O.D., 0.007” I.D.) (Supelco, Bellefonte, PA, USA). The sample injection volume was 50 μL. The mobile phase flow rate was 1 mL/min. The column was a SAX PRP-X100 column (50 mm × 4.1 mm × 5 μm) (Hamilton, Reno, NV, USA). A Tukey test in combination with ANOVA at 95% confidence interval was used to determine whether the obtained results for various PC concentrations were statistically different.

A.9. Analysis of NAs

2 mL of the samples was centrifuged for 10 min at 10,000 revolutions per minutes (rpm). Following centrifugation, 500 µL of the supernatant was placed in a 2 mL glass vial with 450 µL of methanol (Fisher Scientific, Ottawa, ON, Canada), and 50 µL of an internal standard (tetradecanoic acid-1-^{13}C) (Sigma-Aldrich, Oakville, ON, Canada) solution was added to result in a concentration of 200 ng/mL in each sample. A Waters Acquity UPLC® System (Milford, MA, USA) was employed for efficient and rapid chromatographic separation of the NAs and oxidized products. Detection was performed with a high resolution Synapt G2 HDMS mass spectrometer equipped with an electrospray ionization source operating in negative ion mode. The system was controlled using MassLynx® ver. 4.1. Tuning and calibration were performed using standard solutions of lucine enkaphenlin and sodium formate, respectively, provided by Waters Corporation (Milford, MA, USA). TargetLynx® ver. 4.1 was used for data analysis of the target compounds, and the relative ratio of the chromatographic peak area of each analyte to that of the internal standard was calculated for subsequent analysis. Chromatographic separations were run on a Waters UPLC Phenyl BEH column (1.7 μm, 150 mm × 1 mm,) using a mobile phase of: A, 10 mM ammonium acetate solution prepared in Optima-grade water, and B, 10 mM ammonium acetate in 50% methanol 50% acetonitrile, both Optima-grade. Gradient elution was as follows: 1% B for the first 2 min, then ramped to 60% B

by 3 min, to 70% B by 7 min, to 95% B by 13 min, followed by a hold until 14 min and finally returned to 1% B, followed by a further 5.8 min re-equilibration time. The flow was constant at 100 μL/min and column temperature was kept at 50°C, while samples were maintained at 4°C.

A.10. Toxicity Test

A model 500 Microtox® analyzer (Strategic Diagnostic Inc.) was used to measure the light emitted by the *Vibrio fischeri* bacteria as a result of their normal metabolic processes, for the toxicity of the samples before and after treatments. Freeze-dried bacteria, reconstitution solution, diluent and an adjustment solution were purchased from Osprey Scientific Inc. (Edmonton, Canada). Microtox® 81.9% screening and basic test protocols were used for the toxicity assessment of samples (analysis performed using 81.9% of initial sample concentrations). The luminescence of reconstituted *Vibrio fischeri* was measured before and after 15 min of exposure to diluted samples. The toxicity of the samples before and after treatments was evaluated with respect to present of luminescence inhibition (% inhibition) and to volume percent of a sample that caused a 20% or 50% decrease in luminescence (IC_{20} and IC_{50}, respectively). Phenol was used as a positive control for the Microtox® assay. Toxicity analyses were performed in triplicates for each sample.

A.11. Adsorption Isotherms

An adsorption isotherm describes the relation between the equilibrium adsorbate concentration in the solution and that on the surface of the adsorbent. Common isotherms are *Langmuir, Freundlich, and Dubinin-Radushkevich (D-R)*[2, 3]. The *Langmuir* isotherm assumes that all the surface sites on the adsorbent have the same affinity for the adsorbate, while the *Freundlich* isotherm assumes that a distribution of sites exist on the adsorbent, which have different affinities for different adsorbates with each site behaving according to the

Langmuir isotherm. The *D-R* isotherm is more general than the *Langmuir* isotherm with the assumption of non-homogenous surface sites, which helps to determine the physical or chemical nature of the adsorption by the free adsorption energy [4]. The *Langmuir*, *Freundlich*, and *Dubinin-Radushkevich* isotherm equations are shown below:

$q = q_m \, \frac{K_{ads}\, C}{1 + K_{ads}\, C}$ *Langmuir* *(1)*

$q = K C^{1/n}$ *Freundlich* *(2)*

$\ln q_e = \ln q_m - \beta \varepsilon^2$ *Dubinin-Radushkevich* *(3)*

where: q_m is the maximum adsorption capacity in mg/g.

K_{ads} (L/mg) and K [(mg/g)(L/mg)$^{1/n}$] indicate the adsorption affinity of the adsorbate.

n is the adsorption intensity.

K_{ads} is used to determine the affinity of the adsorbate for the adsorbent calculated by separation factor (R_L) as shown below:

$R_L = \frac{1}{1 + K_{ads} C_0}$ *(4)*

where: C_0 is the highest initial NAs concentration.

$0 < R_L < 1$ indicates favorable adsorption, and $R_L > 1$ shows unfavourable adsorption of the NAs onto the adsorbents. $R_L = 1$ and $R_L = 0$ show linear and irreversible adsorption.

β (mol^2/kJ^2) is the adsorption energy constant used to calculate the mean free energy.

