Development and application of Fenton and UV-Fenton processes at natural pH using chelating agents for the treatment of oil sands process-affected water

By

Ying Zhang

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

Doctor of Philosophy

in

Environmental Engineering

Department of Civil and Environmental Engineering

University of Alberta

ABSTRACT

The increasing amount of oil sands process-affected water (OSPW), its high toxicity towards aquatic organisms due to naphthenic acids (NAs) and other organics, and the zero discharge practice of the oil sands industry urge researchers to seek effective approaches for its treatment. Advanced oxidation processes (AOPs) have been successfully used to degrade recalcitrant NAs and reduce the overall toxicity of OSPW towards selected test organisms. Fenton and photo-Fenton processes as very common AOPs have not been applied on the OSPW treatment yet. Due to the precipitation of Fe at pH > 3, nitrilotriacetic acid (NTA) and [S,S]-ethylenediamine-N,N'-disuccinic acid ([S,S]-EDDS) have been employed to form complex with iron and enable Fenton reactions at high pH. The overall goal of this research was, therefore, to investigate the reaction mechanisms and kinetics of the (UV-)chelate-modified Fenton processes on the treatment of OSPW.

In the first stage, this research focused on the optimization of the NTA- and EDDS-Fenton processes in the degradation of cyclohexanoic acid (CHA), a model NA compound. The final CHA removal under the optimum conditions was 87% for NTA-Fenton and 64% for EDDS-Fenton. Hydroxyl radical ($^\bullet OH$) was the main radical responsible for the CHA removal in both processes, while superoxide radical ($^\bullet O_2^-$) played a minor role. Oxy-CHA, hydroxyl-CHA, and dihydroxyl-CHA were detected as the CHA oxidation products. The second-order rate constants of $^\bullet OH$ with CHA, NTA, and EDDS at pH 8 were investigated and obtained as $4.09 \pm 0.39 \times 10^9$, $4.77 \pm 0.24 \times 10^8$, and $2.48 \pm 0.43 \times 10^9$ $M^{-1}s^{-1}$, respectively. The consecutive addition of hydrogen peroxide (H_2O_2) and Fe-EDDS in the EDDS-Fenton process led to a higher removal of CHA compared with adding the reagents at a time. However, the H_2O_2 dosing mode in the

NTA-Fenton process did not have a significant impact on the CHA removal. The mechanisms of Fe(II) oxidation and Fe(III) reduction in the NTA/EDDS-Fenton processes were proposed and discussed based on the redox potentials of Fe(III/II)NTA, Fe(III/II)EDDS, $O_2/O_2^{\bullet-}$, and $H_2O_2/O_2^{\bullet-}$.

In the second stage of the research, UV irradiation was applied in different processes at pH 3 and 8. Compared to UV-H_2O_2, Fenton, UV-Fenton, NTA-Fenton, and UV-Fe-NTA processes, UV-NTA-Fenton at pH 3 exhibited the highest efficiency for the H_2O_2 decomposition, CHA removal, and NTA degradation. H_2O_2-Fe(III)NTA adduct was related to the high amount of Fe in the UV-NTA-Fenton system at pH 8 compared to that in the UV-Fe-NTA system. The co-complexing effect of borate buffer helped to keep iron soluble at pH 8; however, it imposed a negative influence on the CHA degradation in the UV-NTA-Fenton process.

In the third stage of the research, the removals of phenol and hydrogen sulfide (H_2S) as toxic contaminants in OSPW were investigated. Tetrapolyphosphate (TPP) is a chelating agent of iron and the catalytic ability of Fe(III)TPP in the oxidation of H_2S was investigated. The formation of Fe(III)TPP-HS^- intermediate in the reaction of Fe(III)TPP and HS^- was proposed. The second-order rate constant of the direct reaction between Fe(III)TPP and HS^- at pH 9 was obtained as $4.36\pm0.17\ M^{-1}s^{-1}$. The oxidation of Fe(II)TPP by O_2 followed a four-step reaction mechanism, and the reaction kinetic parameters were calculated based on the half-wave potential ($E_{1/2}$) of Fe(III/II)TPP. Low level of phenol degradation was found in the Fe(III)TPP-catalytic desulfurization process.

At the end of the research, the application of the UV-NTA/EDDS-Fenton processes in the treatment of OSPW at natural pH was investigated. The photodecomposition of Fe(III)NTA and Fe(III)EDDS under UV irradiation in MilliQ water and OSPW was described and compared. UV-NTA-Fenton exhibited higher efficiency than UV-EDDS-Fenton in the removal of acid

extractable organic fraction and aromatics. NAs removal in the UV-NTA-Fenton process was much higher than that in the UV-H_2O_2 and NTA-Fenton processes. Both UV-NTA-Fenton and UV-EDDS-Fenton presented promoting effect on the acute toxicity of OSPW towards *Vibrio fischeri*. No significant change of the NTA toxicity occurred during the photolysis of Fe(III)NTA; however, the acute toxicity of EDDS towards *Vibrio fischeri* increased as the photolysis of Fe(III)EDDS proceeded. Considering the contaminants removal and the toxicity effect, NTA is a much better agent than EDDS for the application of UV-Fenton process as a very promising approach for OSPW remediation, and the process deserves more in-depth research on the toxicity depletion and organics removal.

PREFACE

All of the research in this thesis was designed and conducted by myself and supervised by Professor Mohamed Gamal El-Din at the University of Alberta.

Chapter 2 consists of the contents of a journal article published in Chemical Engineering Journal, 292 (2016) 340-347. The contribution of the coauthor is as follows:

- Dr. Nikolaus Klamerth contributed to the experimental plan and manuscript edits.

Chapter 3 contains the contents of a journal article submitted to the Journal of Hazardous Materials. The contributions of the coauthors are as follows:

- Dr. Nikolaus Klamerth contributed to the experimental plan and manuscript edits.
- Dr. Selamawit Ashagre Messele contributed to the manuscript edits.
- Dr. Pamela Chelme-Ayala contributed to the manuscript edits.
- Mr. Béla Reiz from the Department of Chemistry at the University of Alberta contributed to the detection of the CHA degradation products.
- Dr. Ted Sargent's group from the Department of Electrical and Computer Engineering at the University of Toronto contributed to the measurement of half-wave potentials.

Chapter 4 is an adaptation of a journal article, which has been submitted to the Journal of Hazardous Materials. The contributions of the coauthors are as follows:

- Dr. Nikolaus Klamerth contributed to the manuscript edits.
- Dr. Pamela Chelme-Ayala contributed to the manuscript edits.
- Ms. Jing Zheng from the Department of Chemistry at the University of Alberta

contributed to the measurement of CHA.

Chapter 5 presents the results for a journal article, which will be submitted to Applied Catalysis B: Environmental. The contributions of the coauthors are as follows:

- Dr. Ali Safarzadeh-Amiri contributed to the experimental plan and manuscript edits.
- Dr. Nikolaus Klamerth contributed to the manuscript edits.
- Dr. Pamela Chelme-Ayala contributed to the manuscript edits.
- Dr. Ted Sargent's group from the Department of Electrical and Computer Engineering at the University of Toronto contributed to the measurement of half-wave potentials.

Chapter 6 consists of the contents for a journal article, which will be submitted to Environmental Science & Technology. The contributions of the coauthors are as follows:

- Dr. Nikolaus Klamerth contributed to the manuscript edits.
- Dr. Pamela Chelme-Ayala contributed to the manuscript edits.
- Dr. Rongfu Huang contributed to the measurement of naphthenic acid.
- Mr. Guangcheng Chen from the Department of Earth & Atmospheric Sciences at the University of Alberta contributed to the measurement of metal ions.
- Dr. Ted Sargent's group from the Department of Electrical and Computer Engineering at the University of Toronto contributed to the measurement of half-wave potentials.
- Mr. Mark Miskolzie from the Department of Chemistry at the University of Alberta contributed to the NMR analysis.

All the research work was done by myself except the above mentioned contributions from the coauthors.

DEDICATION

This work is dedicated to my lovely father, mother, other relatives, and my dear friends who influence me in a great way.

ACKOWLEDGEMENTS

First and foremost, I would like to express my great appreciation to my supervisor Dr. Gamal El-Din for taking me into the group and for his kindness, support, patience and supervision for the last three years. I also want to thank him for providing me a wonderful internship experience. I would not be able to proceed through the doctoral program and complete my dissertation without his priceless advice and encouragement.

I am deeply grateful to Dr. Nikolaus Klamerth, who gave me valuable suggestions and enormous support during this research. He helped me to think as a researcher and to express my ideas in a clear and concise manner. He reviewed all of my papers and I benefitted a lot from his comments and advice. Thanks to Dr. Yanyan Zhang, my dear sister, who encouraged me a lot and helped me out of glooms every time I felt stressed and depressed. Her kindness and patience always calmed me down. I could not imagine what my life would be like without her.

Truly thanks to Dr. Pamela Chelme-Ayala for reviewing all of my papers, submitting them to the journals, and helping me with the replies to reviewers. Moreover, she gave me valuable suggestions for the thesis preparation. I greatly appreciate everything she did for me. I also would like to thank Miss Maria Demeter and Miss Nian Sun, who taught me many things at the beginning of my project.

I also want to thank Dr. Ali Safarzadeh-Amiri from Trojan Technologies, who supervised me in my internship and gave me some precious advice. Thank Miss Shimiao Dong for helping me doing some experiments. Thanks also go to all the staff in the Department of Civil and Environmental Engineering who made it possible for me to complete my Ph.D. program.

I really acknowledge the support from my dear friends Jingkai Xue, Chunkai Huang, Chengjin Wang, Chao li, Yuan Chen, Shimiao Dong, and Gaoteng Fan. They brought me so many joys and were always around when I needed help.

Special thanks to my father Jikui Zhang, mother Zhaoping Cui, and brother Fuqiang Zhang for their support, understanding, and encouragement, which means everything to me.

I am very grateful for a generous Ph.D. Student Scholarship (2012-2016) from China Scholarship Council.

This research was supported by a research grant from a Natural Sciences and Engineering Research Council of Canada (NSERC) Senior Industrial Research Chair (IRC) in Oil Sands Tailings Water Treatment through the support by Syncrude Canada Ltd., Suncor Energy Inc., Shell Canada, Canadian Natural Resources Ltd., Total E&P Canada Ltd., EPCOR Water Services, IOWC Technologies Inc., Alberta Innovates - Energy and Environment Solution, and Alberta Environment and Parks. The financial supports provided by Trojan Technologies and an NSERC Collaborative Research and Development (CRD) grant are also acknowledged.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

AOP	advanced oxidation process
APCAs	aminopolycarboxylic acids
BTEX	benzene, toluene, ethyl benzene, and xylenes
CHA	cyclohexanoic acid
$CHCl_3$	chloroform
c-NAs	classical naphthenic acids
CO_2	carbon dioxide
DMSO	dimethyl sulfoxide
DTPA	diethylenetriaminepentaacetic acid
E^0	standard electrode potential
$E_{1/2}$	half-wave potential
EDTA	ethylenediaminetetraacetic acid
EGTA	ethylene bis(oxyethyleneitrilo)tetraacetate
FT-IR	Fourier transform infrared spectroscopy
HEDTA	hydroxyethylenediaminetriacetic aicd
H_2O_2	hydrogen peroxide
HPLC	high-performance liquid chromatography
H_2S	Hydrogen sulfide

IDA	iminodiacetic acid
KO_2	potassium superoxide
LP UV lamp	low-pressure UV lamp
LRSR	liquid redox sulfur recovery
MP UV lamp	medium-pressure UV lamp
MW	molecule weight
NAs	naphthenic acids
NHE	normal hydrogen electrode
NMR	^{1}H nuclear magnetic resonance
NTA	nitrilotriacetic acid
$O_2^{\bullet -}$	superoxide radical
OECD	economic cooperation and development
$^{\bullet}OH$	hydroxyl radical
OSHA	Occupational Safety & Health Administration
OSPW	oil sands process-affected water
oxy-NAs	oxidized naphthenic acids
PAH	polyaromatic hydrocarbons
pCBA	para-chlorobenzoic acid
p*K*a	acid dissociation constant

R^2	R-squared values
[R,R]-EDDS	[R,R]-ethylenediamine-N,N’-disuccinic acid
[R,S]-EDDS	[R,S]-ethylenediamine-N,N’-disuccinic acid
SFS	synchronous fluorescence spectrum
SHE	standard hydrogen electrode
[S,S]-EDDS	[S,S]-ethylenediamine-N,N’-disuccinic acid
TBA	tert-butyl alcohol
TOF-MS	time-of-flight mass spectrometer
TPP	Tetrapolyphosphate
UPLC	ultra-performance liquid chromatography
UV	ultraviolet light

1 GENERAL INTRODUCTION

1.1 Background

The global energy demand will probably increase by approximate 50% over the next two decades, and this will enhance the exploration of unconventional and former unprofitable fossil fuel resources such as oil sands (Anderson et al., 2012; Oil Sands Ministerial Strategy Committee, 2006; Veil et al., 2009). Canada's oil sands in the northern Alberta region of Athabasca are the world's 3rd largest known oil deposits, with a volume of 900 billion barrels. 170 billion barrels are currently considered as economically recoverable for the conversion to oil (Burrowes et al., 2005). The bitumen is mined and extracted by an alkaline hot water process at pH~8 (the Clark caustic hot water method) and requires more than 3 barrels of fresh water for every barrel of bitumen (Allen, 2008a; Wang, 2011a). The process leads to the generation of oil sands process-affected water (OSPW), which is highly saline and acutely toxic to plants (Fattah & Wort, 1970; Kamaluddin & Zwiazek, 2002; Kannel & Gan, 2012; Wort & Patel, 1970; Wort et al., 1973), fish (Dokholyan & Magomedov, 1984; Dorn et al., 1992; Kannel & Gan, 2012; Mackinnon & Boerger, 1986), mammals (Kannel & Gan, 2012; Rogers et al., 2002b), zooplanktons (Dokholyan & Magomedov, 1984; Kannel & Gan, 2012), phytoplanktons (Hayes, 2007; Kannel & Gan, 2012; Leung et al., 2003; Leung et al., 2001) and amphibians (Kannel & Gan, 2012; Pollet & Bendell - Young, 2000).

Storage of OSPW in settling ponds has been accepted as a temporary solution due to the zero discharge practice, which the oil companies follow and is in accordance with the provincial environmental legislation (Alberta Environmental Protection and Enhancement Act, 1993). The accumulation of OSPW in the tailing ponds has brought several environmental concerns

(Pourrezaei, 2013; Zubot, 2010). The leaching of OSPW from the ponds to the adjacent rivers can pose a serious threat to the aquatic biota (Allen, 2008a, 2008b; Grewer et al., 2010; Pourrezaei, 2013), and can contaminate the groundwater by long time infiltrating. Surface area of the tailing ponds is more than 70 square kilometers (Allen, 2008a; Dominski, 2007) and more than 1 billion m^3 of OSPWs is estimated to be piled up in the Athabasca region by 2025 (Kannel & Gan, 2012). This can be compared with 150 million m^3 of wastewater that a wastewater treatment plant would treat every year (Afzal, 2013). The increasing OSPW volume and its high toxicity to the environment have been attracting the attention of researchers since 1980s (Allen, 2008a). Numerous articles have been published on the impact of OSPW and the possible treatment solutions (Scott et al., 2008; Tollefsen et al., 2012; Zhou et al., 2008). However, a cost-effective treatment approach for OSPW remediation has not been proposed so far.

1.2 Characteristics of OSPW

The composition of OSPW depends on the ore quality, age, source, and extraction processes, but generally the proportions are 70-80 wt% water, 20-30 wt% solids (i.e., sand, silt, and clays), and 1-3 wt% bitumen (Allen, 2008a; Kannel & Gan, 2012). The pH of OSPW is typically between 7.8-8.5 (Afzal, 2013; Mikula et al., 1996). Dissolved solids in the tailings ponds are in the main form of sodium (~500 to 700 mg/L), chloride (~75 to 550 mg/L), sulphate (~200 to 300 mg/L) (Allen, 2008a), and bicarbonate (700 to 1000 mg/L) (Pourrezaei, 2013). Organic compounds in OSPW include unrecovered bitumen (oil and grease), naphthenic acids (NAs), polyaromatic hydrocarbons (PAHs), BTEX (benzene, toluene, ethyl benzene, and xylenes), and as well as other organic acids such as fulvic and humic acids (Allen, 2008a; Madill et al., 2001; Mohamed et al., 2011; Pourrezaei, 2013; Rogers et al., 2002a). The concentration of the dissolved organic matter (DOM), comprised of organic acids mostly, ranges from 50 to 100 mg/L. NAs hold a percentage up to 80% of DOM and are one of the main species responsible for the OSPW toxicity (Allen, 2008a; Nelson et al., 1993). The general characteristics of OSPW are shown in **Table 1-1**.

Table 1-1. Characterization of Oil Sands Process-Affected Water (Alpatova et al., 2014; Islam et al., 2014; Kim el al., 2013; Pourrezaei et al., 2014; Wang et al., 2013; Wang et al., 2015).

Parameter	Range
pH	8.3-8.7
Turbidity (NTU)	71.6-213.3
Conductivity (μS/cm)	3459-4500
Total suspended solids (TSS) (mg/L)	97-221
Total dissolved solids (TDS) (mg/L)	2477-2859
Zeta potential (mV)	(-40.0)-(-41.3)
Alkalinity (mg/L)	609.3-776.9
Chloride (mg/L)	641.0-715.7
Sulfate (mg/L)	274.7-602.6
Sodium (mg/L)	840.6-846.7
Potassium (mg/L)	14.7-17.0
Magnesium (mg/L)	8.6-15.1
Calcium (mg/L)	10.1-25.3
Organic Parameters	
Chemical oxygen demand (COD) (mg/L)	204-302
Total organic carbon (TOC) (mg/L)	48.3-75.0
Biochemical oxygen demand (BOD_5) (mg/L)	2.7-3.30
UV_{254} (cm^{-1})	0.476±0.512
Naphthenic acids (NAs) (mg/L)	8.92-39.2
Acid extractable fraction (AEF) (mg/L)	48.5-64.2
BTEX (mg/L)	<0.01
PAHs (mg/L)	0.01
Phenols (mg/L)	0.008-1.8

Table 1-1 (concluded).

Parameter	Range
Trace Metals	
Silicon (mg/L)	6.95±0.13
Aluminum (µg/L)	7.66±0.24
Vanadium (µg/L)	8.84±0.62
Chromium (µg/L)	19.29±0.31
Manganese (µg/L)	2.74±1.02
Cobalt (µg/L)	2.13±0.05
Nickel (µg/L)	7.40±0.48
Copper (µg/L)	30.12±4.51
Zinc (µg/L)	1.34±0.15
Arsenic (µg/L)	6.05±0.19
Selenium (µg/L)	11.69±0.35
Strontium (mg/L)	0.67±0.01
Molybdenum (mg/L)	0.19±0.01
Cadmium (µg/L)	0.31±0.02
Antimony (µg/L)	2.76±0.09
Barium (µg/L)	63.67±1.02
Lead (µg/L)	0.10±0.01
Uranium (µg/L)	6.99±0.14
Titanium (mg/L)	0.09±0.03
Gallium (mg/L)	0.001±0.000
Iron (mg/L)	1.0±0.0

1.3 Naphthenic Acids

Naphthenic acids (NAs) are a group of aliphatic and alicyclic carboxylic acids with a general formula of $C_nH_{2n+z}O_x$, where n is the number of carbons, x is equal to two for classical NAs (c-NAs, containing two oxygen atoms) and three or more for oxidized NAs (oxy-NAs) formed after the oxidation of c-NAs (Kannel & Gan, 2012), and Z with a value of zero or an even negative integers (Z=0, no ring; Z= -2, one ring; Z=-4, two rings, etc.) indicates the loss of hydrogen through either the formation of rings or the presence of double bonds (Rogers et al., 2002a). NAs are comprised of mainly C_{11-19} bi- to pentacyclic acids, among which tricyclic (Z=-6) and bicyclic (Z = -4) acids are the major components (Rowland et al., 2011). It is believed that potentially more than 200,000 individual NA structures exist in the oil sands (Anderson et al., 2012). Approximately 2% (by weight) of the total bitumen in the Athabasca oil sands are NAs, which might pollute surface waters by the groundwater mixing and the erosion of the oil deposits of riverbanks (Afzal, 2013; Headley & McMartin, 2004). The concentrations of NAs are reported to have a range of 40-70 mg/L in tailings ponds, but can probably reach 130 mg/L in fresh tailings water (Allen, 2008a; Holowenko et al., 2002; MacKinnon, 2004b), 0.4-51 mg/L in groundwater, and 0.1-0.9 mg/L in river water (Tollefsen et al., 2012).