E (kJ/mol) is the adsorption free energy for the transfer of one mole of adsorbate from the solution to the adsorbent surface. This value determines whether the process is chemisorption ($8 < E < 16$ kJ/mol) or physisorption ($E < 8$ kJ/mol). This value is calculated as follows:

$$E = 1/\sqrt{2\beta}.$$

ε is the Polanyi potential calculated as shown below:

$$\varepsilon = \mathrm{RT}\ln\left(1 + \frac{1}{C_e}\right) \qquad (5)$$

where: R is the gas constant (8.314 J K^{-1} mol^{-1}).

T is the absolute temperature (K).

A.11. References

1. Li, X. S.; Glasauer, S.; Le, X. C., Speciation of vanadium in oil sand coke and bacterial culture by high performance liquid chromatography inductively coupled plasma mass spectrometry (vol 602, pg 17, 2007). *Analytica Chimica Acta* 2009**,** *648*, (1), 128-128.

2. Danish, M.; Hashim, R.; Ibrahim, M. N. M.; Rafatullah, M.; Sulaiman, O.; Ahmad, T.; Shamsuzzoha, M.; Ahmad, A., Sorption of copper(II) and nickel(II) ions from aqueous solutions using calcium oxide activated date (phoenix dactylifera) stone carbon: equilibrium, kinetic, and thermodynamic studies. *Journal of Chemical and Engineering Data* 2011**,** *56*, (9), 3607-3619.

3. Kilic, M.; Apaydin-Varol, E.; Putun, A. E., Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: Equilibrium, kinetics and thermodynamics. *Journal of Hazardous Materials* 2011**,** *189*, (1-2), 397-403.

4. Auta, M.; Hameed, B. H., Preparation of waste tea activated carbon using potassium acetate as an activating agent for adsorption of Acid Blue 25 dye. *Chemical Engineering Journal* 2011**,** *171*, (2), 502-509.

APPENDIX B: Supporting Figures

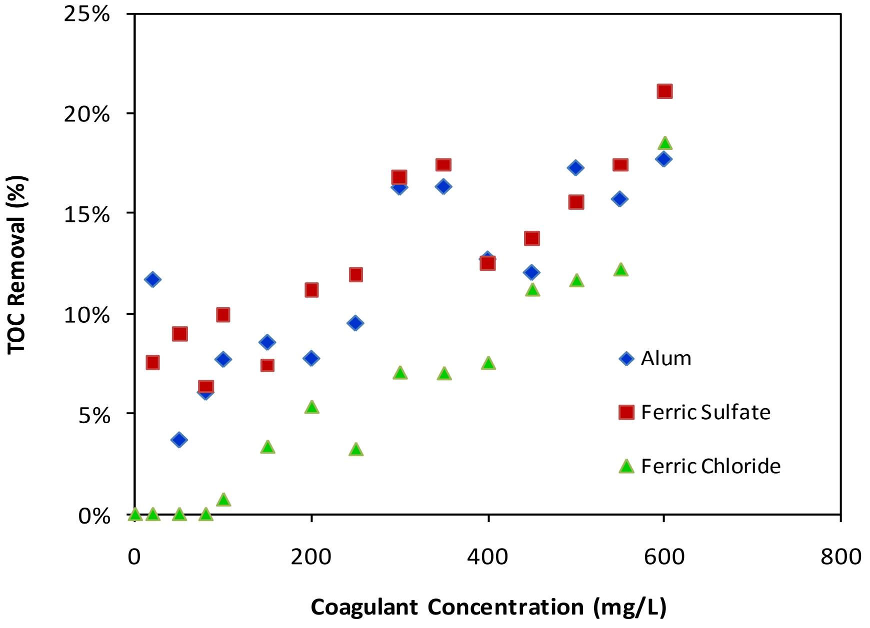

Figure B1. TOC removal with increasing the concentrations of alum, ferric sulfate, and ferric chloride.

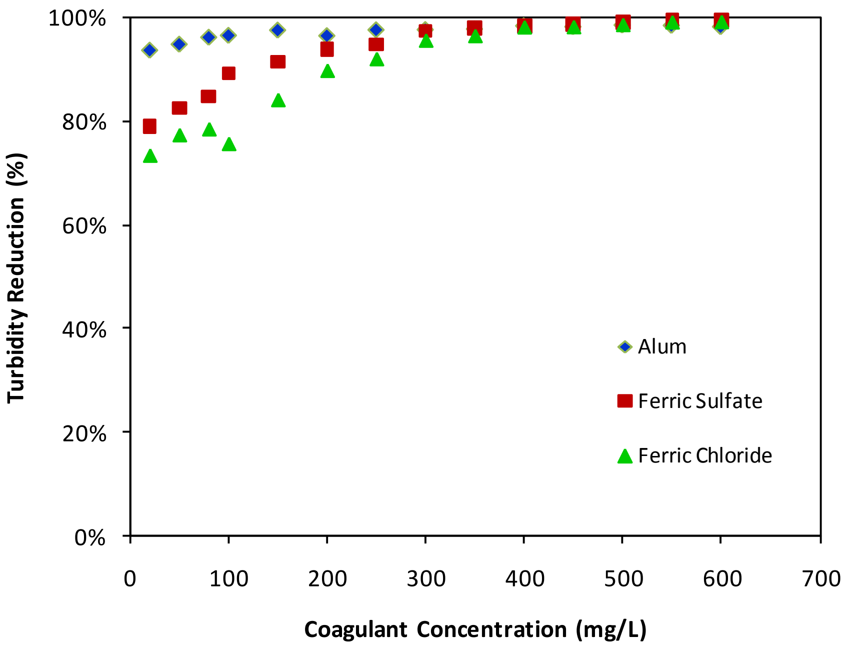

Figure B2. Turbidity reduction with increasing the concentrations of alum, ferric sulfate, and ferric chloride.