NAs with different structures have different solubility. In general, NAs with fewer cyclic rings (low molecule weight (MW) are soluble, while NAs with more rings (high MW) are insoluble (Afzal, 2013; Quagraine et al., 2005). Similar to surfactants, NAs are non-volatile and chemically stable (Headley & McMartin, 2004). The non-polarity and non-volatility of NAs increase with increasing MW, resulting in different chemical, toxicological, and physical properties of individual NAs (Afzal, 2013; Clemente et al., 2003; Headley et al., 2002). The solubility of NAs in aqueous solution also depends on the pH. The p*K*a of NAs was reported to be in a range of 5 to 6 (Afzal, 2013; Kanicky et al., 2000). Due to the alkaline pH of OSPW, NAs in the tailings ponds exist in the form of water soluble salts.

It has been reported that NAs are very harmful to the aquatic environment and have inhibitory influence on a variety of organisms, including fish (Dorn et al., 1992; Kannel & Gan, 2012), plants, zooplankton, rats, and luminescent bacteria (Afzal, 2013; Clemente & Fedorak, 2005). The lethal dosage of NAs for human was reported to be 11 g/kg (Kannel & Gan, 2012; Rockhold, 1955). The oral LD_{50} value for rats is in a range of 3.0-5.2 g/kg for commercial NAs, with death caused by gastrointestinal disturbances (Kannel & Gan, 2012; Lewis, 2000). NAs with large MW tend to have an increased amount of carboxylic groups which reduce their hydrophobicity and the chance of entering biological cells, and hence their toxicity (Frank et al., 2008; Kannel & Gan, 2012). C_{11-13} acids are the most toxic NAs (Jones et al., 2011). NAs with carbon number $n > 22$ have been verified to be less toxic than NAs with carbon numbers $n = 13$-16 using the Microtox^{TM} bacterial bioassay method (Holowenko et al., 2002; Pourrezaei, 2013). Previous research reported that the toxicity of OSPW is dependent not only on the total concentration of NAs, but also on the relative concentrations of specific NAs (Anderson et al., 2012). The toxicity of NAs is also influenced by the pH of OSPW. At high pH (> 6), NAs, mainly in ionized forms, have little chance to pass through biological membranes, and the toxicity of NAs is low. On the contrary, at low pH (< 6), NAs, mainly in unionized forms, are lipid soluble and can enter through biological membranes more easily, and therefore, they are more toxic (Armstrong, 2008; Kannel & Gan, 2012).

1.4 Phenol and H_2S

Wastewater from the petroleum refinery contains both organic and inorganic compounds such as sulfide, phenol, and ammonia with concentrations from 10 to 5000, 5 to 300, and 10 to 3000 mg/L, respectively (Alcántara et al., 2004). As a common toxic contaminant, phenol concentration in OSPW, the Athabasca River, and regional lakes varies from 0.001 mg/L to 1.8 mg/L, as shown in **Table 1-1**. Phenol at high concentrations in wastewater can lead to toxicity towards aquatic organisms (Yan et al., 2008). The maximum inlet phenol concentration for biological wastewater treatment plants is 1-2 mg/L. A presence of 1-10 μg/L phenol in freshwater produces unpleasant odour/taste during chlorination (Arana et al., 2001). The Canadian guideline value of phenol in freshwater for the protection of aquatic life is 4 μg/L (Environment Canada, 1998; Marine, 1999).

High concentration of sulphate (274.7 - 602.6 mg/L) was reported in OSPW, as shown in **Table 1-1**. Hydrogen sulfide (H_2S) considered as extremely toxic and irritating can be generated during the biological sulphate reduction process (Liu, 2015). H_2S ($pKa_1 = 6.9$ and $pKa_2 = 19$) exists mainly as HS^- in water at $pH > 7$ (DeLeon et al., 2012; Olson, 2005). H_2S has a permissible exposure limit of 20 parts per million (ppm), regulated by Occupational Safety & Health Administration (OSHA, USA). Inhalation of 500-1000 (ppm) of H_2S will cause rapid unconsciousness and death through respiratory paralysis and asphyxiation (Doujaiji & Al-Tawfiq, 2010). Therefore, the amount of phenol and H_2S must be reduced to acceptable levels before discharge due to safety and environmental concerns.

1.5 OSPW Treatment Processes

Many processes have been studied to treat OSPW, including wetlands, biodegradation, adsorption/sorption, and oxidation among others. The choice of treatment approach primarily depends on the constituents of OSPW, reuse or release regulations and requirements, cost, and industry processes (Wang, 2011b).

1.5.1 Wetlands

Some researchers have proposed the use of wetlands to remediate OSPW. Many kinds of pollutants (suspended solids, organic carbon, nitrogen compounds, aromatic compounds, and trace metals) can be removed by natural or constructed wetlands (Allen, 2008b; Kadlec & Knight, 1996). However, the low temperature in winter and the leaching problem of OSPW to groundwater raise some concerns about the application of wetlands (Allen, 2008b; Knight et al., 1999; Pourrezaei, 2013). Another question that needs to be answered is whether wetlands can support the aquatic biota (Allen, 2008a; Pourrezaei, 2013). Furthermore, increasing concentration of methane in some tailing ponds may have negative influence on the remediation of fine tailings, particularly with the wet landscape approach (Holowenko et al., 2000; Quagraine et al., 2005).

1.5.2 Biological treatment

Biological treatments have been studied extensively for the removal of organic carbon and nitrogen compounds in the oil industry. However, their application in the treatment of OSPW has been limited due to their sensitivity to the characteristics of the feed water such as salinity and toxicity (Pourrezaei, 2013). Moreover, the biodegradation half-life of NAs in OSPW has been reported to be 12.8-13.6 years (Gruber, 1993; Pourrezaei, 2013). In addition, NAs with large molecular weights are very recalcitrant to biodegradation and cannot be removed completely from OSPW (Pourrezaei, 2013; Quagraine et al., 2005), making biodegradation an unfeasible alternative for the OSPW remediation. However, biodegradation can be considered as a subsequent treatment following the removal of NAs with large molecular weight.

1.5.3 Adsorption/sorption

Adsorbents have been extensively used to remove pollutants from wastewaters produced in the oilfield, including soluble organic carbon compounds (Adhoum & Monser, 2004; Allen, 2008b; Cadena et al., 1990; Chen, 1997), oil and grease (Allen, 2008b; Doyle & Brown, 1997; Gallup et al., 1996; Hansen & Davies, 1994; Yang et al., 2002), and heavy metals (Allen, 2008b; Bose et al., 2002; Schouwenaars & Buitrn, 2000; Scott et al., 1995). Adsorbents commonly used in the treatment of oilfield produced water include activated carbon, natural organic matter, zeolites, clays, and synthetic polymers (Allen, 2008b). Different results have been obtained from the treatment of produced water by activated carbon. Marr et al. (1996) proved the effectiveness of activated carbon in removing NAs from acidified oil sands process waters, while poor performance was observed for the removal of other target pollutants (Allen, 2008b; Gallup et al., 1996; Hansen & Davies, 1994). Inorganic adsorbents such as zeolite, bentonite, and anthracite are considerable alternatives to activate carbon, but most adsorbents used alone in treating wastewaters cannot remove the contaminants in OSPW.

1.5.4 Membrane filtration

Many kinds of contaminants can be removed from wastewaters by membrane filtrations, such as suspended solids, colloidal organic matters, hydrocarbons, NAs, dissolved solids, salts, trace metals, and hardness (Wang, 2011b). Peng et al. (2004) showed that more than 95% of NAs was removed from OSPW by nanofiltation. Moreover, most cations (sodium, calcium, and magnesium) and anions (chloride, sulfate, and bicarbonate) in OSPW can also be removed (Pourrezaei, 2013). Reverse osmosis can remove all contaminants with the exception of H_2O, H^+, and OH^-, and produces high quality water (Wang, 2011b). However, the low flux rates, flux decline, membrane durability, and cost limit the application of membranes for deoiling wastewaters (Zaidi et al., 1992).

1.6 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) have received much attention recently for the treatment of recalcitrant contaminants due to the production of hydroxyl radical ($^{\bullet}OH$). $^{\bullet}OH$ is the second strongest known oxidant after fluorine with a potential of 2.8 V versus normal H electrode (fluorine has a potential of 3.03 V), and it can oxidize almost any organic matter to inorganic ions and CO_2 (Klamerth et al., 2012). AOPs have been proposed as a complementary process to biodegradation remediation because they can degrade recalcitrant NAs and reduce the overall toxicity of OSPW (Fu et al., 2008; Scott et al., 2008; Wang, 2011b). AOPs such as O_3/H_2O_2, UV/O_3, and UV/H_2O_2 have been verified to be suitable to treat recalcitrant organic compounds in OSPW (Allen, 2008a; Pourrezaei, 2013).

Fenton reaction is a homogeneous process based on the formation of $^{\bullet}OH$ from the reaction of hydrogen peroxide (H_2O_2) with iron ions (Bautista et al., 2008; Beeta, 2011; Pereira et al., 2012). Fenton reaction was discovered by Henry John Horstman Fenton in 1894 (Fenton, 1894), but it was not applied as an oxidizing process to degrade organics until the late 1960s (Huang et al., 1993). As a common way of producing $^{\bullet}OH$, Fenton processes are very effective for degrading organic contaminants into harmless compounds, low molecular weight organic acids, inorganic salts, and eventually CO_2 and water (Neyens & Baeyens, 2003). Fenton reactions have drawn lots of attention in the scientific community because they are fast, low cost, and easy to handle at room temperature (Basu & Wei, 1998a; Basu & Wei, 1998b; Kwan & Voelker, 2003; Li et al., 2005; Teel et al., 2001). Moreover, Fenton processes are commonly used to degrade aromatic compounds in wastewaters and reduce the effluent toxicity before biological treatment (ElShafei Gamal et al., 2010).

1.6.1 Classical Fenton

Most of the Fenton studies are carried out at acidic conditions (2.5 < pH < 3-4), under which iron ions remains soluble and Fe(III)-hydroxyl complexes exist in appreciable concentration (De la Cruz et al., 2012). The mechanisms of classical Fenton reaction are presented in **Table 1-2**.

Table 1-2. Main reactions in the classical Fenton process.

Reaction	Rate constant	No.
$Fe(II)+H_2O_2 \rightarrow Fe(III)+HO^- + {}^\bullet OH$ (chain initiation)	$k_1 \approx 70M^{-1}s^{-1}$ (Neyens & Baeyens, 2003; Rigg et al., 1954)	(1-1)
${}^\bullet OH+Fe(II) \rightarrow Fe(III)+HO^-$ (chain termination)	$k_2 = 3.2\times10^8\ M^{-1}s^{-1}$ (Buxton et al., 1988; Neyens & Baeyens, 2003)	(1-2)
$Fe(III)+H_2O_2 \rightarrow Fe(II)+ HO_2^\bullet+H^+$ (Fenton-like reaction)	$K_3 = 0.01\ M^{-1}s^{-1}$ (Bautista et al., 2008)	(1-3)
${}^\bullet OH+H_2O_2 \rightarrow HO_2^\bullet+ H_2O$	$K_4 = 3.3\times10^7\ M^{-1}s^{-1}$ (Buxton et al., 1988; Neyens & Baeyens, 2003)	(1-4)
$Fe(II)+ HO_2^\bullet \rightarrow Fe(III)+HO_2^-$	$K_5 = 1.3\times10^6\ M^{-1}s^{-1}$ at pH 3(Bielski et al., 1985; Neyens & Baeyens, 2003)	(1-5)
$Fe(III)+ HO_2^\bullet \Leftrightarrow Fe(II)+H^++O_2$	$K_6 = 1.2\times10^6\ M^{-1}s^{-1}$ at pH 3 (Bielski et al., 1985; Neyens & Baeyens, 2003)	(1-6)
$Fe(III)+ O_2^{\bullet-} \rightarrow Fe(II)+O_2$	$K_7 = 5\times10^7\ M^{-1}s^{-1}$ at pH < 3.5 (De Latt & Gallard, 1999; Pignatello et al., 2006)	(1-7)

Table 1-2 (concluded).

Reaction	Rate constant	No.
$Fe(II) + O_2^{\bullet -} + H^+ \rightarrow Fe(III) + HO_2^-$	$K_8 = 1\times10^7\ M^{-1}s^{-1}$ pH < 3.5 (De Latt & Gallard, 1999; Pignatello et al., 2006)	(1-8)
$2^{\bullet}OH \Leftrightarrow H_2O_2$	$K_9 = 5.2\times10^9\ M^{-1}s^{-1}$ (Bautista et al., 2008)	(1-9)
$2HO_2^{\bullet} \Leftrightarrow H_2O_2 + O_2$	$K_{10} = 8.6\times10^5\ M^{-1}s^{-1}$ (Burns et al., 2010)	(1-10)
$HO_2^{\bullet} + O_2^{\bullet -} \rightarrow HO_2^- + O_2$	$K_{11} = 1.02\times10^8\ M^{-1}s^{-1}$ (Burns et al., 2010)	(1-11)
$2Fe(II) + H_2O_2 + 2H^+ \rightarrow 2Fe(III) + 2H_2O$	(overall Fenton reaction) (Umar et al., 2010)	(1-12)

The main $^{\bullet}OH$ formation is shown in Eq. 1-1. The recycling of Fe(III) to Fe(II) presented in Eq. 1-3 is several orders of magnitude slower than that in Eq. 1-1, and thus it is considered to be the rate-limiting step in Fenton systems (Georgi et al., 2007).

$^{\bullet}OH$ produced during Fenton reactions can react with organic compounds (RH) to form carbon centered radicals (Beeta, 2011; Pignatello et al., 2006) (Eq. 1-13), or abstract hydrogen atoms (Eq. 1-14) (Beeta, 2011; Huang et al., 1993). $^{\bullet}R$ may be oxidized by Fe(III), reduced by Fe(II), or dimerized as shown in Eqs. 1-17, 1-18 and 1-19 (Neyens & Baeyens, 2003; Tang & Tassos, 1997).

Table 1-3. Degradation of organics in Fenton processes

Reaction	No.
$RH + {}^{\bullet}OH \Leftrightarrow {}^{\bullet}RHOH \rightarrow$ hydroxylated products	(1-13)
$RH + {}^{\bullet}OH \rightarrow {}^{\bullet}R + H_2O \rightarrow$ oxidized products	(1-14)
${}^{\bullet}R + H_2O_2 \rightarrow ROH + {}^{\bullet}OH$	(1-15)
${}^{\bullet}R + O_2 \rightarrow {}^{\bullet}ROO$	(1-16)
${}^{\bullet}R$ + Fe(III)-oxidation $\rightarrow R^+ + Fe(II)$	(1-17)
${}^{\bullet}R$ + Fe(II)-reduction $\rightarrow R^- + Fe(III)$	(1-18)
$2{}^{\bullet}R$-dimerization $\rightarrow$ R-R	(1-19)

The classical Fenton reaction has been widely used to provide $^{\bullet}OH$, but the required low pH conditions prevent further development of this AOP. The main drawback of Fenton processes carried out under acidic conditions is that the acidification of the treated solutions and subsequently neutralization of the water increase the cost of the treatment, the salinity of the solution, and the sludge formation. Moreover, some gases may be released to the environment in the presence of sulfides or cyanides (Lipczynska-Kochany & Kochany, 2008). Thus, scientists and researchers have been working on the modification of classical Fenton reactions to carry out them in a neutral pH environment.

1.6.2 Modified Fenton

Classical Fenton always occur at acidic conditions, which keep Fe(III) ions soluble, therefore, the reaction are very effective. At neutral pH, Fe(III) ions exist in the form of hydroxyl complexes (such as hydrous oxyhydroxides, $Fe_2O_3 \cdot nH_2O$), which are insoluble in water and cannot be cycled in the reduction steps. At the same time, Fe(II) salts may probably co-precipitate with Fe(III) oxyhydroxides at neutral pH (Lipczynska-Kochany & Kochany, 2008). Therefore, ways preventing iron ion from precipitation at high pH have been widely studied by researchers in recent years.

Chelating agents are used in the Fenton remediation at neutral pH to keep iron soluble and thus enhancing the production of $^{\bullet}OH$ and, therefore, the degradation efficiency (Lipczynska-Kochany & Kochany, 2008; Pignatello et al., 2006; Sun & Pignatello, 1992). The influence of the ligands on the reactivity of the Fe-complexes in the modified Fenton processes may come from three ways: (i) by the ligand-field effects on the redox-properties of the metal; (ii) by promoting the reaction of H_2O_2 with the metal; (iii) by competing with substrate for the reaction with the oxidant (Georgi et al., 2007; Sun & Pignatello, 1992). Several chelating reagents have been used in the modified Fenton processes, such as humic substances, glutamic acid, polycarboxylates, polyacrylic acids (PAAs), aminopolycarboxylic acids (APCAs), etc.

1.6.2.1 Humic substances

Humic substances as ubiquitous natural macromolecules resulting from microbial and chemical transformations of organic debris have attracted much attention in recent years. According to the solubility characteristics, humic substances are classified into humic acids, fulvic acids, and humin. Humic and fulvic acids can form chelates with metal ions (such as Fe(III) and Cu(II) as the most common bound metals) by binding to carboxylate, polyphenolic, and nitrogen-containing sites (Georgi et al., 2007; Ghabbour et al., 1997). Beside the chelating ability, humic substances have redox activity and, moreover, they can sorb hydrophobic organic compounds (Georgi et al., 2007). The results of the chelating effect of humic substances are conflicting. Some researchers stated that they had no significant effect on or even inhibited the degradation of organic pollutants in Fenton or Fenton-like reactions (Bissey et al., 2006; Li et al., 1998; Lindsey & Tarr, 2000). However, other researchers found that the addition of humic substances to Fenton systems accelerated the degradation of organic compounds (Georgi et al., 2006; Kochany & Lipczynska-Kochany, 2007; Vione et al., 2004).

1.6.2.2 Polycarboxylates

Polycarboxylates (citrate, malonate and oxalate) are molecules having more than one carboxylate functional group and can react with Fe(III) to form strong complexes, which can undergo rapid photochemical reactions under sunlight irradiation to form oxidative species (Faust & Zepp, 1993; Li et al., 2010; Panias et al., 1996). Good results have been obtained by some researchers using polycarboxylates in the modified Fenton processes (Faust & Zepp, 1993; Li et al., 2005; Ou et al., 2008).

1.6.2.3 Polyacrylic acids

Polyacrylic acids (PAAs) as polymeric chelates have some advantages over other chelating agents due to their multiple binding sites from a single chain (Li et al., 2005). They can combine with Fe(II)/Fe(III) at multiple sites to form chelate Fe(II)-PAA and Fe(III)-PAA, thus improving the solubility of Fe(II) and Fe(III) at neutral pH conditions. Li et al. (2007) demonstrated that PAA-based modified Fenton reactions could degrade 2,2'-polychlorinated biphenyls and biphenyl effectively at neutral pH, and at this condition the Fe(II) oxidation by air was minimized in the presence of PAA and H_2O_2.

1.6.2.4 Aminopolycarboxylic acids

Aminopolycarboxylic acids (APCAs) can act similarly to polycarboxylic acids, solubilize and inactivate metal ions by complex formation, and they are used widely in domestic products, industrial applications, and soil remediation (Abida et al., 2006; Bucheli - Witschel & Egli, 2001; Li et al., 2010). Several APCAs have been used as chelating agents in the modified Fenton processes such as ethylenediaminetetraacetic acid (EDTA), ethylenediamine-*N,N'*-disuccinic acid (EDDS), and nitrilotriacetic acid (NTA). EDTA has been used widely for chelating metal ions. It is considered, however, as a contaminant due to its low biodegradability (Li et al., 2010; Schmidt et al., 2004).

EDDS as a structural isomer of EDTA has two chiral centers in its structure and exists in three stereoisomers, [S,S]-, [R,S]-, and [R,R]-EDDS (Nagaraju et al., 2007). The preparation of EDDS by the most economical method produces a mixture of isomers containing 25% of [S,S]-

EDDS, 25% of [R,R]-EDDS, and 50% of the meso form [R,S]/[S,R] (Metsärinne et al., 2001; Pavelčik & Majer, 1978). These three stereoisomers have different biodegradabilities: [S,S]-EDDS is readily biodegradable, [R,R]-EDDS is resistant, and [R,S]/[S,R]-EDDS is comparatively but not readily biodegradable (Metsärinne et al., 2001; Schowanek et al., 1997). Actually, the final carbon dioxide (CO_2) yield of [S,S]-EDDS exceeds 80% after 20 days of biodegradation, assessed by the modified Sturm test organisation for economic cooperation and development (OECD) 301 B (Jaworska et al., 1999; Jones & Williams, 2001; OECD, 1996; Schowanek et al., 1997). [S,S]-EDDS can form a stable 1:1 complex with Fe at neutral pH and has been recognized as a suitable replacement for EDTA for environmental remediation products due to its strong chelating ability (Li et al., 2010; Nagaraju et al., 2007; Zhang et al., 2008). Its performance is equal to EDTA in most cases and even much better under specific conditions (Jones & Williams, 2001; Whitburn et al., 1999; Willkinson, 1998). Metal-EDDS is found to be low toxic (Fabbricino et al., 2013), and the toxicity of [S,S]-EDDS to fish and *Daphnia* has an $EC_{50} > 1000$ mg/L (Bucheli-Witschel & Egli, 2001).