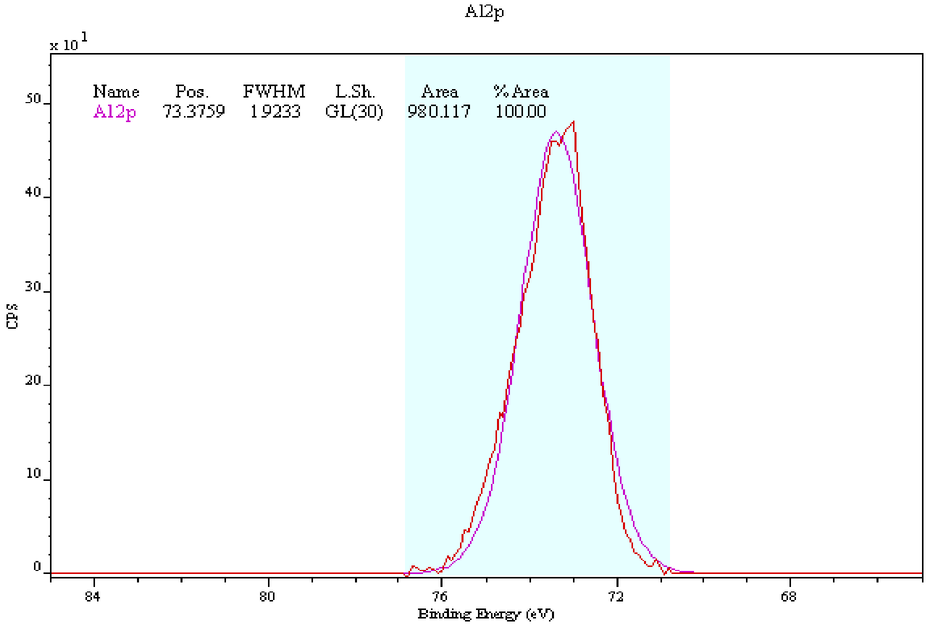

Figure B3. Peak deconvolution of Al_{2p} after CFS treatment with 250 mg/L alum.

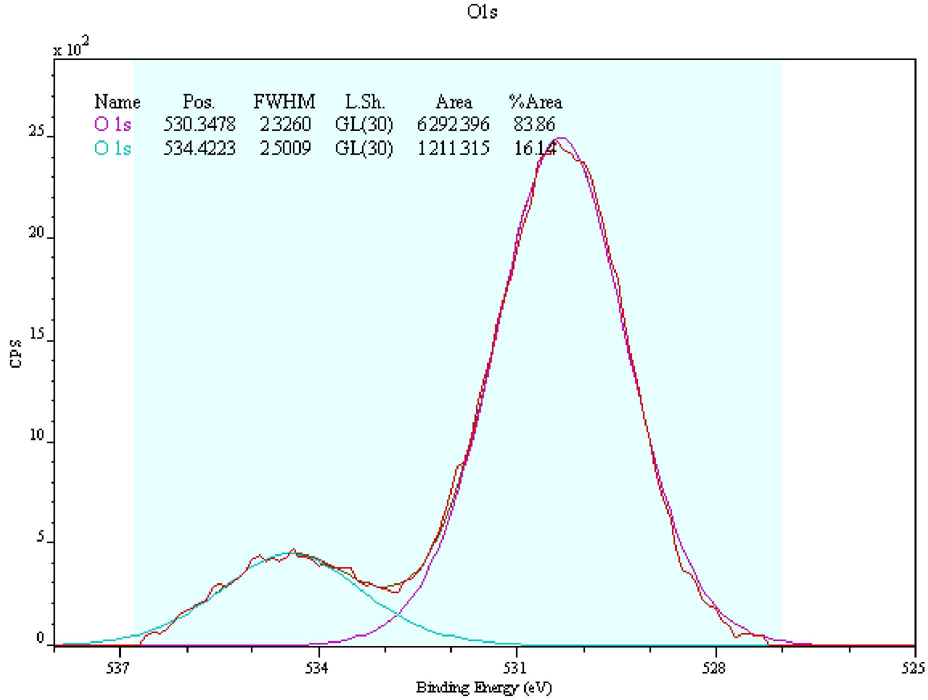

Figure B4. Peak deconvolution of O_{1s} after CFS treatment with 250 mg/L alum.