NTA is another kind of APCAs, which is commonly used as a photo-inductor of organic compounds. NTA has been proven to be one of the most active chelates by Sun and Pignatello (1992) for the decomposition of H_2O_2 and the degradation of 2,4-dichlorophenoxyactic acid among 50 chelating agents. NTA is biodegradable and the metal-NTA complexes have been reported to have rapid photodegradation (Stolzberg & Hume, 1975; Trott et al., 1972). Therefore, the contamination of NTA would not be an environmental concern. Actually, only very low level of NTA has been found in natural waters despite the use of NTA in industrial and consumer products (Anderson et al., 1985). NTA itself shows no adverse effects to aquatic life (Anderson et al., 1985), and its by-products (iminodiacetic acid (IDA), glycine, oxalic acid, ammonia and CO_2) would not cause a toxicity problem to the environment either.

1.6.2.5 Other chelating agents

Park and Choi (2006) reported that amino acids can react with metal ions to form metal chelates with ring structures by neutralizing the cationic charge of metal ions at a pH range of 4.5-6.5. Some studies reported the use of glutamic acid as a chelating agent to enhance the degradation of persistent organic matter with Fenton oxidation processes, and the results were comparable to the results at low pH values (ElShafei Gamal et al., 2010). Tetraamino macrocyclic ligands (TAML) and porphyrins can also be used to chelate Fe(III) at neutral pH by preventing iron from precipitation and producing a reactive oxidant (Keenan & Sedlak, 2008; Koppenol & Liebman, 1984; Lee & Sedlak, 2009). Phosphotungstate ($PW_{12}O_{40}^{3-}$, a type of polyoxometalate) is relatively nontoxic and resistant to oxidation (Kozhevnikov, 1998; Rhule et al., 1998), and can form soluble complexes with Fe(III) at neutral pH (Lee et al., 2008). It is often used combined with silica, and retains its catalytic activity when covalently bound to silica surfaces (Yue et al., 2002).

1.6.3 Photo-Fenton

The efficiency of the Fenton processes can be promoted by the irradiation of UV or visible light (namely photo-Fenton processes) with wavelengths of $\lambda < 580$ nm (Klamerth et al., 2013; Malato et al., 2009). The photolysis of Fe(III) in acidic media yields Fe(II) (Eq. 1-20) and $^{\bullet}OH$ with reaction between Fe(II) and H_2O_2 (Eq. 1-21) (Herney-Ramirez et al., 2010).

$$Fe(OH)^{II} + hv \rightarrow Fe(II) + {}^{\bullet}OH \quad (1\text{-}20)$$

$$Fe(II) + H_2O_2 \rightarrow Fe(OH)^{II} + {}^{\bullet}OH \quad (1\text{-}21)$$

Some reports also pointed out the regeneration of Fe(II) through the photo-reduction of the photochemical organic substrate or its degradation intermediates, as shown in Eq. 1-22 (Herney-Ramirez et al., 2010; Sum et al., 2005).

$$Fe(III)L + hv \rightarrow Fe(II) + L^{\bullet} \; (L = RCOO^{-}, RO^{-}, HO^{-}) \qquad (1\text{-}22)$$

Therefore, the generation of $^{\bullet}$OH and degradation of contaminants in a Fenton system can be accelerated by the light irradiation (Al-Tawabini, 2002). Many studies have been conducted on the treatment of wastewaters by photo-Fenton processes and verified their enhanced effectiveness (Kavitha & Palanivelu, 2003, 2004; Wang et al., 1999).

1.7 Research Scopes and Objectives

Because of the huge amount and high toxicity of OSPW, its accumulation has raised several concerns over the years. The pollution caused by OSPW is waiting eagerly to be resolved. However, none of the existing technologies can be used to economically and effectively treat OSPW to a desirable point. Significant research gaps about the effectiveness and applicability of the treatment approaches of OSPW still exist at the industrial scale. It is of utmost importance to find an effective, economical and feasible approach for the treatment of OSPW.

Classical Fenton oxidation processes are known as economic and effective methods to treat recalcitrant organic contaminants and have been studied widely in the treatment of many kinds of wastewater. However, the acidic condition requirement limits their application. Chelates-modified Fenton oxidation processes have attracted a lot of attention in the scientific community, and they have the potential of being a new and effective way to degrade contaminants in OSPW, especially NAs. UV irradiation can significantly improve the efficiency of the chelates-modified Fenton processes. However, few studies have been conducted on the investigation of the mechanisms and kinetics of the (UV)chelates-modified Fenton processes. Furthermore, no information on the treatment of OSPW by Fenton processes can be found, indicating a new window on the OSPW remediation.

This PhD research focused on the treatment of cyclohexanoic acid (CHA) as a model compound for NAs and OSPW in the (UV)chelates-modified Fenton processes using two chelating agents (NTA and EDDS). The overall goal of this research was to investigate the (UV)chelates-modified Fenton processes in terms of process fundamentals and mechanisms on the treatment of OSPW. The objectives of the research were as follows:

1) To determine the optimal conditions of the NTA/EDDS-Fenton reactions by using factorial experimental design.
2) To investigate the degradation of CHA in the classical Fenton and NTA/EDDS-Fenton processes.
3) To investigate the reaction mechanisms and kinetics of the NTA/EDDS-Fenton processes.
4) To study the reaction kinetics of NTA/EDDS with $^{\bullet}OH$ by using a competition-kinetic method.
5) To investigate the main species responsible for the degradation of contaminants in the NTA/EDDS-Fenton processes.
6) To confirm the role of superoxide radical in the degradation of CHA in the NTA/EDDS-Fenton processes.
7) To investigate the influence of the dosing mode of H_2O_2 and Fe-chelates on the efficiency of the NTA/EDDS-Fenton processes.

8) To compare the efficiency of different processes (UV irradiation, UV-H_2O_2, Fenton, UV-Fenton, NTA-Fenton, UV-NTA-Fenton, and UV-Fe-NTA) on the CHA, H_2O_2, and NTA decomposition at pH 3 and 8.

9) To obtain the kinetic parameters of the oxidation of Fe(II)TPP with O_2.

10) To evaluate the catalytic ability of Fe(III)TPP on the oxidation of HS^- and the degradation of phenol in the process.

11) To verify the efficiency of the NTA/EDDS-modified Fenton processes for the removal of acid extractable organic fraction and aromatics in OSPW.

12) To compare the photolysis of Fe-NTA/EDDS and investigate the influence of OSPW matrix on the photodecomposition of the complexes.

13) To assess the decrease of the toxicity towards *Vibrio fischeri* of OSPW treated by the NTA/EDDS-modified Fenton processes using Microtox® 81.9% screening test.

14) To compare the efficiency of the UV-NTA-Fenton on the degradation of NAs with that of the UV-H_2O_2 and NTA-Fenton.

By achieving these objectives, information about the efficiency, applicability, and mechanisms of the treatment of OSPW by the (UV)NTA/EDDS-Fenton processes were provided. The results of this research were promising and will be the foundation of a new treatment approach for the OSPW remediation.

1.8 Thesis Organization

This thesis contains seven chapters. Chapter 1 consists of background information of OSPW, NAs, and possible treatment approaches of OSPW, as well as the research scopes and objectives. Chapter 2 and 3 contain the results of the CHA degradation by NTA- and EDDS-Fenton processes, respectively. The influence of the doses of H_2O_2 and Fe-chelates and their dosing mode on the CHA removal is presented. The role of the radicals ($^{\bullet}OH$ and $O_2^{\bullet-}$) in the CHA degradation is also provided. Precious information on the second-order rate constants of $^{\bullet}OH$ with NTA, EDDS, and CHA at pH 8 is disclosed. Moreover, Chapter 2 includes interesting discussions on the reaction mechanisms of the NTA-Fenton system. Chapter 3 provides valuable information on the comparison of the $^{\bullet}OH$ attack on pCBA, EDDS, and CHA. Chapter 4 presents the comparison of seven processes, including UV irradiation, UV-H_2O_2, Fenton, UV-Fenton, NTA-Fenton, UV-NTA-Fenton, and UV-Fe-NTA, on CHA removal, H_2O_2 decomposition, and NTA degradation at pH 3 and 8. The minor Fe precipitation in the UV-NTA-Fenton system compared to that in the UV-Fe-NTA system is discussed based on the formation of H_2O_2-Fe(III)NTA adduct. Interesting results of the effect of borate buffer on the CHA removal, H_2O_2 decomposition, Fe-NTA degradation, and Fe concentration in the UV-NTA-Fenton process are also included. The employment of Fe(III)TPP as a catalyst for the oxidation of H_2S is presented in Chapter 5. Valuable information is provided on the oxidation kinetics and mechanisms of Fe(II)TPP by O_2 and the catalytic capability of Fe(III)TPP in the H_2S oxidation. The results of the phenol degradation in the Fe(III)TPP-catalytic oxidation of H_2S are presented. Chapter 6 presents the application and comparison of the UV-NTA/EDDS-Fenton processes for the treatment of OSPW at natural pH. The mechanisms of Fe(II) oxidation and Fe(III) reduction in the NTA/EDDS-Fenton processes are proposed and compared based on the redox potentials of Fe(III/II)NTA, Fe(III/II)EDDS, $O_2/O_2^{\bullet-}$ and $H_2O_2/O_2^{\bullet-}$. The degradation of the chelating agents, the removal of acid extractable organic fraction (AEF) as well as aromatics, and the overall toxicity of raw OSPW in these two processes are presented and compared. The total NA removal in the UV-NTA-Fenton process is exhibited and compared with that in the UV-H_2O_2 and NTA-Fenton processes. Chapter 7 contains general discussions of the results presented in Chapters 2-6, as well as the conclusions of the research and the recommendations for future work. Chapter 8 consists of the supplementary materials of the research, including the analytical instruments and the results of the preliminary experiments. Chapter 9 presents the bibliography of the thesis.

1.9 References

Abida, O., Mailhot, G., Litter, M., & Bolte, M. (2006). Impact of iron-complex (Fe(III)-NTA) on photoinduced degradation of 4-chlorophenol in aqueous solution. *Photochemical & photobiological sciences : Official journal of the European Photochemistry Association and the European Society for Photobiology, 5*(4), 395-402.

Adhoum, N., & Monser, L. (2004). Removal of phthalate on modified activated carbon: application to the treatment of industrial wastewater. *Separation and Purification Technology, 38*(3), 233-239.

Afzal, A. (2013). Application of Advanced Oxidation Processes for Treatment of Napthenic Acids in Oil Sands Process Water. (Doctor of Philosophy), University of Alberta, Edmonton, Alberta, Canada.

Al-Tawabini, B. S. (2002). Treatment of Water Contaminated with Dimethyl Phthalate by Fenton, Photo-Fenton and UV/H_2O_2 Processes. (Docter of Philosophy), King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia.

Alcántara, S., Velasco, A., Muñoz, A., Cid, J., Revah, S., & Razo-Flores, E. (2004). Hydrogen sulfide oxidation by a microbial consortium in a recirculation reactor system: sulfur formation under oxygen limitation and removal of phenols. *Environmental Science & Technology, 38*(3), 918-923.

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

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

Alpatova, A., Kim, E.-S., Dong, S., Sun, N., Chelme-Ayala, P., & Gamal El-Din, M. (2014). Treatment of oil sands process-affected water with ceramic ultrafiltration membrane: Effects of operating conditions on membrane performance. *Separation and Purification Technology*, 122, 170-182.

Anderson, J. C., Wiseman, S. B., Wang, N., Moustafa, A., Perez-Estrada, L., Gamal El-Din, M., . . . Giesy, J. P. (2012). Effectiveness of ozonation treatment in eliminating toxicity of oil sands process-affected water to Chironomus dilutus. *Environmental Science & Technology, 46*(1), 486-493.

Anderson, R. L., Bishop, W. E., Campbell, R. L., & Becking, G. C. (1985). A review of the environmental and mammalian toxicology of nitrilotriacetic acid. *CRC Critical Reviews in Toxicology, 15*(1), 1-102.

Arana, J., Rendón, E. T., Rodrıguez, J. D., Melián, J. H., Dıaz, O. G., & Pena, J. P. (2001). Highly concentrated phenolic wastewater treatment by the Photo-Fenton reaction, mechanism study by FTIR-ATR. *Chemosphere, 44*(5), 1017-1023.

Armstrong, S. A. (2008). Dissipation and phytotoxicity of oil sands naphthenic acids in wetland plants. (Docter of Philosophy), University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

Basu, S., & Wei, I. W. (1998a). Advanced chemical oxidation of 2, 4, 6 trichlorophenol in aqueous phase by fenton's reagent-part i: effects of the amounts of oxidant and catalyst on the treatment reaction. *Chemical Engineering Communications, 164*(1), 111-137.

Basu, S., & Wei, I. W. (1998b). Advanced chemical oxidation of 2, 4, 6 trichlorophenol in aqueous phase by Fenton's Reagent-Part II: Effects of various reaction parameters on the treatment reaction. *Chemical Engineering Communications, 164*(1), 139-151.

Bautista, P., Mohedano, A. F., Casas, J. A., Zazo, J. A., & Rodriguez, J. J. (2008). An overview of the application of Fenton oxidation to industrial wastewaters treatment. *Journal of Chemical Technology and Biotechnology, 83*(10), 1323-1338.

Beeta, S. (2011). Removal of Benzene from Wastewater by Enzyme-Catalyzed Oxidative Polymerization Combined with a Modified Fenton Reaction. (Doctor of Philosophy), University of Windsor, Windsor, Ontario, Canada.

Bielski, B. H. J., Cabelli, D. E., & Arudi, R. L. (1985). Reactivity of H_2O_2/O_2^- radicals in aqueous solution. *Journal of Physical and Chemical Reference Data, 4*, 1041-1100.

Bissey, L. L., Smith, J. L., & Watts, R. J. (2006). Soil organic matter-hydrogen peroxide dynamics in the treatment of contaminated soils and groundwater using catalyzed H_2O_2 propagations (modified Fenton's reagent). *Water Research, 40*(13), 2477-2484.

Bose, P., Aparna, B. M., & Kumar, S. (2002). Critical evaluation of treatment strategies involving adsorption and chelation for wastewater containing copper, zinc and cyanide. *Advances in Environmental Research, 7*(1), 179-195.

Bucheli - Witschel, M., & Egli, T. (2001). Environmental fate and microbial degradation of aminopolycarboxylic acids. *FEMS Microbiology Reviews, 25*(1), 69-106.

Burns, J. M., Craig, P. S., Shaw, T. J., & Ferry, J. L. (2010). Multivariate Examination of Fe(II)/Fe(III) Cycling and Consequent Hydroxyl Radical Generation†. *Environmental Science & Technology, 44*(19), 7226-7231.

Burrowes, A., Marsh, R., Ramdin, N., Evans, C., Kirsch, M., Philp, L., . . . Sankey, G. (2005). Alberta's reserves 2004 and supply/demand outlook 2005-2014. Calgary, Alberta, Canada: Alberta Energy and Utilities Board.

Buxton, G. V., Greenstock, C. L., Helman, W. P., & Ross, A. B. (1988). Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals. *Journal of Physical and Chemical Reference Data, 17*, 513-886.

Cadena, F., Garcia, R., & Peters, R. W. (1990). Adsorption of benzene from aqueous solutions by bentonite treated with quaternary amines. *Environmental Progress, 9*(4), 245-253.

Chen, P. H. (1997). Adsorption of organic compounds in water using a synthetic adsorbent. *Environment International, 23*(1), 63-73.

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

Clemente, J. S., Prasad, N., MacKinnon, M. D., & Fedorak, P. M. (2003). A statistical comparison of naphthenic acids characterized by gas chromatography-mass spectrometry. *Chemosphere, 50*(10), 1265-1274.

De la Cruz, N., Gimenez, J., Esplugas, S., Grandjean, D., de Alencastro, L. F., & Pulgarin, C. (2012). Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. *Water Research, 46*(6), 1947-1957.

De Latt, J., & Gallard, H. (1999). Catalytic decomposition of hydrogen peroxide by Fe(III) in homogenerous aqueous solution: Mechanism and kinetic modeling. *Environmental Science & Tecbnology, 33*, 2726-2732.

DeLeon, E. R., Stoy, G. F., & Olson, K. R. (2012). Passive loss of hydrogen sulfide in biological experiments. *Analytical Biochemistry, 421*(1), 203-207.

Dokholyan, B. K., & Magomedov, A. K. (1984). The effect of sodium naphthenate on the viability and physiological and biochemical indices of fish. *Voprosy Ikhtiologii, 23*(6), 11-26.

Dominski, M. (2007). Surface mined oil sands: tailings practices, performance, and projections. Paper presented at the The 3rd international Heavy Oil Conference, Calgary, AB, Canada.

Dorn, P. B., Van Compernolle, R., Mueller, G. R., Sun, P. J., Glaze, D. E., Hwang, J. C., & Hansen, S. R. (1992). *Toxicity identification and derivation of a water quality based effluent limit for a west coast refinery*. Lancasyer, PA, USA: Technomic Pub Inc.

Doujaiji, B., & Al-Tawfiq, J. A. (2010). Hydrogen sulfide exposure in an adult male. *Annals of Saudi Medicine, 30*(1), 76-80.

Doyle, D. H., & Brown, A. B. (1997). Field test of produced water treatment with polymer modified bentonite. Paper presented at the SPE Rocky Mountain Regional Meeting.

ElShafei Gamal, M. S., Yehia, F. Z., Dimitry, O. I. H., Badawi, A. M., & Eshaq, G. (2010). Degradation of nitrobenzene at near neutral pH using Fe^{2+}-glutamate complex as a homogeneous Fenton catalyst. *Applied Catalysis B: Environmental, 99*(1-2), 242-247.

Environment Canada. (1998). Canadian water quality guidelines for phenols. Ottawa, Canada: Unpub.

Fabbricino, M., Ferraro, A., Del Giudice, G., & d'Antonio, L. (2013). Current views on EDDS use for ex situ washing of potentially toxic metal contaminated soils. *Reviews in Environmental Science and Bio/Technology, 12*(4), 391-398.

Fattah, Q., & Wort, D. (1970). Metabolic responses of bush bean plants to naphthenate application. *Canadian Journal of Botany, 48*(5), 861-866.

Faust, B. C., & Zepp, R. G. (1993). Photochemistry of aqueous iron(III)-polycarboxylate complexes: Roles in the chemistry of atmospheric and surface waters. *Environmental Science & Technology, 27*(12), 2517-2522.

Fenton, H. J. H. (1894). Oxidation of Tartaric acid in the presence of iron. *Journal of the Chemical Society, Transactions, 65*, 899-910.

Frank, R. A., Fischer, K., Kavanagh, R., Burnison, B. K., Arsenault, G., Headley, J. V., . . . Solomon, K. R. (2008). Effect of carboxylic acid content on the acute toxicity of oil sands naphthenic acids. *Environmental Science & Technology, 43*(2), 266-271.

Fu, H., Gamal El-Din, M., Smith, D. W., MacKinnon, M., & Zubot, W. (2008). Ozone treatment of naphthenic acids in Athabasca oil sands process-affected water. Paper presented at the First International Oil Sands Tailings Conference,, Edmonton, AB, Canda.

Gallup, D. L., Isacoff, E. G., & Smith, D. N. (1996). Use of Ambersorb® carbonaceous adsorbent for removal of BTEX compounds from oil-field produced water. *Environmental Progress, 15*(3), 197-203.

Georgi, A., Schierz, A., & Kopinke, F. D. (2006). Activation of hydrogen peroxide by complexes of iron(III) with humic acid for chemical degradation of organic compounds in water. Paper presented at the Proceeding of the EAAOP Conference (Environmental Applications of Advanced Oxidation Processes), Chania, Greece, September.

Georgi, A., Schierz, A., Trommler, U., Horwitz, C. P., Collins, T. J., & Kopinke, F. D. (2007). Humic acid modified Fenton reagent for enhancement of the working pH range. *Applied Catalysis B: Environmental, 72*(1-2), 26-36.

Ghabbour, E. A., Jansen, S. A., Paciolla, M. D., Sein, L. T., Fataftah, A., Cherkasskiy, A., . . . Kolla, S. (1997). Tight metal binding by humic acids and its role in biomineralization†. *Journal of the Chemical Society, Dalton Transactions* (21), 4047-4060.

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

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

Gulley, J. R. (1992). Study of Oilsands Sludge Reclamation Under the Tailings Sludge Abandonment Research Program: Suncor Incorporated.

Hansen, B. R., & Davies, S. R. (1994). Review of potential technologies for the removal of dissolved components from produced water. *Chemical Engineering Research & Design, 72*(2), 176-188.

Hayes, T. M. E. (2007). Examining the ecological effects of naphthenic acids and major ions on phytoplankton in the Athabasca oil sands region. (Docter of Philosophy), University of Waterloo, Waterloo, ON, Canada.

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

Headley, J. V., Peru, K. M., McMartin, D. W., & Winkler, M. (2002). Determination of dissolved naphthenic acids in natural waters by using negative-ion electrospray mass spectrometry. *Journal of AOAC International, 85*(1), 182-187.