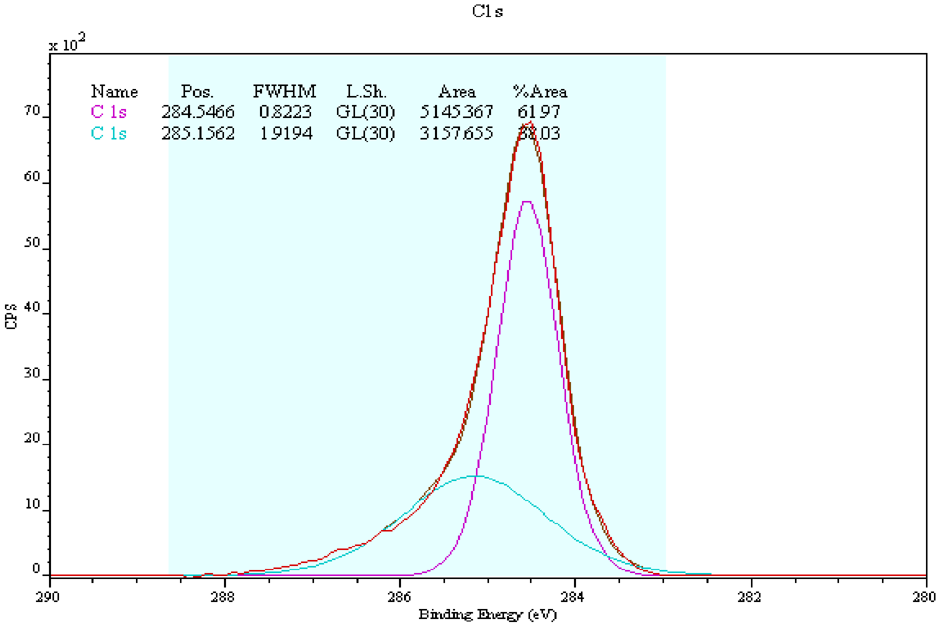

Figure B5. Peak deconvolution of C_{1s} after CFS treatment with 250 mg/L alum.

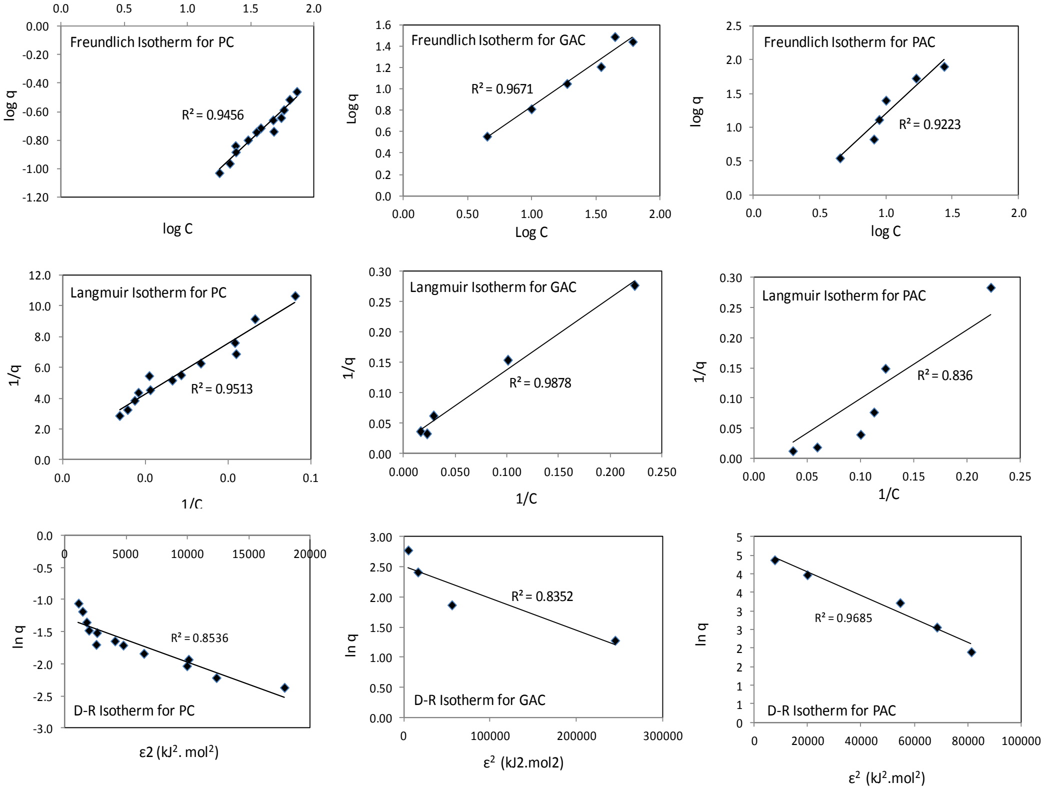

Figure B6. *Freundlich*, *Langmuir*, and *Dubinin-Radushkevich* isotherm plots for PC, GAC, and PAC.

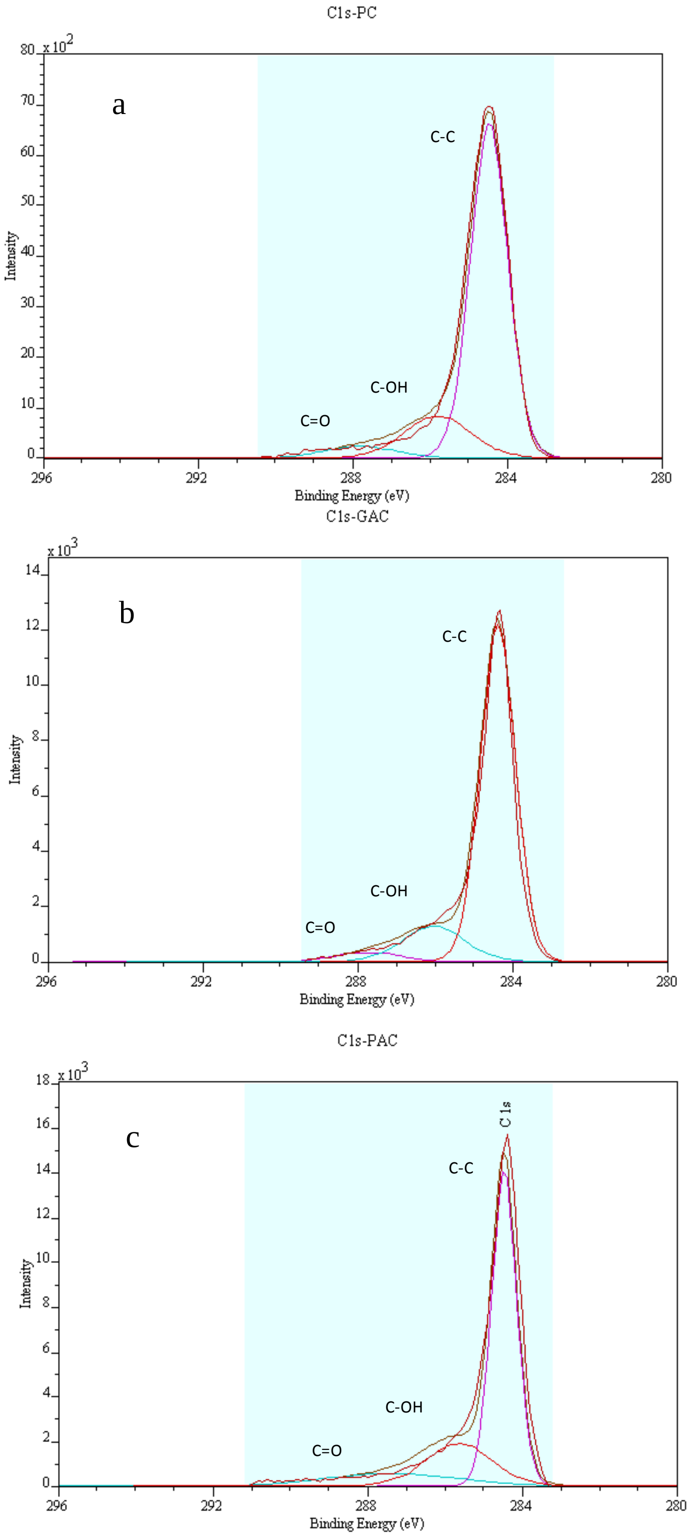

Figure B7. Peak deconvolution of C_{1s} of (a) PC, (b) GAC, and (c) PAC.

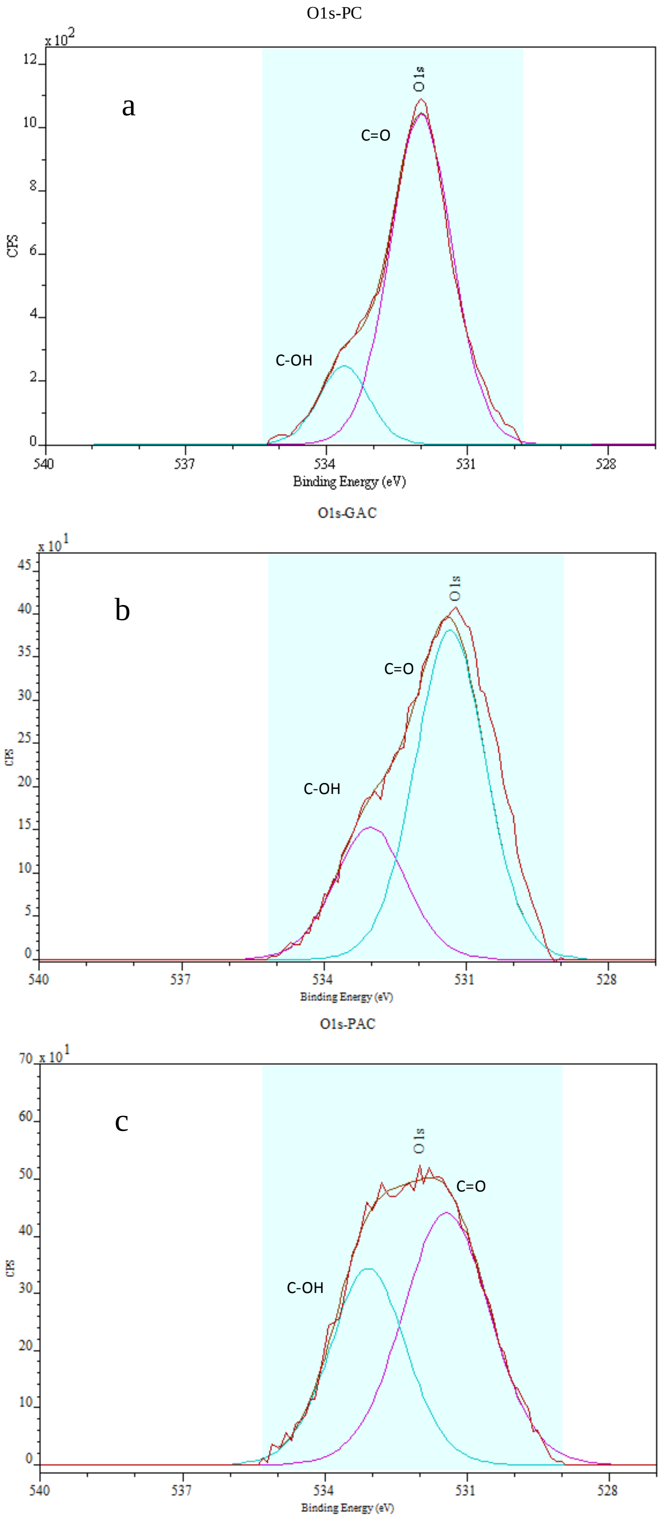

Figure B8. Peak deconvolution of O_{1s} for (a) PC, (b) GAC, and (c) PAC.