Herney-Ramirez, J., Vicente, M. A., & Madeira, L. M. (2010). Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review. *Applied Catalysis B: Environmental, 98*(1), 10-26.

Holowenko, F. M., MacKinnon, M. D., & Fedorak, P. M. (2000). Methanogens and sulfate-reducing bacteria in oil sands fine tailings waste. *Canadian Journal of Microbiology, 46*(10), 927-937.

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

Huang, C. P., Dong, C. D., & Tang, Z. H. (1993). Advanced chemical oxidation: its present role and potential future in hazardous waste treatment. *Waste Management, 13*(5), 361-377.

Islam, M. S., Dong, T., Sheng, Z., Zhang, Y., Liu, Y., & Gamal El-Din, M. (2014). Microbial community structure and operational performance of a fluidized bed biofilm reactor treating oil sands process-affected water. *International biodeterioration & biodegradation*, 91, 111-118.

Jaworska, J. S., Schowanek, D., & Feijtel, T. C. (1999). Environmental risk assessment for trisodium [S, S]-ethylene diamine disuccinate, a biodegradable chelator used in detergent applications. *Chemosphere, 38*(15), 3597-3625.

Jones, D., Scarlett, A. G., West, C. E., & Rowland, S. J. (2011). Toxicity of individual naphthenic acids to Vibrio fischeri. *Environmental Science & Technology, 45*(22), 9776-9782.

Jones, P. W., & Williams, D. R. (2001). Chemical speciation used to assess [S, S′]-ethylenediaminedisuccinic acid (EDDS) as a readily-biodegradable replacement for EDTA in radiochemical decontamination formulations. *Applied Radiation and Isotopes, 54*(4), 587-593.

Kadlec, R. H., & Knight, R. L. (1996). Treatment wetlands. Boca Raton: CRC Lewis Publishers.

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

Kanicky, J., Poniatowski, A., Mehta, N., & Shah, D. (2000). Cooperativity among molecules at interfaces in relation to various technological processes: effect of chain length on the p K a of fatty acid salt solutions. *Langmuir, 16*(1), 172-177.

Kannel, P. R., & Gan, T. Y. (2012). 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, 47*(1), 1-21.

Kasperski, K. (2001). Extraction and water chemistry. Canadian Oil Sands Network for Research and Development (CONRAD) Oil sands extraction fundamentals and process water workshop. May 7-8, 2004.

Kavitha, V., & Palanivelu, K. (2003). Degradation of 2-chlorophenol by Fenton and photo-Fenton processes-A comparative study. *Journal of Environmental Science and Health, Part A, 38*(7), 1215-1231.

Kavitha, V., & Palanivelu, K. (2004). The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere, 55*(9), 1235-1243.

Keenan, C. R., & Sedlak, D. L. (2008). Ligand-enhanced reactive oxidant generation by nanoparticulate zero-valent iron and oxygen. *Environmental Science & Technology, 42*(18), 6936-6941.

Kim, E.-S., Liu, Y., & Gamal El-Din, M. (2013). An in-situ integrated system of carbon nanotubes nanocomposite membrane for oil sands process-affected water treatment. *Journal of Membrane Science*, 429, 418-427.

Klamerth, N., Malato, S., Aguera, A., & Fernandez-Alba, A. (2013). Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: a comparison. *Water Research, 47*(2), 833-840.

Klamerth, N., Malato, S., Aguera, A., Fernandez-Alba, A., & Mailhot, G. (2012). Treatment of municipal wastewater treatment plant effluents with modified photo-Fenton as a tertiary treatment for the degradation of micro pollutants and disinfection. *Environmental Science & Technology, 46*(5), 2885-2892

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

Kochany, J., & Lipczynska-Kochany, E. (2007). Fenton reaction in the presence of humates. Treatment of highly contaminated wastewater at neutral pH. *Environmental Technology, 28*(9), 1007-1013.

Koppenol, W. H., & Liebman, J. F. (1984). The oxidizing nature of the hydroxyl radical. A comparison with the ferryl ion (FeO^{2+}). *The Journal of Physical Chemistry, 88*(1), 99-101.

Kozhevnikov, I. V. (1998). Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. *Chemical Reviews, 98*(1), 171-198.

Kwan, W. P., & Voelker, B. M. (2003). Rates of hydroxyl radical generation and organic compound oxidation in mineral-catalyzed Fenton-like systems. *Environmental Science & Technology, 37*(6), 1150-1158.

Lee, C., & Sedlak, D. L. (2009). A Novel Homogeneous Fenton-like System with Fe(III)-Phosphotungstate for Oxidation of Organic Compounds at Neutral pH Values. *Journal of Molecular Catalysis. A, Chemical, 311*(1-2), 1-6.

Lee, C. H., Keenan, C. R., & Sedlak, D. L. (2008). Polyoxometalate-enhanced oxidation of organic compounds by nanoparticulate zero-valent iron and ferrous ion in the presence of oxygen. *Environmental Science & Technology, 42*(13), 4921-4926.

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

Leung, S. S. C., MacKinnon, M. D., & Smith, R. E. (2001). Aquatic reclamation in the Athabasca, Canada, oil sands: naphthenate and salt effects on phytoplankton communities. *Environmental Toxicology and Chemistry, 20*(7), 1532-1543.

Lewis, R. L. (2000). Dangerous Properties of Industrial Materials. New York: Wiley Intersicence.

Li, J., Mailhot, G., Wu, F., & Deng, N. S. (2010). Photochemical efficiency of Fe(III)-EDDS complex: OH radical production and 17β-estradiol degradation. *Journal of Photochemistry and Photobiology A: Chemistry, 212*(1), 1-7.

Li, Y. C., Bachas, L. G., & Bhattacharyya, D. (2005). Kinetics studies of trichlorophenol destruction by chelate-based Fenton reaction. *Environmental Engineering Science, 22*(6), 756-771.

Li, Y. C., Bachas, L. G., & Bhattacharyya, D. (2007). Selected chloro-organic detoxifications by polychelate (poly (acrylic acid)) and citrate-based Fenton reaction at neutral pH environment. *Industrial & Engineering Chemistry Research, 46*(24), 7984-7992.

Li, Z. M., Shea, P. J., & Comfort, S. D. (1998). Nitrotoluene destruction by UV-catalyzed Fenton oxidation. *Chemosphere, 36*(8), 1849-1865.

Limited, G. A. (2002). Oil sands regional aquatics monitoring program (RAMP) 2001. Vol. 1- Chemical and biological monitoring *Reported prepared for the RAMP Steering Committee*. Fort McMurray, Alberta.

Lindsey, M. E., & Tarr, M. A. (2000). Inhibition of hydroxyl radical reaction with aromatics by dissolved natural organic matter. *Environmental Science & Technology, 34*(3), 444-449.

Lipczynska-Kochany, E., & Kochany, J. (2008). Effect of humic substances on the Fenton treatment of wastewater at acidic and neutral pH. *Chemosphere, 73*(5), 745-750.

Liu, H. (2015). Community Structure and Microbial Activity of Sulfate Reducing Bacteria in Wastewater Biofilms and Mature Fine Tailings Analyzed by Microsensors and Molecular Biology Techniques. (Doctor of Philosophy), University of Alberta, Edmonton, Alberta, Canada.

MacKinnon, M. (2004a). Oil sands water quality issues: properties, treatment, and discharge options [online]. Canadian Oil Sands Network for Research and Development (CONRAD) Oil Sands Water Usage Workshop, February 24–25, 2005.

Mackinnon, M., & Boerger, H. (1986). Description of two treatments for detoxifying oil sands tailings pond water. *Water Pollution Research Journal of Canada, 21*, 496-512.

MacKinnon, M., & Sethi, A. (1993). A comparison of the physical and chemical properties of the tailings ponds at the Syncrude and Suncor oil sands plants. Paper presented at the Proceedings of the Fine Tailings Symposium: Oil Sands-Our Petroleum Future Conference.

Mackinnon, M. D. (2001). Process-affected waters: impact of operating factors on recycle water quality. *Canadian Oil Sands Network for Research and Development (CONRAD) Oil Sands Extraction Fundamentals and Process Water Workshop, May 7-8, 2004*. Athabasca, Alberta: Athabasca University.

MacKinnon, M. D. (2004b). Oild sands water quality issues: properties, treatment, and discharge options, from http://www.conrad.ab.ca/seminars/water_usage/2004/Agenda.htm

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

Malato, S., Fernández-Ibáñez, P., Maldonado, M. I., Blanco, J., & Gernjak, W. (2009). Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today, 147*(1), 1-59.

Marine, N. (1999). Canadian Water Quality Guidelines for the Protection of Aquatic Life. *Canadian Council of Ministers of the Environment, Winnipeg*, 1-5.

Marr, J. B., Mohammed, M., MacKinnon, M., & Rogers, M. (1996). Removal of naphthenic acid from water via pH adjustment, coagulation and sand filtration. Paper presented at the International Water Conference, Pittsburgh.

Metsärinne, S., Tuhkanen, T., & Aksela, R. (2001). Photodegradation of ethylenediaminetetraacetic acid (EDTA) and ethylenediamine disuccinic acid (EDDS) within natural UV radiation range. *Chemosphere, 45*(6), 949-955.

Mikula, R. J., Kasperski, K. L., Burns, R. D., & MacKinnon, M. D. (1996). Nature and fate of oil sands fine tailings. *Advances in Chemistry Series*(251).

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

Nagaraju, V., Goje, T., & Crouch, A. M. (2007). Determination of Copper and Iron Using [S, S']-Ethylenediaminedisuccinic Acid as a Chelating Agent in Wood Pulp by Capillary Electrophoresis. *Analytical Sciences, 23*(4), 493-496.

Nelson, L. R., MacKinnon, M., & Gulley, J. R. (1993). Application of toxicity testing in the evaluation of reclamation options for oil sands fine tails. Paper presented at the Oil Sands-Our Petroleum Future Conference,, Edmonton, Alberta, Canada.

Neyens, E., & Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials, 98*(1-3), 33-50.

Nix, P. G. (1983). Detoxification of tailings pond top water. *Report prepared for Suncor Energy Inc.* Fort McMurray, Alberta.

OECD. (1996). OECD Guidelines for Testing of Chemicals. *Degradation and Accumulation*. Paris.

Oil Sands Ministerial Strategy Committee. (2006). Responding to the rapid growth of oil sands development, from http://alberta.ca/home/395.cfm

Olson, K. R. (2005). Vascular actions of hydrogen sulfide in nonmammalian vertebrates. *Antioxidants & Redox Signaling, 7*(5-6), 804-812.

Ou, X. X., Quan, X., Chen, S. Y., Zhang, F. J., & Zhao, Y. Z. (2008). Photocatalytic reaction by Fe (III)–citrate complex and its effect on the photodegradation of atrazine in aqueous solution. *Journal of Photochemistry and Photobiology A: Chemistry, 197*(2), 382-388.

Panias, D., Taxiarchou, M., Paspaliaris, I., & Kontopoulos, A. (1996). Mechanisms of dissolution of iron oxides in aqueous oxalic acid solutions. *Hydrometallurgy, 42*(2), 257-265.

Park, M. G., & Choi, M. H. (2006). United States Patent No. US/0128799 A1.

Pavelčik, F., & Majer, J. (1978). New complexanes. XXXIV. Preparation and properties of the meso and rac forms of ethy! enediamine-iV, iV'-disuccinic acid. *Chemické Zvesti, 32*(1), 37-41.

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

Pereira, M. C., Oliveira, L. C. A., & Murad, E. (2012). Iron oxide catalysts: Fenton and Fentonlike reactions - a review. *Clay Minerals, 47*(3), 285-302.

Pignatello, J. J., Oliveros, E., & MacKay, A. (2006). Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology, 36*(1), 1-84.

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

Pourrezaei, P. (2013). Physico-Chemical Processes for Oil Sands Process-Affected Water Treatment. (Doctor of Philosophy), University of Alberta, Edmonton, A.B.

Pourrezaei, P., Alpatova, A., Khosravi, K., Drzewicz, P., Chen, Y., Chelme-Ayala, P., & Gamal El-Din, M. (2014). Removal of organic compounds and trace metals from oil sands process-affected water using zero valent iron enhanced by petroleum coke. *Journal Of Environmental Management*, 139, 50-58.

Quagraine, E. K., Peterson, H. G., & Headley, J. V. (2005). 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, 40*(3), 685-722.

Rhule, J. T., Hill, C. L., Judd, D. A., & Schinazi, R. F. (1998). Polyoxometalates in medicine. *Chemical Reviews, 98*(1), 327-358.

Rigg, T., Taylor, W., & Weiss, J. (1954). The rate constant of the reaction between hydrogen peroxide and ferrous ions. *The Journal of Chemical Physics, 22*(4), 575-577.

Rockhold, W. (1955). Toxicity of naphthenic acids and their metal salts. *A.M.A. Archives of Industrial Health, 12*, 477-482.

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

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

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

Schmidt, C. K., Fleig, M., Sacher, F., & Brauch, H. J. (2004). Occurrence of aminopolycarboxylates in the aquatic environment of Germany. *Environmental Pollution, 131*(1), 107-124.

Schouwenaars, R., & Buitrn, G. (2000). Production of activated carbon from petroleum coke and itsapplication in water treatment for the removal of metals and phenol. *Water Science & Technology, 42*(5-6), 119-126.

Schowanek, D., Feijtel, T. C., Perkins, C. M., Hartman, F. A., Federle, T. W., & Larson, R. J. (1997). Biodegradation of [S, S],[R, R] and mixed stereoisomers of ethylene diamine disuccinic acid (EDDS), a transition metal chelator. *Chemosphere, 34*(11), 2375-2391.

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

Scott, J. A., Karanjkar, A. M., & Rowe, D. L. (1995). Biofilm covered granular activated carbon for decontamination of streams containing heavy metals and organic chemicals. *Minerals Engineering, 8*(1), 221-230.

Stolzberg, R. J., & Hume, D. N. (1975). Rapid formation of iminodiacetate from photochemical degradation of iron(III) nitrilotriacetate solutions. *Environmental Science & Technology, 9*(7), 654-656.

Sum, O. S. N., Feng, J. Y., Hub, X. J., & Yue, P. L. (2005). Photo-assisted fenton mineralization of an azo-dye acid black 1 using a modified laponite clay-based Fe nanocomposite as a heterogeneous catalyst. *Topics in Catalysis, 33*(1-4), 233-242.

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

Tang, W. Z., & Tassos, S. (1997). Oxidation kinetics and mechanisms of trihalomethanes by Fenton's reagent. *Water Research, 31*(5), 1117-1125.

Teel, A. L., Warberg, C. R., Atkinson, D. A., & Watts, R. J. (2001). Comparison of mineral and soluble iron Fenton's catalysts for the treatment of trichloroethylene. *Water Research, 35*(4), 977-984.

Tollefsen, K. E., Petersen, K., & Rowland, S. J. (2012). Toxicity of synthetic naphthenic acids and mixtures of these to fish liver cells. *Environmental Science & Technology, 46*(9), 5143-5150.

Trott, T., Henwood, R. W., & Langford, C. H. (1972). Sunlight photochemistry of ferric nitrilotriacetate complexes. *Environmental Science & Technology, 6*(4), 367-368.

Umar, M., Aziz, H. A., & Yusoff, M. S. (2010). Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate. *Waste Management, 30*(11), 2113-2121.

Veil, J. A., Quinn, J. J., & Garcia, J. P. (2009, March 23-25, 2009). Water issues relating to heavy oil production. Paper presented at the 2009 SPE Americas E & P Environmental and Safety Conference, San Antonio.

Vione, D., Merlo, F., Maurino, V., & Minero, C. (2004). Effect of humic acids on the Fenton degradation of phenol. *Environmental Chemistry Letters, 2*(3), 129-133.

Wang, C., Alpatova, A., McPhedran, K. N., & Gamal El-Din, M. (2015). Coagulation/flocculation process with polyaluminum chloride for the remediation of oil sands process-affected water: Performance and mechanism study. *Journal of Environmental Management*, 160, 254-262.

Wang, N. (2011a). Ozonation and biodegradation of oil sands process water. (Master of Science), University of Alberta, Edmonton, AB, Canada.

Wang, N., Chelme-Ayala, P., Perez-Estrada, L., Garcia-Garcia, E., Pun, J., Martin, J. W., . . . Gamal El-Din, M. (2013). Impact of ozonation on naphthenic acids speciation and toxicity of oil sands process-affected water to Vibrio fischeri and mammalian immune system. *Environmental Science & Technology*, 47(12), 6518-6526.

Wang, T. H., Kang, S. F., & Lin, Y. H. (1999). Comparison among Fenton-related processes to remove 2, 4-dinitrophenol. *Journal of Environmental Science & Health Part A, 34*(6), 1267-1281.

Wang, Y. N. (2011b). Application of Coagulation-Flocculation Process for Treating Oil Sands Process-Affected Water. (Master of Science), University of Alberta, Edmonton, AB, Canada.

Whitburn, J. S., Wilkinson, S. D., & Williams, D. R. (1999). Chemical speciation of ethylenediamine-N, N′ -disuccinic acid (EDDS) and its metal complexes in solution. *Chemical Speciation & Bioavailability, 11*(3), 85-93.

Willkinson, S. D. (1998). Chemical Speciation of a Biodegradable Replacement Ligand for EDTA. (Doctor of Philosophy), University of Wales, Cardiff.

Wort, D. J., & Patel, K. M. (1970). Response of Plants to Naphthenic and Cycloalkanecarboxylic Acids. *Agronomy Journal, 62*(5), 644-&.

Wort, D. J., Severson, J. G., & Peirson, D. R. (1973). Mechanism of Plant Growth Stimulation by Naphthenic Acid Effects on Nitrogen Metabolism of Phaseolus Vulgaris L. *Plant Physiology, 52*(2), 162-165.

Yan, Q., Yu, D., Wang, Z., Zou, H., & Ruan, W. (2008). Phenol inhibition and restoration of the bioactivity of anaerobic granular sludge. *Applied Biochemistry and Biotechnology, 150*(3), 259-265.

Yang, Y., Zhang, X., & Wang, Z. (2002). Oilfield produced water treatment with surface-modified fiber ball media filtration. *Water Science & Technology, 46*(11-12), 165-170.

Yue, B., Zhou, Y., Xu, J. Y., Wu, Z. Z., Zhang, X., Zou, Y. F., & Jin, S. L. (2002). Photocatalytic degradation of aqueous 4-chlorophenol by silica-immobilized polyoxometalates. *Environmental Science & Technology, 36*(6), 1325-1329.

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

Zhang, L. H., Zhu, Z. L., Zhang, R. H., Zheng, C. S., Zhang, H., Qiu, Y. L., & Zhao, J. F. (2008). Extraction of copper from sewage sludge using biodegradable chelant EDDS. *Journal of Environmental Sciences, 20*(8), 970-974.

Zhou, S. Q., Huang, H. P., & Liu, Y. M. (2008). Biodegradation and origin of oil sands in the Western Canada sedimentary basin. *Petroleum Science, 5*(2), 87-94.

Zubot, W. A. (2010). Removal of Naphthenic Acids from Oil Sands Process Water using Petroleum Coke. (Master of Science), University of Alberta, Edmonton, AB, Canada.

2 DEGRADATION OF CYCLOHEXANOIC ACID BY NITRILOTRIACETIC ACID-MODIFIED FENTON PROCESS[1]

2.1 Introduction

Canada's oil sands in the northern Alberta region of Athabasca are the world's 3rd largest known oil deposits, with a volume of 170 billion barrels being currently considered as economically recoverable (ERCB, 2012; Swart & Weaver, 2012). About 20% of the bitumen is surface mineable and is extracted from the oil sands by an alkaline hot water process at pH ~ 8 (Allen, 2008; Wang, 2011a). The produced suspension separates into three distinct layers of water, sands, and raw bitumen (also called bitumen froth), which is skimmed off the top to be further refined and upgraded to synthetic crude oil. This process leads to the production of oil sands process-affected water (OSPW), which is highly saline, and shows acute and chronic toxicity to aquatic organisms (He et al., 2011). Organic compounds in OSPW include unrecovered bitumen (oil and grease), naphthenic acids (NAs), polyaromatic hydrocarbons (PAH), BTEX (benzene, toluene, ethyl benzene, and xylenes), and other organic acids such as fulvic and humic acids (Allen, 2008; Madill et al., 2001; Mohamed et al., 2011; Pourrezaei, 2013; Rogers et al., 2002).

NAs are believed to be the main responsible compounds for OSPW toxicity. They are a group of aliphatic and alicyclic carboxylic acids with a general formula: $C_nH_{2n+z}O_x$, where n is the number of carbons, x is the number of oxygen, with $x = 2$ for classical NAs (c-NAs), $x \geq 3$ for oxidized NAs (oxy-NAs) which are formed after the oxidation of c-NAs (Kannel & Gan,

---

[1] A version of this chapter has been published previously: Ying Zhang, Nikolaus Klamerth, & Mohamed Gamal El-Din. (2016). Degradation of a Model Naphthenic Acid by Nitrilotriacetic Acid-Modified Fenton Process. *Chemical Engineering Journal, 292*, 340-347.

2012), and z is zero or an even negative integer indicating the loss of hydrogen through either the formation of rings or the presence of double bonds (Rogers et al., 2002). NAs concentration in tailings ponds has been reported to be in a range of 40-130 mg/L, depending on pond age and extracted ore (Allen, 2008; Holowenko et al., 2002; MacKinnon, 2004). Due to the toxicity and recalcitrance of NAs to biodegradation, their removal from OSPW has been attracting attentions from researchers since 1980s (Afzal et al., 2012; Allen, 2008).

Advanced oxidation processes (AOPs) have received much attention in the last decades for the treatment of recalcitrant contaminants due to their high oxidative ability promoted by the production of hydroxyl radical ($^{\bullet}$OH). AOPs have been proposed as a complementary technology to biological treatment of OSPW due to their ability to degrade recalcitrant NAs and reduce overall toxicity towards selected organisms (Fu et al., 2008; Scott et al., 2008; Wang, 2011b). $^{\bullet}$OH is a known oxidant, second to the strongest oxidant - Fluorine, with a potential of 2.8 V versus normal H electrode. $^{\bullet}$OH is produced in the Fenton process through the reaction of hydrogen peroxide (H_2O_2) with Fe(II) at acidic pH (around 3.0) (Bautista et al., 2008; Beeta, 2011; Pouran et al., 2015). This radical can oxidize almost any organic matter to short-chain organic acids, inorganic ions and CO_2 (Esplugas et al., 2007; Klamerth et al., 2012; Malato et al., 2009). Fenton reactions have drawn lots of attention in the scientific community because they are fast, low cost, and easy to handle at room temperature (Basu & Wei, 1998a; Basu & Wei, 1998b; Kwan & Voelker, 2003; Li et al., 2005; Teel et al., 2001). However, the acidic condition requirement limits their application in the treatment of wastewaters.

Some researchers have studied modified Fenton processes at neutral pH by using chelating agents to prevent the precipitation of iron and to produce $^{\bullet}$OH (Klamerth et al., 2011; Lipczynska-Kochany & Kochany, 2008; Pignatello et al., 2006; Rastogi et al., 2009; Sun &

Pignatello, 1992; Wang et al., 2013; Xue et al., 2009). Due to their structure and properties, polycarboxylic acids and aminopolycarboxylic acids (APCAs) can chelate metal ions by the formation of complexes (Huang et al., 2013). Several APCAs have been used as chelating agents in modified Fenton processes such as ethylenediaminetetraacetic acid (EDTA), ethylenediamine-*N,N'*-disuccinic acid (EDDS), and nitrilotriacetic acid (NTA). The use of EDTA considered as the most widely used chelating agent, has been limited due to its low biodegradability (Huang et al., 2013). NTA has been proven to be one of the most active chelates by Sun and Pignatello (1992) for the decomposition of H_2O_2 and the degradation of 2,4-dichlorophenoxyactic acid among 50 chelating agents. NTA is biodegradable and the metal-NTA complexes have been reported to have rapid photodegradation (Stolzberg & Hume, 1975; Trott et al., 1972). Therefore, the contamination of NTA would not be an environmental concern. Actually, only very low level of NTA has been found in natural waters despite the use of NTA in industrial and consumer products (Anderson et al., 1985). NTA itself shows no adverse effects to aquatic life (Anderson et al., 1985), and its by-products (iminodiacetic acid (IDA), glycine, oxalic acid, ammonia and carbon dioxide) would not cause a toxicity problem to the environment either. In this paper, NTA was used as a chelating agent to modify Fenton process at pH 8.

A reaction sequence was suggested for NTA-Fenton process based on the reaction mechanisms between haem iron and H_2O_2 proposed by Petersen et al. (1989) and by Gutteridge et al. (1990) for the reaction between Fe(III)EDTA and H_2O_2, as in Eqs. 2-1 to 2-12 (Eqs. 2-5 to 2-12 from De Laat et al. (2011)):

$$Fe(II)NTA + H_2O_2 \rightarrow Fe(III)NTA + {}^{\bullet}OH + OH^- \tag{2-1}$$

$$Fe(III)NTA + H_2O_2 \rightarrow Fe(III)OOH^-NTA + H^+ \tag{2-2}$$

$$Fe(III)OOH^{-}NTA + H_2O_2 \rightarrow FeO^{II}NTA + HO_2^{\bullet} + H_2O \tag{2-3}$$

$$FeO^{II}NTA + H_2O_2 \rightarrow Fe(III)NTA + HO_2^{\bullet} + OH^{-} \tag{2-4}$$

$$Fe(III)NTA + HO_2^{\bullet}/O_2^{\bullet -} \rightarrow Fe(II)NTA + O_2 \tag{2-5}$$

$$Fe(II)NTA + HO_2^{\bullet}/O_2^{\bullet -} \rightarrow Fe(III)NTA + O_2 \tag{2-6}$$

$$Fe(II)NTA + {}^{\bullet}OH \rightarrow Fe(III)NTA + OH^{-} \tag{2-7}$$

$$Fe(III)NTA/free\ NTA\ + {}^{\bullet}OH \rightarrow Products \tag{2-8}$$

$${}^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O_2 \tag{2-9}$$

$${}^{\bullet}OH + HO_2^{-} \rightarrow O_2^{\bullet -} + H_2O \tag{2-10}$$

$$HO_2^{\bullet} \rightarrow H^{+} + O_2^{\bullet -} \tag{2-11}$$

$$O_2^{\bullet -} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^{-} \tag{2-12}$$

Although several chelate driven Fenton processes have been described in the literature, there are no reports of these processes for the treatment of OSPW or NAs model compounds so far. Iron concentration in OSPW ranges from 0.8 to 3 mg/L (Allen, 2008), which can be used in Fenton, making the process more economically acceptable. NAs with at least one ring are the main constituents in OSPW (Afzal et al., 2012; Headley & McMartin, 2004). CHA, as one of the simplest cyclic NAs, was selected as a model compound to study the degradation mechanism of NAs by the NTA-Fenton process at pH 8 and ambient temperature. Its structure is the typical structure of NAs and its reaction with radicals can represent the typical reaction between NAs and radicals. Moreover, CHA was used as a reference compound in some AOP papers and its degradation was well studied in previous studies (Afzal et al., 2012; Drzewicz et al., 2010). To mimic the pH of real OSPW, the experiments were conducted using pH 8 buffer solution.

The parameters investigated in this study were as follows: the dose of H_2O_2 and Fe(III)NTA, the ratio of NTA to Fe, the second-order rate constants of $^{\bullet}OH$ with CHA and NTA, the dosing mode of H_2O_2, the oxidant species responsible for the degradation of CHA (tert-butyl alcohol (TBA) as a scavenger of $^{\bullet}OH$ and chloroform ($CHCl_3$) as a scavenger of $O_2^{\bullet-}$), and the reaction between CHA and $O_2^{\bullet-}$ generated with KO_2 dissolved in DMSO/water solution. Moreover, through the analysis of the species in the NTA-Fenton reaction, the reaction mechanisms proposed were discussed.

2.2 Materials and Methods

2.2.1 Reagents and sample preparation

Cyclohexanoic acid (CHA) was purchased from TCI (Portland, OR, USA). NaOH, H_2O_2 (30%), $FeSO_4 \cdot 7H_2O$, 98% H_2SO_4, sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$), 1,10-phenanthroline, acetic acid, dimethyl sulfoxide (DMSO), and sodium acetate were purchased from Fisher Scientific Co. Canada. Nitrilotriacetic acid (NTA) (99%), para-chlorobenzoic acid (pCBA), tetrabutylammonium bromide, and bovine catalase were purchased from Sigma Aldrich. KO_2, tert-butyl alcohol (TBA), and chloroform were purchased from ACROS Organics. Titanium (IV) oxysulfate and ammonium acetate were purchased from Fluka Analytical. All chemicals were ACS grade. Filters used in the experiments were millex syringe-driven 0.2 μm nylon membrane filters provided by Thermo Scientific. All reagents for chromatographic analyses were HPLC grade (optima methanol and acetonitrile) purchased from Sigma Aldrich.

CHA stock solution (15.6 mM) was prepared in 18 MΩ MilliQ water (Millipore Corporation). 0.39 mM CHA test solution was prepared using the stock solution and a pH 8 buffer solution (a mixture of 0.05M sodium tetraborate and 0.05 M sulfuric acid). Fe(II) solution was prepared prior to Fenton reactions by dissolving $FeSO_4 \cdot 7H_2O$ in MilliQ water at pH 3 to prevent any iron precipitation. NTA stock solution was made by dissolving NTA in MilliQ water and the pH of the solution was adjusted to 4 (Abida et al., 2006).

2.2.2 CHA degradation experiments

Experiments were performed in pH 8 buffer solutions (100 mL) with 0.39 mM CHA in 250-mL Erlenmeyer flasks, which were covered in aluminium foil to prevent photochemical processes and put on a platform shaker (New Brunswick Scientific, Innova®2100). NTA and Fe(II) stock solution were added to form Fe(III)NTA complex (Fe(II) was oxidized to Fe(III) instantly once it was added into the solution containing NTA), and afterwards H_2O_2 was added. It has been stated in the literature that Fe(III)EDTA complex prepared by the oxidation of Fe(II)EDTA was more effective in some radical reactions than the complex prepared directly from a ferric salt (Gutteridge et al., 1990). In our study, therefore, we used Fe(II) source to prepare Fe(III)NTA complex. The total volume of the stock solutions added into one sample was less than 2 mL. Samples were taken at 2, 10, 30, 60, 120, 180 and 240 min using 10-mL syringes. H_2O_2 and Fe were analyzed immediately by spectrophotometric methods. Control experiments were conducted without the addition of NTA. Samples for CHA analysis were mixed with drops of bovine catalase (1g/L) to destroy excess H_2O_2, filtered with 0.2 μm nylon membrane filters, and analyzed by LC-MS.

2.2.3 Measurement of the second-order rate constants of $^{\bullet}OH$ with CHA and NTA

A competition-kinetic method using pCBA as a reference compound was used to determine the second-order rate constants of $^{\bullet}OH$ with CHA and NTA according to the approach described by Shu et al. (2013) and Onstein et al. (1999). The doses for CHA, NTA, and pCBA were 0.2 mM, and 50 mM for H_2O_2. The irradiance of the mixture of CHA and pCBA and the mixture of NTA and pCBA was obtained by placing the reactor under a collimated beam (Model PSI-I-120, Calgon Carbon Corporation, USA) equipped with a 1-kw medium pressure Hg-lamp (Calgon Carbon, Pittsburgh, PA, USA). The emission of the lamp is from 200 nm to 530 nm. Sample (80 mL) was held in a 100-mL beaker with a 5.4-cm diameter. Distance from the lamp to the surface was set at 275 mm for the measurement of the rate constant between NTA and $^{\bullet}OH$, and 295 mm for CHA and $^{\bullet}OH$. Smaller distance was used for the slower reaction between NTA and $^{\bullet}OH$ compared to the reaction between CHA and $^{\bullet}OH$.

2.2.4 Reactions between $O_2^{\bullet-}$ and CHA

To investigate the reaction between CHA and $O_2^{\bullet-}$ as a sole reactive oxidant, KO_2 dissolved in DMSO/water solution was used to generate $O_2^{\bullet-}$, based on the methodology proposed by Marklund (1976). Reaction was carried out in a 50-mL Erlenmeyer flask containing 10 mL of a solution of 80% DMSO in water, 0-200 mM TBA, 10 mM NaOH, and 0.39 mM CHA. Low temperature can extend the half-life of $O_2^{\bullet-}$; therefore, the mixture was kept at 4 °C in fridge before experiments. The reactions were initiated by the addition of 0.1-0.5 M solid KO_2 into the mixture, and total reaction time was 24 hours to make sure the reactions were complete.

2.2.5 Analytical methods

Spectrophotometric (GENESYS™ 10S UV-Vis spectrophotometer) methods were used to measure H_2O_2 by titanium (IV) oxysulfate method (DIN 38402H15) at 410 nm (Klamerth et al., 2011; Munoz et al., 1990), and the concentration of Fe(II) and Fe(III) by 1.10-phenanthroline (ISO 6332) at 510 nm (Klamerth et al., 2012). pH measurement was controlled with a pH meter (Fisher Scientific, AR 50) using 0.1 M NaOH and 0.1 M H_2SO_4. NTA in the form of Fe-NTA and pCBA were analyzed by HPLC-UV (Agilent Technologies, 1260 Infinity) at 254 nm and 238 nm, respectively. The mobile phase for NTA analysis consisted of 0.03 M sodium acetate, 0.002 M tetrabutylammonium bromide, and 5% methanol. pH of the solution was adjusted to 2.78 using acetic acid. Flow rate was 0.8 mL/min. The mobile phase for pCBA analysis was 70% A (acetonitrile) and 30% B (10 mM phosphate buffer solution). pH of the solution was adjusted to 2. Flow rate was 1 mL/min. The column used for the NTA and pCBA analysis was C18, 5 μm, 250 mm×4.6 mm, from Phenomenex. CHA analysis was done by HPLC-ion trap MS (Varian 500-MS). The column used for CHA analysis was C8, 5 μm, 250 mm×4.6 mm, from Phenomenex. Column temperature was kept at 40°C. The chromatographic conditions were: 50% A (4 mM aqueous ammonium acetate with 0.1% acetic acid) and 50% B (100% acetonitrile) for the first 16 min, then B solution increased to 100% in 1.5 min and held for 2 min before decreased to 50%. Flow rate was 200 μL/min. Injection volume was 20 μL.

2.3 Results and Discussions

2.3.1 Effect of the dose of Fenton reagents

To investigate the impact of Fe(III)NTA complex and H_2O_2 dose on the degradation of CHA, five different doses of H_2O_2 (0.29, 1.47, 2.94, 4.41, and 5.88 mM) and three different doses of Fe(III)NTA (0.27, 0.45, and 0.89 mM, NTA:Fe = 1:1) were tested in the pH 8 buffer solutions. The doses of H_2O_2 and Fe-NTA were chosen based on literature (Dao & De Laat, 2011; Huang et al., 2013) and the preliminary tests conducted in our study to achieve high CHA removal. CHA removal increased with increasing H_2O_2 dose from 20% at 0.29 mM H_2O_2 to 95% at 5.88 mM H_2O_2, while the impact of the Fe(III)NTA dose on CHA removal was marginal

(**Figure 2-1**). The only significant impact of Fe(III)NTA was on the overall time needed to completely decompose different amounts of H_2O_2 (**Table 2-1**).

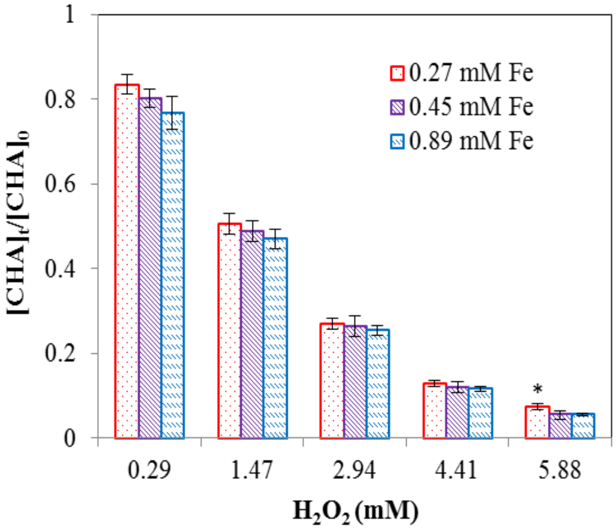


Figure 2-1. Degradation of CHA by NTA-Fenton with different doses of H_2O_2 and Fe(III)NTA ($[NTA:Fe]_0 = 1:1$) (Reaction was not complete in 48 hours under the condition labeled by *, and CHA removal was the removal at 48 hours).

Table 2-1. Time needed for completely decomposing different amount of H_2O_2 with different dose of Fe(III)NTA ($[NTA:Fe]_0 = 1:1$).

Fe(III)NTA (mM) **H_2O_2 (mM)**	**0.27**	**0.45**	**0.89**
5.88	> 48 h	8 h	4 h
4.41	18 h	5 h	1.5 h
2.94	9 h	2 h	0.8 h

For 0.27 mM Fe(III)NTA, when the dose of H_2O_2 increased from 4.41 mM to 5.88 mM (H_2O_2 was not completely consumed in 48 hours, and CHA removal was the removal at 48 hours), CHA removal increased only by 5.4%, from 87.2% to 92.6%. By considering the removal efficiency and the reaction time, 4.41 mM H_2O_2 and 0.27 mM Fe(III)NTA were chosen

as the initial doses. The 48-h reactions were only conducted for very high H_2O_2 dose (5.88 mM) and very low Fe dose (0.27mM). Control experiments were conducted in borate buffer solutions (pH 8), with the addition of 4.41 mM H_2O_2, 0.27 mM Fe(II), and 0 mM NTA, and the CHA removal was less than 5%.

At a given NTA:Fe ratio of 1:1, over 95% NTA was bound in the Fe(III)NTA complex (from our test), thus leaving the Fe(III)NTA complex (the scavenging effect of free NTA on $^{\bullet}OH$ was negligible), CHA, and H_2O_2 to interact with $^{\bullet}OH$. Under these conditions, the second order rate constant between CHA and $^{\bullet}OH$ measured in this paper was $4.09\times10^{9}\ M^{-1}s^{-1}$, between Fe(III)NTA and $^{\bullet}OH$ was $1.6\times10^{8}\ M^{-1}s^{-1}$ at pH 2 (De Laat et al., 2011; Sharma & Sahul, 1982), and between H_2O_2 and $^{\bullet}OH$ was $2.7\times10^{7}\ M^{-1}s^{-1}$ (De Laat & Gallard, 1999; Gallard & De Laat, 2000; Huang et al., 2013). The percentage of $^{\bullet}OH$ scavenged by those species can be estimated using the scavenging term k_ic_i (k_i represents the second-order rate constant between $^{\bullet}OH$ and a solute i, and c_i is the concentration of the solute i) (Dao & De Laat, 2011), as shown in Eq. 2-13.

$$R = \frac{k_i c_i}{k_i c_i + \sum k_j c_j} \tag{2-13}$$

where R denotes the percentage of $^{\bullet}OH$ consumed by a specific species i; k_i represents the second-order rate constant between $^{\bullet}OH$ and i; c_i is the concentration of the solute i; and j denotes the other scavengers except i in the system.

$^{\bullet}$OH scavenged by the species in the NTA-Fenton process is given in **Table 2-2**.

Table 2-2. $^{\bullet}$OH scavenged by the species in the NTA-Fenton process ($[NTA:Fe]_0 = 1:1$).

H_2O_2 dose (mM)	Fe(III)NTA dose (mM)	$^{\bullet}$OH scavenged by H_2O_2 (%)	$^{\bullet}$OH scavenged by Fe(III)NTA (%)	$^{\bullet}$OH for CHA degradation (%)
0.29	0.27	0.5	2.6	96.9
5.88	0.27	8.8	2.4	88.8
0.29	0.45	0.5	4.3	95.2
5.88	0.45	8.7	3.9	87.4
0.29	0.89	0.5	8.2	91.4
5.88	0.89	8.2	7.5	84.3

2.3.2 Effect of the ratio of NTA to Fe

The formation of the Fe(III)NTA complex can be observed by spectrophotometry. NTA (0.54 mM) and NTA (0.54 mM) + H_2O_2 (4.41 mM) had low absorbance below 250 nm and almost none above 250 nm (**Figure 2-2**). The Fe(III)NTA (NTA:Fe = 1:1) complex without the presence of H_2O_2, on the other hand, displayed a significant absorbance below 400 nm. Abida et al. (2006) also reported a similar absorption spectrum of Fe(III)NTA (NTA:Fe = 1:1) from 200 to 400 nm ($\varepsilon = 6000\ M^{-1}cm^{-1}$ at 260 nm). Increasing the NTA concentration, i.e., molar ratio of NTA to Fe from 1:1 to 10:1, did not change the absorbance (see **Figure 2-2**), indicating the similar structure for the formed complexes. For NTA:Fe 0.5:1 (not shown in the Figure), the absorbance (from 200 nm to 300 nm) was much lower than the absorbance for higher NTA:Fe ratios (1:1 to 10:1), and higher than the absorbance for higher ratios above 300 nm. All these data indicated that Fe and NTA formed 1:1 complex, which is confirmed by other researchers (Kołodyńska, 2011; Motekaitis & Martell, 1994; Owens et al., 2000; Sun et al., 2013).

Motekaitis and Martell (1994) also declared that [FeNTA] predominates below pH 3, while the main specie at pH 8 is $[Fe(OH)_2NTA]^{2-}$.