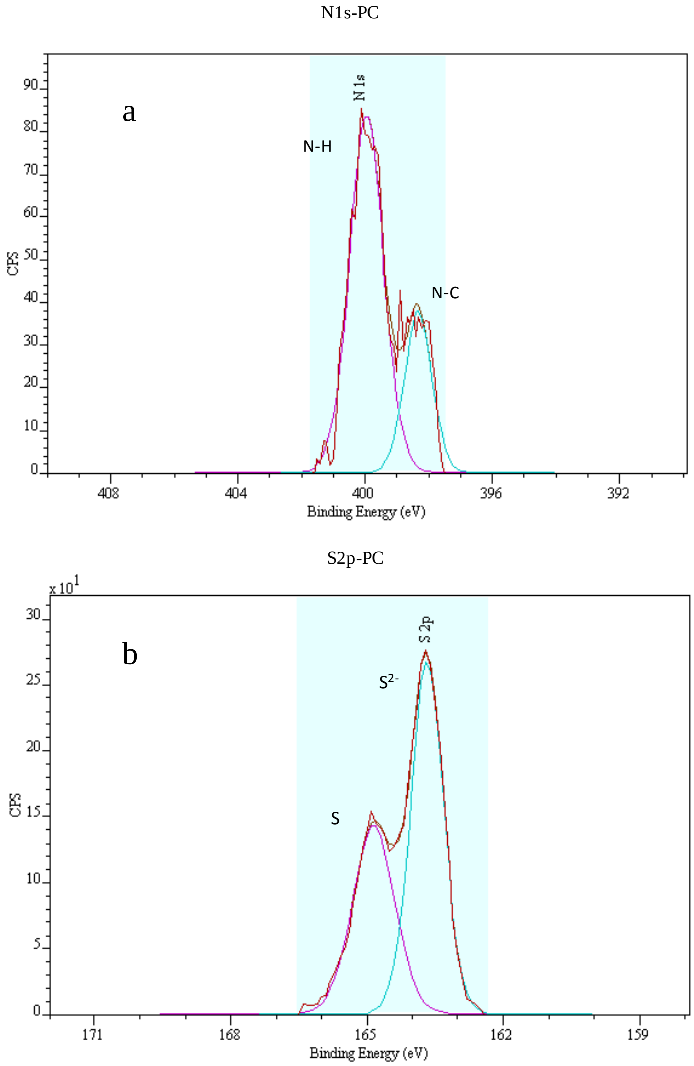

Figure B9. Peak deconvolution of (a) N_{1s} and (b) S_{2p} in PC.

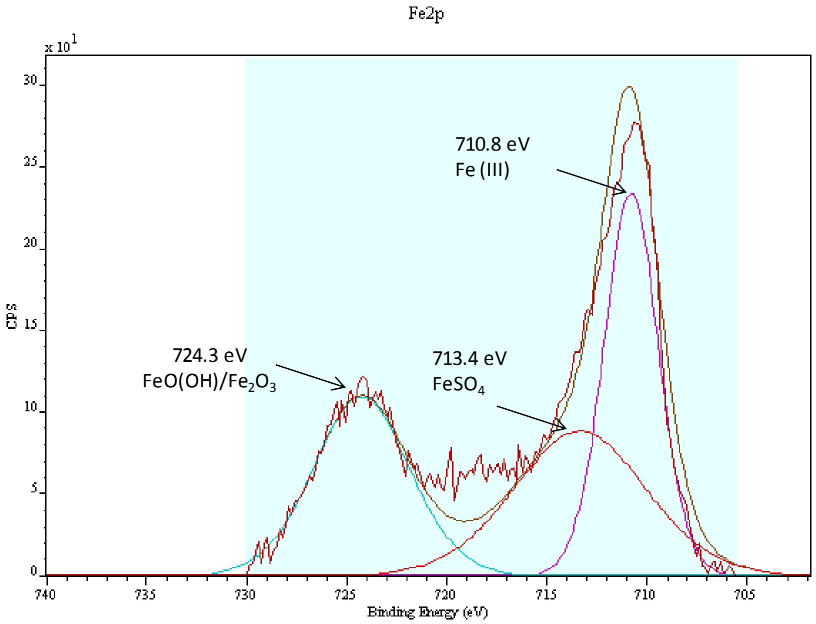

Figure B10. Peak deconvolution of Fe_{2p} on the ZVI surface at 25 g/L of ZVI.