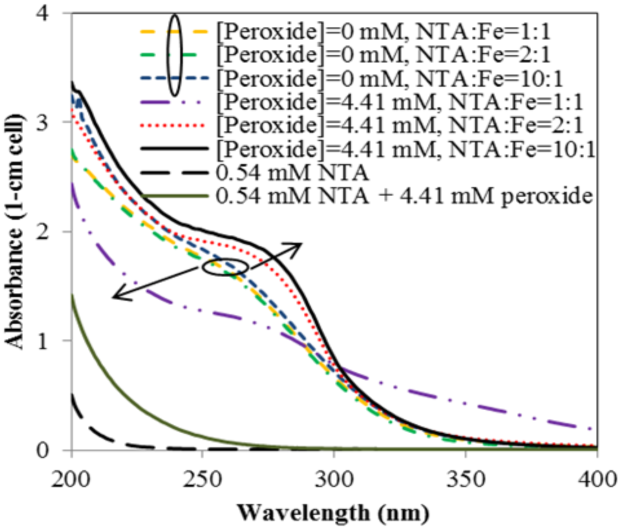


Figure 2-2. Absorption spectra of the samples with different ratios of NTA to Fe ($[Fe]_0$ = 0.27 mM).

For samples with the addition of H_2O_2, the spectrum was recorded after the complete consumption of H_2O_2. The addition of 4.41 mM H_2O_2 changed the original absorption spectra of the samples (NTA:Fe = 1:1) to lower absorption values below 300 nm and to higher values above 300 nm. This change was due to the progressive oxidation of the ligands and subsequent polymerization of the ferric species (Rush & Koppenol, 1988). The study conducted by De Laat et al. (2011) also showed that the addition of 0.5-4 M H_2O_2 to the solution of Fe(III)NTA (Fe(III) = 0.89 mM, NTA:Fe = 1.2:1) led to the generation of species absorbing light in the region of 350 - 600 nm where Fe(III)NTA complex and H_2O_2 do not absorb. While, by adding 4.41 mM H_2O_2 to the samples with the ratio of NTA:Fe higher than 1:1 (2:1 and 10:1), the absorbance of the samples showed an increase between 230 nm and 300 nm with an obvious shoulder at around 260 nm, compared to the original absorbance (see **Figure 2-2**). The absorbance below 230 nm and above 300 nm almost did not change. Unfortunately, explanations for the change of the absorbance of the Fe(III)NTA/H_2O_2 system with excess NTA (NTA:Fe = 2:1 or 10:1) could not be found in the literature. However, the change of the absorbance may be related to with the formation of peroxocomplexes, which is the first step of the decomposition of H_2O_2 by iron-aminopolycarboxylate (De Laat et al., 2011; Francis et al., 1985; Tachiev et al., 2000; Walling et al., 1970). In the case of the reaction of H_2O_2 with Fe(III)EDTA, the formation of purple intermediates has been reported by several researchers (De Laat et al., 2011; Francis et al., 1985; Walling et al., 1970). No literature has been reported yet on the kinetics of the peroxocomplex formed in the Fe(III)NTA/H_2O_2 system.

NTA would be degraded as the reaction proceeds, therefore, excess of NTA (a critical ratio of NTA:Fe > 1:1) is required to keep iron soluble in the solution and to achieve high efficiency of the process. Taking all the results into consideration, 2:1 was chosen as the initial ratio of NTA:Fe.

2.3.3 Effect of the dosing mode of H_2O_2

The effect of the initial H_2O_2 dose versus total consumed H_2O_2 concentration was investigated to see whether it was beneficial to add H_2O_2 consecutively. The reason behind this lies in the fact that high initial H_2O_2 doses have a negative effect on $^{\bullet}OH$ due to the scavenging effect of H_2O_2. Consecutive dosing mode of H_2O_2 should decrease the percentage of $^{\bullet}OH$ scavenged by H_2O_2, and thus increasing the CHA removal. For four consecutive doses of 1.47 mM and eight doses of 0.74 mM of H_2O_2, we added every dose of H_2O_2 after the total consumption of H_2O_2 in the solution. CHA removal was recorded when H_2O_2 in the sample was completely decomposed.

No significant difference in the CHA degradation could be observed whether H_2O_2 was added in 1 dose of 5.88 mM, 4 consecutive doses of 1.47 mM, or 8 doses of 0.74 mM. The CHA removal with 1 dose was 94.7%, with 4 doses was 97.9%, and with 8 doses was 98.3% with only an increase of 3.6% compared to the 1 dose removal (see **Figure 2-3**). This is due to the fact that, as discussed in Section 2.3.1, the second-order rate constant between $^{\bullet}OH$ and H_2O_2 is one magnitude smaller than the rate constant between $^{\bullet}OH$ and Fe(III)NTA, and two magnitudes smaller than the constant between $^{\bullet}OH$ and CHA. The percentage of $^{\bullet}OH$ scavenged by H_2O_2 at 5.88 mM H_2O_2 and 0.27 mM Fe(III)NTA (NTA:Fe = 2:1) was only 8.6%. Under the experimental conditions, the H_2O_2 dosing mode did not have a significant impact on the CHA removal.

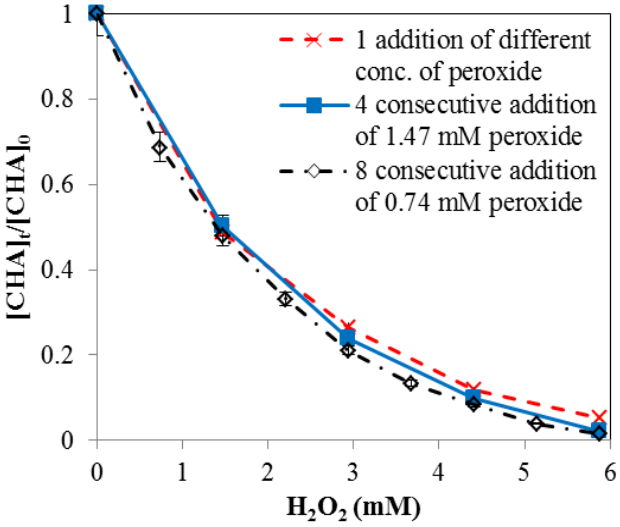


Figure 2-3. Effect of the dosing mode of H_2O_2 on the CHA removal ($[Fe]_0$ = 0.27 mM and $[NTA:Fe]_0$ = 2:1).

2.3.4 Kinetics of the reaction of $^{\bullet}$OH with CHA and NTA

The second-order rate constants between $^{\bullet}$OH and NTA and $^{\bullet}$OH and CHA were investigated using a competition-kinetic approach. pCBA was chosen to be the reference compound because of its widely accepted second-order rate constant with $^{\bullet}$OH of 5.0×10^{9} $M^{-1}s^{-1}$ (Buxton et al., 1988; Shu et al., 2013). Because the initial H_2O_2 concentration was much higher than the concentration of NTA, CHA, and pCBA, the degradation of those compounds can be described in Eq. 2-14 (Shu et al., 2013):

$$k'_P = k'_{Ref}\frac{k_{OH}/_{P}}{k_{OH}/_{Ref}} \tag{2-14}$$

where k'_P (for NTA and CHA) and k'_{Ref} (for pCBA) are the pseudo-first-order rate constants deduced from a plot of $\ln([C]_t/[C]_0)$ vs. reaction time.

The second-order rate constants between organics and $^{\bullet}$OH are in a range of 10^{6} to 10^{10} $M^{-1}s^{-1}$ (Pereira et al., 2007; Shu et al., 2013). The values of the rate constants of $^{\bullet}$OH with NTA and CHA obtained in the present study at pH 8 were $4.77\pm0.24\times10^{8}$ $M^{-1}s^{-1}$ and $4.09\pm0.39\times10^{9}$ $M^{-1}s^{-1}$, respectively (see **Figure 2-4**). We investigated the degradation of pCBA, CHA and NTA by photolysis, and we found photolysis could not directly degrade these compounds under the experimental conditions. The value for CHA and $^{\bullet}$OH agrees well with a literature value of 5.5×10^{9} $M^{-1}s^{-1}$ at pH 9 (Afzal et al., 2012; Buxton et al., 1988). However, for NTA and $^{\bullet}$OH, the value obtained in this study differs from values reported in the literature as 5.5×10^{8} $M^{-1}s^{-1}$ at pH 6 and 4.2×10^{9} $M^{-1}s^{-1}$ at pH 10 (De Laat et al., 2011; Sahul & Sharma, 1987). One reason for this could be attributed to the pH difference. Different processes used to generate $^{\bullet}$OH, such as gamma radiolysis in the study conducted by Sahul and Sharma (1987), might generate different accompanied oxidants compared to the UV/H_2O_2 process (Peller et al., 2003; Shu et al., 2013).

Reactor types, system geometry, reference compound, and the concentration of reactants would also have something to do with the difference (Shu et al., 2013).

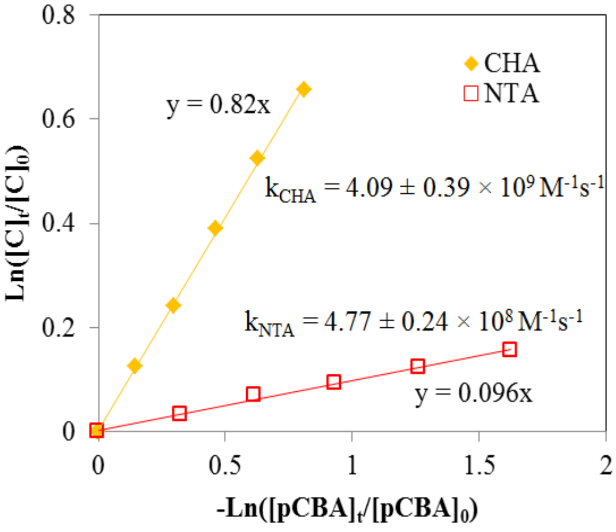


Figure 2-4. Plots of the competitive kinetic equation for the determination of the second-order rate constants of $^{\bullet}$OH with CHA and NTA ($[H_2O_2]_0$ = 50 mM and $[pCBA]_0 = [CHA]_0 = [NTA]_0$ = 0.2 mM).

2.3.5 Radicals responsible for the degradation of CHA

The impact of $^{\bullet}$OH scavengers on the decomposition of H_2O_2 or degradation of target compounds has been investigated by some researchers (Dao & De Laat, 2011; De Laat et al., 2011). In these studies, it was considered that $^{\bullet}$OH was the most dominant radical. However, the effect of $O_2^{\bullet -}$ on the degradation of target compounds has not been thoroughly investigated.

To investigate if other radicals apart from $^{\bullet}$OH had some impact on the CHA degradation, TBA was used as a scavenger of $^{\bullet}$OH with a second-order rate constant of 6×10^8 $M^{-1}s^{-1}$ (Dao & De Laat, 2011) in experiments using 0.27 mM Fe(III)NTA (2:1) and 4.41 mM H_2O_2. CHA degradation decreased from 87% to 6% with increasing TBA concentration (0, 0.5, 5, 20, 40, 200, and 400 mM). When TBA concentration was equal to or higher than 200 mM, all the $^{\bullet}$OH was scavenged, a 6% degradation of CHA could still be observed (**Figure 2-5**a). This confirmed that the main species responsible for CHA degradation in the NTA-Fenton process was $^{\bullet}OH$, which lies in agreement with other researchers (Dao & De Laat, 2011; De Laat et al., 2011). Degradation products of CHA by $^{\bullet}OH$-driven processes have been identified as hydroxy-CHA, dihydroxy-CHA, oxo-CHA, heptadioic acid, and other simple carboxylic acids (Afzal et al., 2012; Drzewicz et al., 2010), so these compounds were to be expected in the NTA-Fenton process as well. The results also indicated that $^{\bullet}OH$ was not the only radical responsible for the degradation of CHA under the experimental conditions. It is commonly accepted that the reaction of H_2O_2 with free Fe(II) at low pH produces $^{\bullet}OH$, while other oxidant species may be yielded at neutral pH (Dao & De Laat, 2011; De Laat & Legube, 1998; Hug & Leupin, 2003; Katsoyiannis et al., 2008; Keenan & Sedlak, 2008; Rivas et al., 2001), which may cause some degradation of CHA.

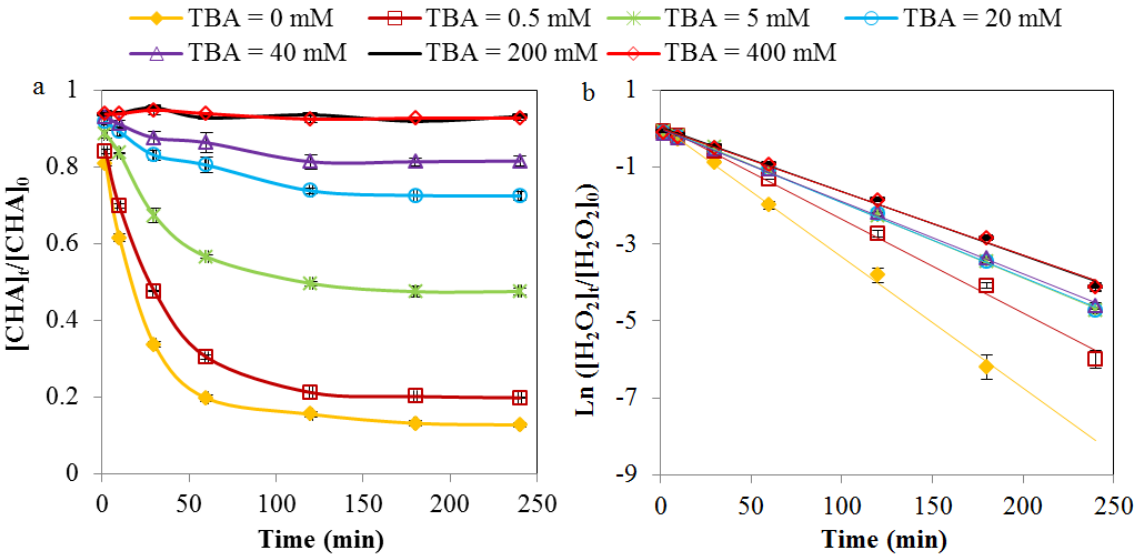


Figure 2-5. a) Effect of TBA concentration on the CHA degradation and b) pseudo-first-order plots of H_2O_2 decomposition as a function of TBA concentration ($[H_2O_2]_0$ = 4.41 mM, $[Fe]_0$ = 0.27 mM, and $[NTA:Fe]_0$ = 2:1).

The pseudo-first-order values of H_2O_2 decomposition rates decreased with increasing TBA concentration (**Figure 2-5**b). One of the main reasons for this behaviour was that TBA decreased the steady-state concentration of $^{\bullet}OH$, leading to the decrease of the decomposition of H_2O_2 by $^{\bullet}OH$ (Dao & De Laat, 2011), and thus the total decomposition rate of H_2O_2.

To verify the presence of $O_2^{\bullet-}$ and to investigate its role in CHA degradation, $CHCl_3$ was used as a scavenger. The second-order rate constants of $CHCl_3$ with $O_2^{\bullet-}$ and $^{\bullet}OH$ are 3×10^{10} $M^{-1}s^{-1}$ and 5×10^{6} $M^{-1}s^{-1}$, respectively (Buxton et al., 1988; Huang et al., 2013), with $CHCl_3$ being highly reactive with $O_2^{\bullet-}$ and much less reactive with $^{\bullet}OH$. The solubility of $CHCl_3$ in water is very low and much higher in organic solvents; therefore, $CHCl_3$ stock solution was made in 40 mM TBA solution. 40 mM was chosen because low concentration of TBA would not dissolve enough $CHCl_3$, while high concentration of TBA could introduce too much TBA into the test solutions that would scavenge all the $^{\bullet}OH$. The effect of the $CHCl_3$ concentration on the degradation of CHA is shown in **Figure 2-6**.

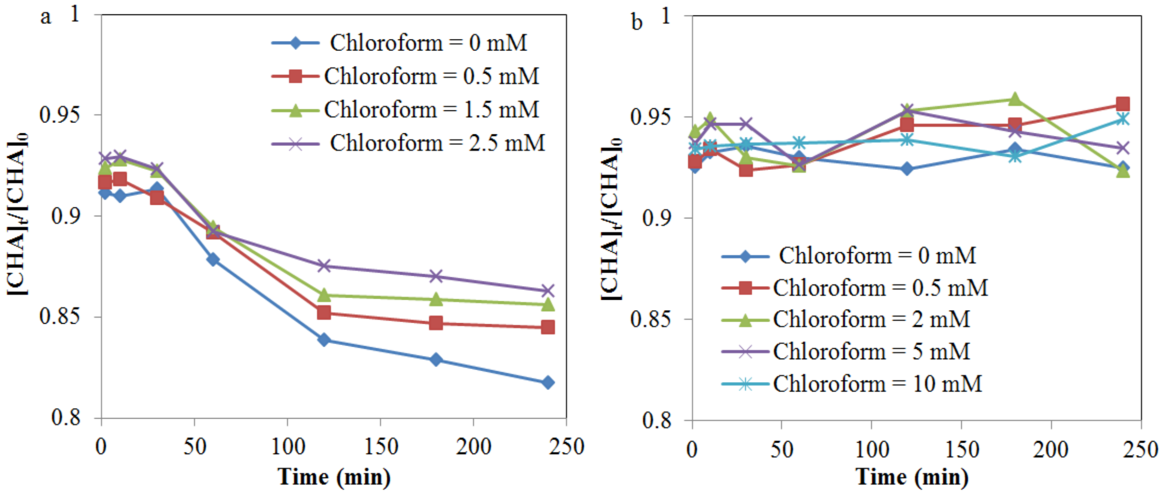


Figure 2-6. Effect of chloroform in a) 40 mM TBA and b) 200 mM TBA on the CHA degradation ($[H_2O_2]_0$ = 4.41 mM, $[Fe]_0$ = 0.27 mM, and $[NTA:Fe]_0$ = 2:1).

In **Figure 2-6**a, at 40 mM TBA, the degradation of CHA decreased with increasing $CHCl_3$ concentration, signifying that $O_2^{\bullet-}$ was produced and had an influence on the degradation of CHA. When the TBA concentration increased to 200 mM (**Figure 2-6**b), all the $^{\bullet}OH$ were scavenged, and there was no significant difference in the CHA degradation with different $CHCl_3$ doses. This indicated that no $O_2^{\bullet-}$ existed in the solution or $O_2^{\bullet-}$ alone couldn't degrade CHA under the experimental conditions. Around 6% CHA degradation was still observed when all the $^{\bullet}OH$ were scavenged, in agreement with the results shown in **Figure 2-5**a.

2.3.6 Reaction between superoxide radical and CHA

To investigate if $O_2^{\bullet-}$ indeed had a significant impact on the CHA degradation, KO_2 as a $O_2^{\bullet-}$ producing agent was applied. $^{\bullet}OH$ could be formed by the reaction of $O_2^{\bullet-}$ with H_2O_2 generated through Eqs. 2-15 to 2-17. TBA in different concentrations (0, 1, 10, 50, 100, and 200 mM) were added into the solution to exclude the influence of $^{\bullet}OH$ on the degradation of CHA. CHA removal increased with the increase of TBA concentration, as shown in **Figure 2-7**, which was probably due to the change of the solution polarity. For example, when TBA dose increased from 0 mM to 200 mM, the degradation of CHA increased from 3.2% to 5.4% at the dose of KO_2 of 0.1 M. While, at 0.3 M KO_2 (0.08 mM $O_2^{\bullet-}$) and 0.5 M KO_2 (0.13 mM $O_2^{\bullet-}$), CHA degradation increased from 13.3% to 17.1% and from 5.3% to 10.2%, respectively.

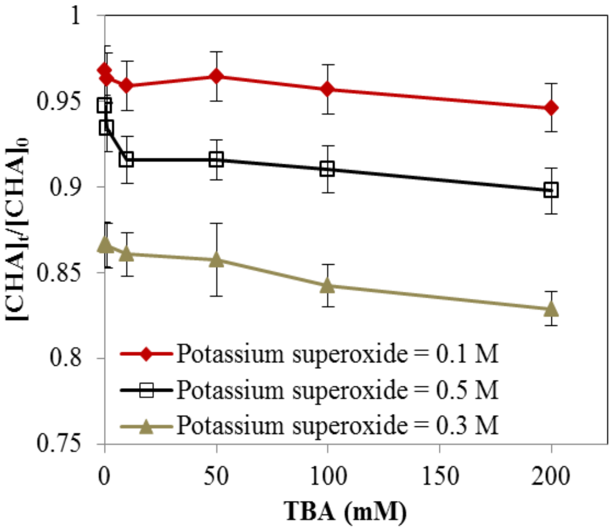


Figure 2-7. Effect of TBA on the CHA degradation in KO_2 solution ($[CHA]_0$ = 0.39 mM, $[NaOH]_0$ = 10 mM, and $[DMSO/water]_0$ = 80%/20%).

The low removal of CHA at high dose of KO_2 can be explained by the spontaneous disproportion of $O_2^{\bullet-}$ interpreted in the following mechanisms (Behar et al., 1970; Marklund, 1976; Rabani & Nielsen, 1969):

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad k = 0.76 \times 10^6 M^{-1}S^{-1} \tag{2-15}$$

$$HO_2^{\bullet} + O_2^{\bullet-} \xrightarrow{H_2O} H_2O_2 + O_2 + OH^- \quad k = 8.5 \times 10^7 M^{-1}S^{-1} \tag{2-16}$$

$$O_2^{\bullet-} + O_2^{\bullet-} \xrightarrow{2H_2O} H_2O_2 + O_2 + 2OH^- \quad k \leq 100\ M^{-1}S^{-1} \tag{2-17}$$

According to Eqs. 2-15 to 2-17, $O_2^{\bullet-}$ and $HO_2^{\bullet}$ can act as scavengers of $O_2^{\bullet-}$. At high dose of KO_2, 0.5 M in this case, part of the $O_2^{\bullet-}$ generated may probably be scavenged by oxidant radicals in the solution, leading to the lower degradation of CHA than that at 0.3 M KO_2.

The activity of $O_2^{\bullet-}$ in water is low due to the high degree solvation of the radical by water molecules. Smith et al. (2004) summarized that the reactivity of $O_2^{\bullet-}$ is increased by the presence of species less polar than water, due to the changes in the solvent shell surrounding $O_2^{\bullet-}$

in water-solvent system. $O_2^{\bullet-}$ produced from KO_2 in anhydrous DMSO is very stable, while in the presence of water it disproportionates according to Eq. 2-18 (Samoilova et al., 2011):

$$2O_2^{\bullet-} + 2H^+ \rightarrow H_2O_2 + O_2 \tag{2-18}$$

A similar study about the production of $O_2^{\bullet-}$ conducted by Marklund (1976) stated that the decay of $O_2^{\bullet-}$ in the solution was second-order with a rate constant of 0.5 $M^{-1}s^{-1}$, giving it a first half-time of 125 s. According to the study of Lokesh and Cunningham (1986), about 375±32 nmol $O_2^{\bullet-}$ was formed per 0.014 mmol KO_2 at pH 7.8. Assuming that 375 nmol $O_2^{\bullet-}$ was produced per 0.014 mmol KO_2 under the experimental conditions, the total amount of $O_2^{\bullet-}$ produced in the samples with 0.1 M KO_2 in 10 mL 80% DMSO/water solution was 0.0266 mmol, leading to around 4% degradation of 0.39 mM CHA, as shown in **Figure 2-7**. Therefore, around 170.9 moles of $O_2^{\bullet-}$ was needed for the degradation of one mole of CHA under the experimental conditions. Because that the reactivity of $O_2^{\bullet-}$ in water is much lower than that in DMSO solution, much more $O_2^{\bullet-}$ would be needed for degrading one mole of CHA in the borate buffer solution. No significant CHA degradation was observed in the control experiments (same condition without the addition of KO_2).

2.3.7 Reaction mechanisms of the NTA-modified Fenton process

In the proposed mechanism described in the Introduction, Fe(II)NTA was oxidized to Fe(III)NTA instantaneously at the beginning of the reaction, and after that $^{\bullet}OH$ was generated by using $O_2^{\bullet-}$ as an intermediate and not directly through the reaction of Fe(III)NTA and H_2O_2. In a study about EDDS-modified Fenton process conducted by Huang et al. (2013), it was also suggested that 80% $^{\bullet}OH$ were produced through $O_2^{\bullet-}$, while 20% from the direct Fenton reactions. In our study, no Fe(II) was detected in the NTA-Fenton process, which is consistent with a similar study conducted by Dao and De Laat (2011), who also stated that no Fe(II) was detected in the Fe(III)NTA/H_2O_2 system. In a study conducted by Gutteridge et al. (1990), Fe(III)EDTA, Fe(III)-dipyridyl and Fe(III)-Ferene S complexes were used, and no reduction of any ferric complex by H_2O_2 was observed. It was suggested that H_2O_2 was unlikely to reduce complexed iron (Gutteridge et al., 1990; Melnyk et al., 1981; Wood, 1988), and the reduction of Fe(III)-chelates was $O_2^{\bullet-}$-dependent not H_2O_2-dependent (Gutteridge et al., 1990), which is in agreement with the proposed mechanism in this paper. Because the generation of $O_2^{\bullet-}$ was already proved in the NTA-Fenton process in Section 2.3.6, the fact that no Fe(II) was detected in the system could be attributed to three reasons: i) the reactivity of $O_2^{\bullet-}$ in the buffer solution was too low; ii) the life-time of $O_2^{\bullet-}$ in the buffer solution was too short; and iii) Fe(II)NTA was generated by the reaction of Fe(III)NTA with $O_2^{\bullet-}$; However, it was oxidized instantly to Fe(III)NTA by O_2. This mechanism is still under investigation and needs further assessment.

2.4 Conclusions

NTA-Fenton was proposed as a potential technology for the treatment of OSPW. Iron in OSPW would make the process more economically acceptable compared to the treatment of other wastewaters. The results obtained in the present work showed that NTA-Fenton processes were very efficient in degrading CHA at pH 8. The degradation was closely related to the dose of H_2O_2, while Fe(III)NTA dose affected primarily the overall reaction time. Absorption spectra of the solution of Fe(III)NTA confirmed the 1:1 ratio of NTA:Fe in the Fe(III)NTA complex and was presented as a proof of the degradation of Fe(III)NTA. The dosing mode of H_2O_2 did not have a significant impact on the CHA removal. $^{\bullet}OH$ was proved to be the main radical responsible for CHA degradation. $O_2^{\bullet-}$ had some influence on the degradation of CHA probably through its influence on the production of $^{\bullet}OH$. Around 170.9 moles of $O_2^{\bullet-}$ was needed for the degradation of one mole of CHA in DMSO/water solution. The reaction mechanisms of NTA-modified Fenton process were proposed and discussed based on the discovery that no Fe(II) was detected in the system. The findings obtained in this study can further be applied to the planning and design of effective advanced oxidation processes for OSPW treatment.

2.5 References

Abida, O., Mailhot, G., Litter, M., & Bolte, M. (2006). Impact of iron-complex (Fe(III)-NTA) on photoinduced degradation of 4-chlorophenol in aqueous solution. *Photochemical & photobiological sciences : Official journal of the European Photochemistry Association and the European Society for Photobiology, 5*(4), 395-402.

Afzal, A., Drzewicz, P., Martin, J. W., & Gamal El-Din, M. (2012). Decomposition of cyclohexanoic acid by the UV/H_2O_2 process under various conditions. *Science of the Total Environment, 426*, 387-392.

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

Anderson, R. L., Bishop, W. E., Campbell, R. L., & Becking, G. C. (1985). A review of the environmental and mammalian toxicology of nitrilotriacetic acid. *CRC Critical Reviews in Toxicology, 15*(1), 1-102.

Basu, S., & Wei, I. W. (1998a). Advanced chemical oxidation of 2, 4, 6 trichlorophenol in aqueous phase by fenton's reagent-part i: effects of the amounts of oxidant and catalyst on the treatment reaction. *Chemical Engineering Communications, 164*(1), 111-137.

Basu, S., & Wei, I. W. (1998b). Advanced chemical oxidation of 2, 4, 6 trichlorophenol in aqueous phase by Fenton's Reagent-Part II: Effects of various reaction parameters on the treatment reaction. *Chemical Engineering Communications, 164*(1), 139-151.

Bautista, P., Mohedano, A. F., Casas, J. A., Zazo, J. A., & Rodriguez, J. J. (2008). An overview of the application of Fenton oxidation to industrial wastewaters treatment. *Journal of Chemical Technology and Biotechnology, 83*(10), 1323-1338.

Beeta, S. (2011). Removal of Benzene from Wastewater by Enzyme-Catalyzed Oxidative Polymerization Combined with a Modified Fenton Reaction. (Doctor of Philosophy), University of Windsor, Windsor, Ontario, Canada.

Behar, D., Czapski, G., Rabani, J., Dorfman, L. M., & Schwarz, H. A. (1970). Acid dissociation constant and decay kinetics of the perhydroxyl radical. *Journal of Physical Chemistry, 74*(17), 3209-3213.

Buxton, G. V., Greenstock, C. L., Helman, W. P., & Ross, A. B. (1988). Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals. *Journal of Physical and Chemical Reference Data, 17*, 513-886.

Dao, Y. H., & De Laat, J. (2011). Hydroxyl radical involvement in the decomposition of hydrogen peroxide by ferrous and ferric-nitrilotriacetate complexes at neutral pH. *Water Research, 45*(11), 3309-3317.

De Laat, J., Dao, Y. H., Hamdi El Najjar, N., & Daou, C. (2011). Effect of some parameters on the rate of the catalysed decomposition of hydrogen peroxide by iron(III)-nitrilotriacetate in water. *Water Research, 45*(17), 5654-5664.

De Laat, J., & Gallard, H. (1999). Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modeling. *Environmental Science & Technology, 33*(16), 2726-2732.

De Laat, J., & Legube, B. (1998). Influence du pH sur la vitesse d'oxydation de compose′ s organiques par Fe^{II}/H_2O_2. Me′ canismes re′ actionnels et mode′ lisation. *New Journal of Chemistry, 22*(3), 263-268.

Drzewicz, P., Afzal, A., Gamal El-Din, M., & Martin, J. W. (2010). 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, 114*(45), 12067-12074.

ERCB, E. R. C. B. (2012). Alberta's Energy Reserves 2011 and Supply/Demand Outlook 2012-2021. In Government of Alberta, C., AB, Canada, 2012 (Ed.).

Esplugas, S., Bila, D. M., Krause, L. G. T., & Dezotti, M. (2007). Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. *Journal of Hazardous Materials, 149*(3), 631-642.

Francis, K. C., Cummins, D., & Oakes, J. (1985). Kinetic and structural investigations of [Fe^{III} (edta)]–[edta= ethylenediaminetetra-acetate (4–)] catalysed decomposition of hydrogen peroxide. *Journal of the Chemical Society, Dalton Transactions*(3), 493-501.

Fu, H., Gamal El-Din, M., Smith, D. W., MacKinnon, M., & Zubot, W. (2008). Ozone treatment of naphthenic acids in Athabasca oil sands process-affected water. Paper presented at the First International Oil Sands Tailings Conference,, Edmonton, AB, Canda.

Gallard, H., & De Laat, J. (2000). Kinetic modelling of Fe(III)/H_2O_2 oxidation reactions in dilute aqueous solution using atrazine as a model organic compound. *Water Research, 34*(12), 3107-3116.

Gutteridge, J., Maidt, L., & Poyer, L. (1990). Superoxide dismutase and Fenton chemistry. Reaction of ferric-EDTA complex and ferric-bipyridyl complex with hydrogen peroxide without the apparent formation of iron (II). *Biochemical Journal, 269*, 169-174.

He, Y. H., Wiseman, S. B., Hecker, M., Zhang, X. W., Wang, N., Perez, L. A., . . . Giesy, J. P. (2011). Effect of ozonation on the estrogenicity and androgenicity of oil sands process-affected water. *Environmental Science & Technology, 45*(15), 6268-6274.

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

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

Huang, W. Y., Brigante, M., Wu, F., Mousty, C., Hanna, K., & Mailhot, G. (2013). Assessment of the Fe(III)–EDDS complex in Fenton-like processes: from the radical formation to the degradation of bisphenol A. *Environmental Science & Technology, 47*(4), 1952-1959.

Hug, S. J., & Leupin, O. (2003). Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. *Environmental Science & Technology, 37*(12), 2734-2742.

Kannel, P. R., & Gan, T. Y. (2012). 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, 47(1), 1-21.

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

Keenan, C. R., & Sedlak, D. L. (2008). Ligand-enhanced reactive oxidant generation by nanoparticulate zero-valent iron and oxygen. *Environmental Science & Technology, 42*(18), 6936-6941.

Klamerth, N., Malato, S., Aguera, A., Fernandez-Alba, A., & Mailhot, G. (2012). Treatment of municipal wastewater treatment plant effluents with modified photo-Fenton as a tertiary treatment for the degradation of micro pollutants and disinfection. *Environmental Science & Technology, 46*(5), 2885-2892.

Klamerth, N., Malato, S., Maldonado, M. I., Agüera, A., & Fernández-Alba, A. (2011). Modified photo-Fenton for degradation of emerging contaminants in municipal wastewater effluents. *Catalysis Today, 161*(1), 241-246.

Kołodyńska, D. (2011). Chelating agents of a new generation as an alternative to conventional chelators for heavy metal ions removal from different waste waters: INTECH Open Access Publisher.

Kwan, W. P., & Voelker, B. M. (2003). Rates of hydroxyl radical generation and organic compound oxidation in mineral-catalyzed Fenton-like systems. *Environmental Science & Technology, 37*(6), 1150-1158.

Li, Y. C., Bachas, L. G., & Bhattacharyya, D. (2005). Kinetics studies of trichlorophenol destruction by chelate-based Fenton reaction. *Environmental Engineering Science, 22*(6), 756-771.

Lipczynska-Kochany, E., & Kochany, J. (2008). Effect of humic substances on the Fenton treatment of wastewater at acidic and neutral pH. *Chemosphere, 73*(5), 745-750.

Lokesh, B. R., & Cunningham, M. L. (1986). Further studies on the formation of oxygen radicals by potassium superoxide in aqueous medium for biochemical investigations. *Toxicology letters, 34*(1), 75-84.

MacKinnon, M. D. (2004). Oild sands water quality issues: properties, treatment, and discharge options, from http://www.conrad.ab.ca/seminars/water_usage/2004/Agenda.htm

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

Malato, S., Fernández-Ibáñez, P., Maldonado, M. I., Blanco, J., & Gernjak, W. (2009). Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today, 147*(1), 1-59.

Marklund, S. (1976). Spectrophotometric study of spontaneous disproportionation of superoxide anion radical and sensitive direct assay for superoxide dismutase. *Journal of Biological Chemistry, 251*(23), 7504-7507.

Melnyk, D. L., Horwitz, S. B., & Peisach, J. (1981). Redox potential of iron-bleomycin. *Biochemistry, 20*(18), 5327-5331.

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

Motekaitis, R. J., & Martell, A. E. (1994). The iron(III) and iron(II) complexes of nitrilotriacetic acid. *Journal of Coordination Chemistry, 31*(1), 67-78.

Munoz, M., Alonso, J., Bartroli, J., & Valiente, M. (1990). Automated spectrophotometric determination of titanium (IV) in water and brines by flow injection based on its reaction with hydrogen peroxide. *Analyst, 115*(3), 315-318.

Onstein, P., Stefan, M. I., & Bolton, J. R. (1999). Competition kinetics method for the determination of rate constants for the reaction of hydroxyl radicals with organic pollutants using the UV/H_2O_2 advanced oxidation technology: the rate constants for the tert-butyl formate ester and 2, 4-dinitrophenol. *Journal of Advanced Oxidation Technologies, 4*(2), 231-236.

Owens, G., Ferguson, V. K., McLaughlin, M. J., Singleton, I., Reid, R. J., & Smith, F. (2000). Determination of NTA and EDTA and speciation of their metal complexes in aqueous solution by capillary electrophoresis. *Environmental Science & Technology, 34*(5), 885-891.

Peller, J., Wiest, O., & Kamat, P. V. (2003). Mechanism of Hydroxyl Radical-Induced Breakdown of the Herbicide 2, 4-Dichlorophenoxyacetic Acid (2, 4-D). *Chemistry-A European Journal, 9*(21), 5379-5387.

Pereira, V. J., Weinberg, H. S., Linden, K. G., & Singer, P. C. (2007). UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm. *Environmental Science & Technology, 41*(5), 1682-1688.

Peters, L. E., MacKinnon, M., Van Meer, T., van den Heuvel, M. R., & Dixon, D. G. (2007). Effects of oil sands process-affected waters and naphthenic acids on yellow perch (Perca flavescens) and Japanese medaka (Orizias latipes) embryonic development. *Chemosphere, 67*(11), 2177-2183.

Petersen, R. L., Symons, M. C., & Taiwo, F. (1989). Application of radiation and electron spin resonance spectroscopy to the study of ferryl myoglobin. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 85*(8), 2435-2443.

Pignatello, J. J., Oliveros, E., & MacKay, A. (2006). Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology, 36*(1), 1-84.

Pouran, S. R., Aziz, A. A., & Daud, W. M. A. W. (2015). Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters. *Journal of Industrial and Engineering Chemistry, 21*, 53-69.

Pourrezaei, P. (2013). Physico-Chemical Processes for Oil Sands Process-Affected Water Treatment. (Doctor of Philosophy), University of Alberta, Edmonton, A.B.

Rabani, J., & Nielsen, S. O. (1969). Absorption spectrum and decay kinetics of O_2^- and HO_2 in aqueous solutions by pulse radiolysis. *Journal of Physical Chemistry, 73*(11), 3736-3744.

Rastogi, A., Al-Abed, S. R., & Dionysiou, D. D. (2009). Effect of inorganic, synthetic and naturally occurring chelating agents on Fe(II) mediated advanced oxidation of chlorophenols. *Water Research, 43*(3), 684-694.

Rivas, F. J., Beltran, F. J., Frades, J., & Buxeda, P. (2001). Oxidation of p-hydroxybenzoic acid by Fenton's reagent. *Water Research, 35*(2), 387-396.

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

Rush, J., & Koppenol, W. (1988). Reactions of iron(II) nitrilotriacetate and iron (II) ethylenediamine-N, N'-diacetate complexes with hydrogen peroxide. *Journal of the American Chemical Society, 110*(15), 4957-4963.

Sahul, K., & Sharma, B. (1987). Gamma radiolysis of nitrilotriacetic acid (NTA) in aqueous solutions. *Journal of Radioanalytical and Nuclear Chemistry, 109*(2), 321-327.

Samoilova, R. I., Crofts, A. R., & Dikanov, S. A. (2011). Reaction of superoxide radical with quinone molecules. *Journal of Physical Chemistry A, 115*(42), 11589-11593.

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

Sharma, B. K., & Sahul, K. (1982). Co-60 gamma radiolysis of iron(III)-nitrilotriacetate in aqueous solutions. *Radiation Physics and Chemistry, 20*, 341-346.

Shu, Z., Bolton, J. R., Belosevic, M., & Gamal El-Din, M. (2013). Photodegradation of emerging micropollutants using the medium-pressure UV/H_2O_2 Advanced Oxidation Process. *Water Research, 47*(8), 2881-2889.

Smith, B. A., Teel, A. L., & Watts, R. J. (2004). Identification of the reactive oxygen species responsible for carbon tetrachloride degradation in modified Fenton's systems. *Environmental Science & Technology, 38*(20), 5465-5469.

Stolzberg, R. J., & Hume, D. N. (1975). Rapid formation of iminodiacetate from photochemical degradation of iron(III) nitrilotriacetate solutions. *Environmental Science & Technology, 9*(7), 654-656.

Sun, S.-P., Zeng, X., & Lemley, A. T. (2013). Kinetics and mechanism of carbamazepine degradation by a modified Fenton-like reaction with ferric-nitrilotriacetate complexes. *Journal of Hazardous Materials, 252*, 155-165.

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

Swart, N. C., & Weaver, A. J. (2012). The Alberta oil sands and climate. *Nature Climate Change, 2*(3), 134-136.

Tachiev, G., Roth, J., & Bowers, A. (2000). Kinetics of hydrogen peroxide decomposition with complexed and "free" iron catalysts. *International Journal of Chemical Kinetics, 32*(1), 24-35.

Teel, A. L., Warberg, C. R., Atkinson, D. A., & Watts, R. J. (2001). Comparison of mineral and soluble iron Fenton's catalysts for the treatment of trichloroethylene. *Water Research, 35*(4), 977-984.

Trott, T., Henwood, R. W., & Langford, C. H. (1972). Sunlight photochemistry of ferric nitrilotriacetate complexes. *Environmental Science & Technology, 6*(4), 367-368.

Walling, C., Kurz, M., & Schugar, H. J. (1970). Iron(III)-ethylenediaminetetraacetic acid-peroxide system. *Inorganic Chemistry, 9*(4), 931-937.

Wang, N. (2011a). Ozonation and biodegradation of oil sands process water. (Master of Science), University of Alberta, Edmonton, AB, Canada.

Wang, Y. N. (2011b). Application of Coagulation-Flocculation Process for Treating Oil Sands Process-Affected Water. (Master of Science), University of Alberta, Edmonton, AB, Canada.

Wang, Z., Bush, R. T., & Liu, J. (2013). Arsenic(III) and iron(II) co-oxidation by oxygen and hydrogen peroxide: Divergent reactions in the presence of organic ligands. *Chemosphere, 93*(9), 1936-1941.

Wood, P. M. (1988). The potential diagram for oxygen at pH 7. *Biochemical Journal, 253*(1), 287-289.

Xue, X., Hanna, K., Despas, C., Wu, F., & Deng, N. (2009). Effect of chelating agent on the oxidation rate of PCP in the magnetite/H_2O_2 system at neutral pH. *Journal of Molecular Catalysis A: Chemical, 311*(1), 29-35.