APPENDIX C: Naphthenic Acid Speciation Tables

Table C1. Concentration of NA species in OSPW control sample as a function of the carbon number (*n*) and the cyclicity (-*Z*)

n	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**
10	0.029408	0.058774				
11	0.046943	0.189781	0.062416			
12	0.141541	0.806238	0.221337			
13	0.203017	1.653681	0.953381	0.091292		
14	0.200181	2.079854	1.940645	0.298808		
15	0.124829	1.998283	2.94565	0.764818	0.327834	
16	0.052371	0.941033	2.050173	0.977018	0.645687	
17		0.207893	0.700812	0.674231	0.780152	1.723173
18		0.045881	0.1765	0.266455	0.672847	1.636531
19				0.061413	0.282464	1.064756
20					0.095097	0.523753
21						0.099783

Table C2. Concentration and removal of NA species in ZVI at 25 g/L as a function of the carbon number (*n*) and the cyclicity (-*Z*)

	Concentration of NA species						**Removal of NA species**					
n	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**
10	0.019176	0.035743					34.8	39.2				
11	0.0	0.104992	0.046684				100.0	44.7	25.2			
12	0.089234	0.330434	0.128028				37.0	59.0	42.2			
13	0.096463	0.673715	0.408417	0.072556			52.5	59.3	57.2	20.5		
14	0.084092	0.780473	0.738091	0.161242			58.0	62.5	62.0	46.0		
15	0.050048	0.753164	1.075887	0.301774	0.161089		59.9	62.3	63.5	60.5	50.9	
16	0.0	0.328688	0.683584	0.353476	0.272561		100.0	65.1	66.7	63.8	57.8	
17		0.065014	0.234807	0.241174	0.316093	0.583898		68.7	66.5	64.2	59.5	66.1
18		0.0	0.059081	0.083894	0.197237	0.548264		100.0	66.5	68.5	70.7	66.5
19				0.0	0.080272	0.35879				100.0	71.6	66.3
20					0.0	0.178526					100.0	65.9
21						0.042974						56.9

Table C3. Concentration and removal of NA species in CZVI at 25 gZVI/L as a function of the carbon number (*n*) and the cyclicity (-*Z*)

Concentration of NA species							**Removal of NA species**					
n	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**
10	0.0	0.02928					100.0	50.2				
11	0.0	0.057461	0.036945				100.0	69.7	40.8			
12	0.0	0.123075	0.074664				100.0	84.7	66.3			
13	0.033588	0.210521	0.154239	0.059402			83.5	87.3	83.8	34.9		
14	0.0	0.208104	0.197081	0.076612			100.0	90.0	89.8	74.4		
15	0.0	0.122112	0.21492	0.103104	0.059789		100.0	93.9	92.7	86.5	81.8	
16	0.0	0.028373	0.083998	0.067152	0.082134		100.0	97.0	95.9	93.1	87.3	
17		0.0	0.0	0.0	0.053342	0.107239		100.0	100.0	100.0	93.2	93.8
18		0.0	0.0	0.0	0.023352	0.085329		100.0	100.0	100.0	96.5	94.8
19				0.0	0.0	0.0				100.0	100.0	100.0
20					0.0	0.0					100.0	100.0
21						0.0						100.0

Table C4. Concentration and removal of NA species in PC (200 g/L) as a function of the carbon number (*n*) and the cyclicity (-*Z*)

Concentration of NA species							**Removal of NA species**					
n	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**
10	0.029684	0.048202					0.0	18.0				
11	0.068953	0.17286	0.034539				0.0	8.9	44.7			
12	0.12389	0.709164	0.207992				12.5	12.0	6.0			
13	0.16412	1.513328	0.861824	0.099737			19.2	8.5	9.6	0.0		
14	0.160493	1.797417	1.702622	0.259647			19.8	13.6	12.3	13.1		
15	0.093555	1.581941	2.530034	0.678226	0.283773		25.1	20.8	14.1	11.3	13.4	
16	0.0	0.560727	1.449445	0.78782	0.544954		100.0	40.4	29.3	19.4	15.6	
17		0.082172	0.391728	0.454775	0.597355	1.301685		60.5	44.1	32.5	23.4	24.5
18		0.0	0.060798	0.139142	0.393872	1.103219		100.0	65.6	47.8	41.5	32.6
19				0.0	0.104182	0.597328				100.0	63.1	43.9
20					0.0	0.247703					100.0	52.7
21						0.0						100.0

Table C5. Concentration of the oxidized NA species in OSPW control as a function of the carbon number (*n*) and the cyclicity (-*Z*)

n	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**
10	0.060038	0.092074				
11	0.104223	0.303592	0.240138			
12	0.187831	0.520307	0.576697			
13	0.228443	0.798373	1.081598	0.564392		
14	0.19746	1.110212	2.032725	1.24767		
15	0.130749	0.876348	1.836855	1.446507	0.457619	
16	0.074018	0.515252	1.154271	1.115856	0.586859	
17		0.199415	0.510553	0.592184	0.530318	0.501069
18			0.219318	0.336493	0.390208	0.563251
19				0.171045	0.217255	0.447037
20				0.091487	0.14274	0.290122
21						0.154827

Table C6. Concentration and increase of oxidized NA species in ZVI at 25 g/L as a function of the carbon number (*n*) and the cyclicity (-*Z*)

	Concentration of NA species						**Increase in the oxidized NA species concentration**					
n	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**
10	0	0.12462					0.0	35.3				
11	0.14074	0.29767	0.33137				35.0	0.0	38.0			
12	0.23166	0.71123	0.84121				23.3	36.7	45.9			
13	0.22740	1.17564	1.55244	0.68435			0.0	47.3	43.5	21.3		
14	0.26627	1.70931	2.88558	1.62989			34.8	54.0	42.0	30.6		
15	0.12980	1.21841	2.66980	1.87820	0.59000		0.0	39.0	45.3	29.8	28.9	
16	0.0	0.63645	1.66617	1.54734	0.72840			23.5	44.3	38.7	24.1	
17		0.21676	0.64614	0.78976	0.64028	0.68526		8.7	26.6	33.4	20.7	36.8
18			0.25202	0.31981	0.48852	0.78331			14.9	0.0	25.2	39.1
19			0.09628	0.10926	0.24702	0.54244			0.0	0.0	13.7	21.3
20					0.10826	0.30153					0.0	3.9
21						0.0						0.0

Table C7. Concentration and removal of oxidized NA species in CZVI at 25 g/L as a function of carbon number (*n*) and the cyclicity (-*Z*)

Concentration of NA species							**Removal of oxidized NA species**					
n	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**
10	0	0.09373					100.0	0.0				
11	0.08033	0.24193	0.21978				22.9	20.3	8.5			
12	0.12279	0.51356	0.58821				34.6	1.3	0.0			
13	0.14356	0.74707	0.94899	0.47367			37.2	6.4	12.3	16.1		
14	0.15848	1.14376	1.86752	0.99406			19.7	0.0	8.1	20.3		
15	0.07714	0.72033	1.58724	1.11153	0.38408		41.0	17.8	13.6	23.2	16.1	
16		0.30498	0.77701	0.78673	0.40416			40.8	32.7	29.5	31.1	
17			0.21471	0.30503	0.28486	0.37436		100.0	57.9	48.5	46.3	25.3
18				0.10246	0.17040	0.33380				69.5	56.3	40.7
19						0.11351						74.6
20						0.07262						75.0
21						0.0						100.0

Table C8. Concentration of NA species in de-oxygenated OSPW control as a function of the carbon number (*n*) and the cyclicity (-*Z*)

n	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**
10	0.065499	0.080268				
11	0.162026	0.402688	0.115799			
12	0.307374	1.579319	0.510823			
13	0.463102	3.575214	2.006466	0.222444		
14	0.369834	4.296581	3.975926	0.545615		
15	0.301898	4.342384	6.47507	1.751853	0.742233	
16	0.10423	2.022695	4.222258	2.223254	1.440698	
17		0.433029	1.604388	1.316388	1.767072	3.730893
18			0.304515	0.663288	1.334031	3.549312
19					0.705258	2.225318
20					0.211421	1.288232
21						0.280185

Table C9. Concentration and removal of NA species in de-oxygenated ZVI at 25 g/L as a function of the carbon number (*n*) and the cyclicity (-*Z*)

Concentration of NA species							**Removal of NA species**					
n	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**
10	0.052785	0.081864					19.4					
11	0.14789	0.26047	0.10425				8.7	35.3	10.0			
12	0.217397	1.162915	0.373324				29.3	26.4	26.9			
13	0.335441	2.669358	1.482361	0.156335			27.6	25.3	26.1	29.7		
14	0.263583	3.301604	2.765969	0.438136			28.7	23.2	30.4	19.7		
15	0.238471	2.988023	4.818667	1.187686	0.476551		21.0	31.2	25.6	32.2	35.8	
16	0.06918	1.441713	3.14227	1.489908	1.085512		33.6	28.7	25.6	33.0	24.7	
17		0.291116	1.093288	0.96423	1.282963	2.63372		32.8	31.9	26.8	27.4	29.4
18			0.26388	0.420223	1.012426	2.697208			13.3	36.6	24.1	24.0
19					0.469184	1.545728					33.5	30.5
20					0.138398	0.884441					34.5	31.3
21						0.209658						25.2

Table C10. Concentration and removal of NA species in de-oxygenated CZVI at 25 g/L as a function of the carbon number (*n*) and the cyclicity (-*Z*)

Concentration of NA species							**Removal of NA species**					
n	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**	**-*Z*=2**	**-*Z*=4**	**-*Z*=6**	**-*Z*=8**	**-*Z*=10**	**-*Z*=12**
10	0.040118	0.063944					38.8	20.3				
11	0.094185	0.222426	0.072267				41.9	44.8	37.6			
12	0.151036	0.799821	0.266959				50.9	49.4	47.7			
13	0.220312	1.689221	1.021954	0.127584			52.4	52.8	49.1	42.6		
14	0.144786	2.007412	1.857379	0.265208			60.9	53.3	53.3	51.4		
15	0.052675	1.387687	2.489522	0.796995	0.35708		82.6	68.0	61.6	54.5	51.9	
16	0.0	0.439985	1.231241	0.792994	0.604082		100.0	78.2	70.8	64.3	58.1	
17		0.0	0.234485	0.333281	0.552615	1.369326		100.0	85.4	74.7	68.7	63.3
18			0.0	0.093791	0.291438	1.056078			100.0	85.9	78.2	70.2
19					0.106156	0.394346					84.9	82.3
20					0.0	0.144376					100.0	88.8
21						0.0						100.0

Copyright Clearance Center RightsLink®

Home Account Info Help

ACS Publications High quality. High impact.

Title:	The Impact of Metallic Coagulants on the Removal of Organic Compounds from Oil Sands Process-Affected Water
Author:	Parastoo Pourrezaei, Przemysław Drzewicz, Yingnan Wang, Mohamed Gamal El-Din, Leonidas A. Perez-Estrada, Jonathan W. Martin, Julie Anderson, Steve Wiseman, Karsten Liber, and John P. Giesy
Publication:	Environmental Science & Technology
Publisher:	American Chemical Society
Date:	Oct 1, 2011

Logged in as:
Parastoo Pourrezaei

LOGOUT

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.