3 KINETICS STUDY ON THE DEGRADATION OF CYCLOHEXANOIC ACID WITH [S,S]-ETHYLENEDIAMINE-N,N'-DISUCCINIC ACID-MODIFIED FENTON PROCESS[2]

3.1 Introduction

Oil sands process-affected water (OSPW) produced during the bitumen extraction processes is highly saline and acutely toxic to aquatic organisms (He et al., 2011). Naphthenic acids (NAs) as one of the organic components in OSPW are a group of aliphatic and alicyclic carboxylic acids, and they are the main species responsible for OSPW toxicity (Kannel & Gan, 2012). The removal of NAs from OSPW has been a focus of researchers since 1980s due to their toxicity and persistence (Afzal et al., 2012; Allen, 2008). Advanced oxidation processes (AOPs) with the generation of hydroxyl radical ($^{\bullet}$OH), the second strongest known oxidant to fluorine, have been proposed as a complementary technology for the OSPW remediation, due to their strong ability of degrading NAs and reducing the overall toxicity of OSPW towards selected test organisms (Fu et al., 2008; Scott et al., 2008; Wang, 2011).

With the generation of $^{\bullet}$OH through the reaction of H_2O_2 with Fe(II) at acidic pH (around 3.0), Fenton processes have been successfully applied to degrade diverse contaminants in wastewaters (Basu & Wei, 1998a; Basu & Wei, 1998b; Kwan & Voelker, 2003; Li et al., 2005; Teel et al., 2001). However, the acidic condition requirement limits their application. At neutral

---

[2] A version of this chapter has been submitted previously: Ying Zhang, Nikolaus Klamerth, Selamawit Ashagre Messele, Pamela Chelme-Ayala, & Mohamed Gamal El-Din. Kinetics Study on the Degradation of a Model Naphthenic Acid by Ethylenediamine-N,N'-Disuccinic Acid-Modified Fenton Process. *Journal of Hazardous Materials* (Submitted date: May 05, 2016).

pH, Fe(III) ions exist in the form of hydroxyl complexes (such as hydrous oxyhydroxides, $Fe_2O_3 \cdot nH_2O$), which are insoluble in water and, therefore, cannot be cycled in the reduction steps. At the same time, Fe(II) salts may probably co-precipitate with Fe(III) oxyhydroxides at neutral pH (Lipczynska-Kochany & Kochany, 2008). In order to carry out Fenton reactions at neutral pH, chelating agents have been used to keep iron soluble and, therefore, to improve the efficiency of the process (Lipczynska-Kochany & Kochany, 2008; Pignatello et al., 2006; Sun & Pignatello, 1992). The ligands may affect the modified Fenton processes by: (i) the ligand-field effects on the redox-properties of the metal; (ii) promoting the reaction of H_2O_2 with the metal; and (iii) competing with substrate for the oxidants (Georgi et al., 2007; Sun & Pignatello, 1992).

Aminopolycarboxylic acids (APCAs) have been used as chelating agents in the modified Fenton processes. The use of ethylenediaminetetraacetic acid (EDTA) considered as the most widely used chelating agent, has been limited due to its low biodegradability (Huang et al., 2013). Ethylenediamine-N,N'-disuccinic acid (EDDS) as a structural isomer of EDTA has two chiral centers in its structure and exists in three stereoisomers: [S,S]-, [R,S]-, and [R,R]-EDDS (Nagaraju et al., 2007). The preparation of EDDS by the most economical method produces a mixture of isomers containing 25% of [S,S]-EDDS, 25% of [R,R]-EDDS, and 50% of the meso form [R,S]/[S,R] (Metsärinne et al., 2001; Pavelčik & Majer, 1978). These three stereoisomers have different biodegradabilities: [S,S]-EDDS is readily biodegradable, [R,R]-EDDS is resistant, and [R,S]/[S,R]-EDDS is comparatively but not readily biodegradable (Metsärinne et al., 2001; Schowanek et al., 1997). The final carbon dioxide (CO_2) yield of [S,S]-EDDS exceeds 80% after 20 days biodegradation, assessed by the modified Sturm test organisation for economic cooperation and development (OECD) 301 B (Jaworska et al., 1999; Jones & Williams, 2001; OECD, 1996; Schowanek et al., 1997). [S,S]-EDDS can form a stable 1:1 complex with Fe at neutral pH. Its performance is equal to EDTA in most cases and even much better under specific conditions (Jones & Williams, 2001; Whitburn et al., 1999; Willkinson, 1998). Based on the reactions in the classical Fenton process, the main reactions in the EDDS-Fenton process are summarized as follows (Eqs. 3-1 to 3-3 (Huang et al., 2013) and Eqs. 3-6 to 3-8 (De Laat et al., 2011)):

$$Fe(II)EDDS + H_2O_2 \rightarrow Fe(III)EDDS + {}^{\bullet}OH + OH^- \tag{3-1}$$

$$Fe(III)EDDS + H_2O_2 \rightarrow Fe(II)EDDS + HO_2^{\bullet}/O_2^{\bullet-} + H^+ \tag{3-2}$$

$$Fe(III/II)EDDS + {}^{\bullet}OH \rightarrow oxidized\ products \tag{3-3}$$

$$Fe(II)EDDS + HO_2^{\bullet}/O_2^{\bullet-} \rightarrow Fe(III)EDDS + H_2O_2 \tag{3-4}$$

$$Fe(III)EDDS + HO_2^{\bullet}/O_2^{\bullet-} \rightarrow Fe(II)EDDS + O_2 \tag{3-5}$$

$${}^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \tag{3-6}$$

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{3-7}$$

$${}^{\bullet}OH + HO_2^- \rightarrow O_2^{\bullet-} + H_2O \tag{3-8}$$

$$HO_2^{\bullet} \rightarrow H^+ + O_2^{\bullet-} \tag{3-9}$$

$$O_2^{\bullet-} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- \tag{3-10}$$

To date, no study about the degradation of NAs by the EDDS-Fenton process has been reported yet. Cyclohexanoic acid **(**CHA) was selected as a model NA compound to study the mechanisms and kinetics of the EDDS-Fenton process at pH 8, and CHA degradation products were also investigated. Possible interference of OSPW matrix on the process was discussed. This is the first paper that reported the time profiles of the main species in the EDDS-Fenton process, especially the degradation of EDDS. The second-order rate constant between EDDS and ${}^{\bullet}$OH was investigated at pH 8 for the first time. We also investigated the dosing mode of H_2O_2 and Fe-EDDS to improve the removal of CHA, which was never done by the other researchers in the EDDS-Fenton system. The reaction mechanisms of $^{\bullet}OH$ with NAs, para-chlorobenzoic acid (pCBA), and EDDS were described and compared. Tert-butyl alcohol (TBA) and chloroform ($CHCl_3$) were used to investigate the impact of $^{\bullet}OH$ and $O_2^{\bullet-}$, respectively, on the CHA degradation. The half-wave potential ($E_{1/2}$) of Fe(III/II)EDDS was measured at pH 7 to 9 and used for the estimation of ΔG_0 for the first time.

3.2 Materials and Methods

3.2.1 Chemicals and sample preparation

Cyclohexanoic acid (CHA) was purchased from TCI (Portland, OR, USA). NaOH, H_2O_2 (30%), $FeSO_4 \cdot 7H_2O$, 98% H_2SO_4, sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$), 1,10-phenanthroline, acetic acid, and sodium acetate were purchased from Fisher Scientific Co., Canada. Para-chlorobenzoic acid (pCBA), tetrabutylammonium hydrogen sulfate, ethylenediamine-N,N'-disuccinic acid (EDDS) (35% in water), bovine catalase, and optima methanol and acetonitrile were purchased from Sigma Aldrich. Tert-butyl alcohol (TBA) and chloroform ($CHCl_3$) were purchased from ACROS Organics. Titanium (IV) oxysulfate and ammonium acetate were purchased from Fluka Analytical. Filters used in the experiments were millex syringe-driven 0.2 μm nylon membrane filters provided by Thermo Scientific.

CHA stock solution (15.6 mM) was prepared in 18-MΩ MilliQ water (Millipore Corporation). To mimic the pH of real OSPW, the experiments were conducted using pH 8 buffer solutions (a mixture of 0.05M sodium tetraborate and 0.05 M sulfuric acid). 0.39 mM CHA test solution was prepared by diluting the CHA stock solution using the buffer solution. 45

mM Fe(II) stock solution was prepared prior to Fenton reactions by dissolving $FeSO_4 \cdot 7H_2O$ in MilliQ water at pH 3 to prevent any iron precipitation. 180 mM EDDS stock solution was prepared by diluting 35% EDDS solution.

3.2.2 CHA degradation experiments

Experiments were carried out in 100 mL CHA samples in 250-mL Erlenmeyer flasks covered by aluminium foil on a platform shaker (New Brunswick Scientific, Innova®2100). EDDS and $FeSO_4$ stock solutions were added into the samples first, and H_2O_2 was added last. Samples were taken at 0, 2, 10, 30, 60, 120, 180, 300, and 420 min using 10-mL syringes and immediately analyzed for H_2O_2 and Fe. Samples for CHA analysis were mixed with drops of bovine catalase (1 g/L) to destroy the remaining H_2O_2, and filtered with 0.2 μm nylon membrane filters. No loss of CHA was observed during the filtration (recovery ranged from 96 to 106%). Control experiments were conducted without the addition of EDDS. All the experiments were conducted in at least duplicates.

3.2.3 Measurement of the second-order rate constant between EDDS and $^{\bullet}OH$

In a competition-kinetic scheme, the decay of a target compound is compared with that of a “reference” compound. pCBA as a “reference” compound was used in this study to determine the second-order rate constant between EDDS and $^{\bullet}OH$ according to the protocol described by Shu et al. (2013) and Onstein et al. (1999). The dose for EDDS and pCBA was 0.2 mM, and 50 mM for H_2O_2. Because that the initial H_2O_2 concentration in this approach was much higher than that of EDDS and pCBA, an assumption can be made that $^{\bullet}OH$ only reacted with the target compound, the reference compound, and H_2O_2. Some researchers have employed this approach in the UV/H_2O_2 system to determine the rate constants of $^{\bullet}OH$ and organic contaminants (García

Einschlag et al., 2002; Onstein et al., 1999; Pereira et al., 2007; Shu et al., 2013), indicating the validity of the approach. The degradation of EDDS and pCBA can be described in Eq. 3-11 (Shu et al., 2013):

$$k'_p = k'_{Ref} \frac{k_{OH/P}}{k_{OH/Ref}} \tag{3-11}$$

where k'_{P} (for EDDS) and k'_{Ref} (for pCBA) are the pseudo-first-order rate constants deduced from a plot of $\ln([C]_t/[C]_0)$ vs. reaction time.

Irradiation of the mixture of EDDS and pCBA was held in a 100-mL beaker with a 5.4-cm diameter and placed under a collimated beam (Model PSI-I-120, Calgon Carbon Corporation, USA) equipped with a 1-kw medium pressure Hg-lamp (Calgon Carbon, Pittsburgh, PA, USA). The emission of the lamp was from 200 nm to 530 nm. The pH of the sample was adjusted to 8 prior to the experiment and the change of the pH during the reaction was less than 0.2.

3.2.4 Analytical methods

Spectrophotometric (GENESYS™ 10S UV-Vis spectrophotometer) methods were used to measure H_2O_2 by titanium (IV) oxysulfate method (DIN 38402H15) at 410 nm (Klamerth et al., 2011; Munoz et al., 1990), and Fe(II) and Fe(III) by 1.10-phenanthroline method (ISO 6332) at 510 nm (Klamerth et al., 2012). pH was controlled with a pH meter (Fisher Scientific, AR 50) using 0.1 M NaOH and 0.1 M H_2SO_4. Chemical oxygen demand (COD) measurement was carried out with a colorimetric method (Standard Methods for the Examination of Water and Wastewater 5220D) using a COD reactor (Bioscience, Inc.) and a visible spectrophotometer (Thermo Scientific GENESYS™ 20). The concentration of pCBA and EDDS was measured by HPLC-UV (Agilent Technologies, 1260 Infinity) equipped with a C18 reverse phase column (5 μm, 250 mm×4.6 mm, from Phenomenex). The mobile phase for pCBA analysis (at 238 nm) was 70% A (acetonitrile) and 30% B (10 mM phosphate buffer solution). pH of the phosphate buffer solution was adjusted to 2. The flow rate was 1 mL/min. The analysis of EDDS in the form of Fe-EDDS was performed at 240 nm with a mobile phase of a 10%/90% mixture of methanol and formate buffer (2 mM tetrabutylammonium hydrogen sulfate and 15 mM sodium formate) at a flow rate of 0.8 mL/min. The pH of the sodium formate solution was adjusted to 4 with formic acid. CHA analysis was done with a high-pressure liquid chromatograph (HPLC)-ion trap mass spectrometry (MS) (Varian 500-MS) with a C8 column (5 μm, 250 mm×4.6 mm, from Phenomenex). The column temperature was kept at 40 °C. The chromatographic conditions were: 50% A (4 mM aqueous ammonium acetate with 0.1% acetic acid) and 50% B (100% acetonitrile) for the first 16 min, then B solution increased to 100% in 1.5 min and held for 2 min before decreased to 50%. Flow rate was 200 μL/min. Injected volume was 20 μL. Products of CHA degradation were analyzed with an Agilent 1200 HPLC coupled with an Agilent 6220 TOF mass spectrometer (Santa Clara, CA, USA) in negative scan/SIM (selected-ion monitoring) mode. The column used for the detection was Kinetex 2.6 μm, XB-C18, 100 Å, 2.1×100 mm. The temperature was set at 40 °C. Solvents used were A of 4 mM aqueous ammonium acetate with 0.1% acetic acid and B of 100% acetonitrile. The solvent gradient for CHA products detection is given in **Table 3-1**.

Table 3-1. HPLC solvent gradient for CHA products detection.

Time (min)	The percentage of solvent B (%)	Flow rate (mL/min)
0	2	0.35
1	2	0.35
8	95	0.35
11	95	0.35

Cyclic voltammetry was conducted with a Metrohm Autolab electrochemical workstation using a three-electrode system. Platinum electrode, silver chloride electrode, and glassy carbon electrode were used as counter, reference, and working electrodes, respectively. The electrolyte used in this study was 0.1 M NaCl. Scan rate was 1.2 V/s. The buffer solutions used were Tris buffer at pH 7 (a mixture of 0.1 M Tris and 0.1 M HCl), and borate buffers at pH 8 and pH 9 (a mixture of 0.05 M sodium tetraborate and 0.1 M HCl).

3.3 Results and Discussions

3.3.1 Species in the EDDS-Fenton process

The species in the EDDS-Fenton process at pH 8 were investigated under the optimum conditions ($[H_2O_2]_0$ = 2.94 mM, $[Fe]_0$ = 0.45 mM, and $[EDDS:Fe]_0$ = 2:1), which were determined based on the H_2O_2 and Fe dose and the results of the factorial experiments (**Table 3-2** and **Figure 3-1**).

Table 3-2. Results of the factorial experiments (t = 7 h).

H_2O_2 dose (mM)	**Fe dose (mM)**	**EDDS: Fe**	**H_2O_2 residue (mM)**	**Fe(II) residue (mM)**	**Fe(III) residue (mM)**	**CHA removal (%)**
2.94	0.89	0.5:1	0.50	0.04	0.18	61.6±1.3
2.94	0.89	1:1	0.04	0.09	0.64	75.1±0.7
2.94	0.89	2:1	0.14	0.12	0.77	74.9±0.7
2.94	0.45	0.5:1	1.57	0.04	0.28	41.3±2.9
2.94	0.45	1:1	0.61	0.08	0.37	55.2±2.7
2.94	0.45	2:1	0.03	0.12	0.38	64.4±2.3
2.94	0.18	0.5:1	2.31	0.01	0.11	19.6±2.1
2.94	0.18	1:1	1.81	0.02	0.14	28.0±1.2
2.94	0.18	2:1	1.14	0.04	0.16	33.6±0.6
1.47	0.89	0.5:1	0.00	0.03	0.17	61.4±1.9
1.47	0.89	1:1	0.03	0.05	0.70	66.3±1.6
1.47	0.89	2:1	0.14	0.06	0.76	64.7±1.6
1.47	0.45	0.5:1	0.43	0.04	0.33	42.1±3.2
1.47	0.45	1:1	0.00	0.06	0.37	56.7±2.7
1.47	0.45	2:1	0.04	0.08	0.38	55.9±2.7
1.47	0.18	0.5:1	1.03	0.01	0.10	19.0±3.1
1.47	0.18	1:1	0.58	0.02	0.14	27.7±2.1
1.47	0.18	2:1	0.09	0.04	0.17	38.3±0.8
0.74	0.89	0.5:1	0.00	0.02	0.31	54.8±0.1
0.74	0.89	1:1	0.00	0.03	0.73	58.8±1.0
0.74	0.89	2:1	0.05	0.02	0.76	50.6±1.4
0.74	0.45	0.5:1	0.04	0.04	0.33	41.6±3.5
0.74	0.45	1:1	0.00	0.04	0.37	48.2±2.4
0.74	0.45	2:1	0.02	0.04	0.38	45.0±1.8
0.74	0.18	0.5:1	0.37	0.01	0.11	19.8±1.4
0.74	0.18	1:1	0.09	0.02	0.15	28.8±0.0
0.74	0.18	2:1	0.00	0.03	0.17	33.1±0.9

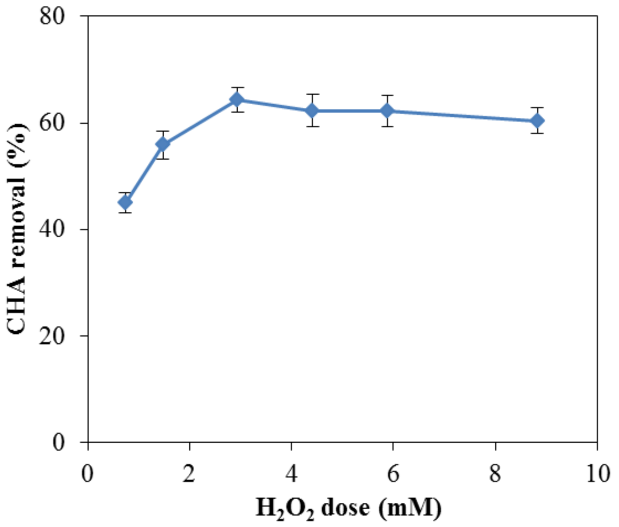


Figure 3-1. The influence of H_2O_2 dose on the CHA removal ($[Fe]_0$ = 0.45 mM and $[EDDS:Fe]_0$ = 2:1).

A complete decomposition of H_2O_2 was observed at 420 min under the optimum conditions (**Figure 3-2**). Fe-EDDS in the main form of Fe(III)EDDS decreased with time, and only 0.14 mM (30% of its initial dose of 0.45 mM) was left at the end of the reaction, while the amount of total iron only decreased from 0.45 mM to 0.42 mM (6% removal) in 420 min. These results indicated that EDDS was degraded into other organics, which were still able to keep iron soluble in the solution. CHA decreased from 0.39 mM to 0.26 mM (32% removal) in the first 2 min, and then slowly decreased to 0.14 mM (64% removal) at the end of the reaction. The very fast CHA degradation at the beginning of the reaction was due to the fact that most of the iron was in the form of Fe(II), which reacted very fast with H_2O_2. Similar results were observed at 4.41 mM H_2O_2, 0.45 mM Fe(II), and EDDS:Fe of 2:1. CHA removal reached 40% in the first two minutes at these conditions, and slowly increased to 62% at the end of the reaction. We also obtained a two-stage CHA degradation in the nitrilotriacetic acid (NTA)-Fenton system (4.41 mM H_2O_2, 0.27 mM Fe, and NTA:Fe =2:1) in our previous study (Zhang et al., 2016). CHA removal in that process reached 20% in the first two minutes, and slowly increased to 87% at 240 min. Furthermore, De Laat et al. (2011) reported a two-stage H_2O_2 decomposition with 0.2 mM Fe, 0.5 mM NTA, and four different concentrations of H_2O_2 (0.2-0.9 mM), a very fast decomposition in the first 20 s and a slow decomposition in the following 13 min. Most of Fe(II) was fast oxidized to Fe(III) at the beginning of the reaction, as shown in **Figure 3-2**.

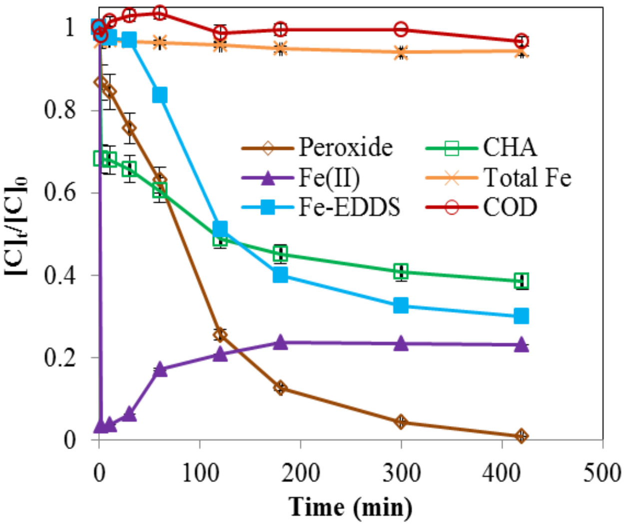
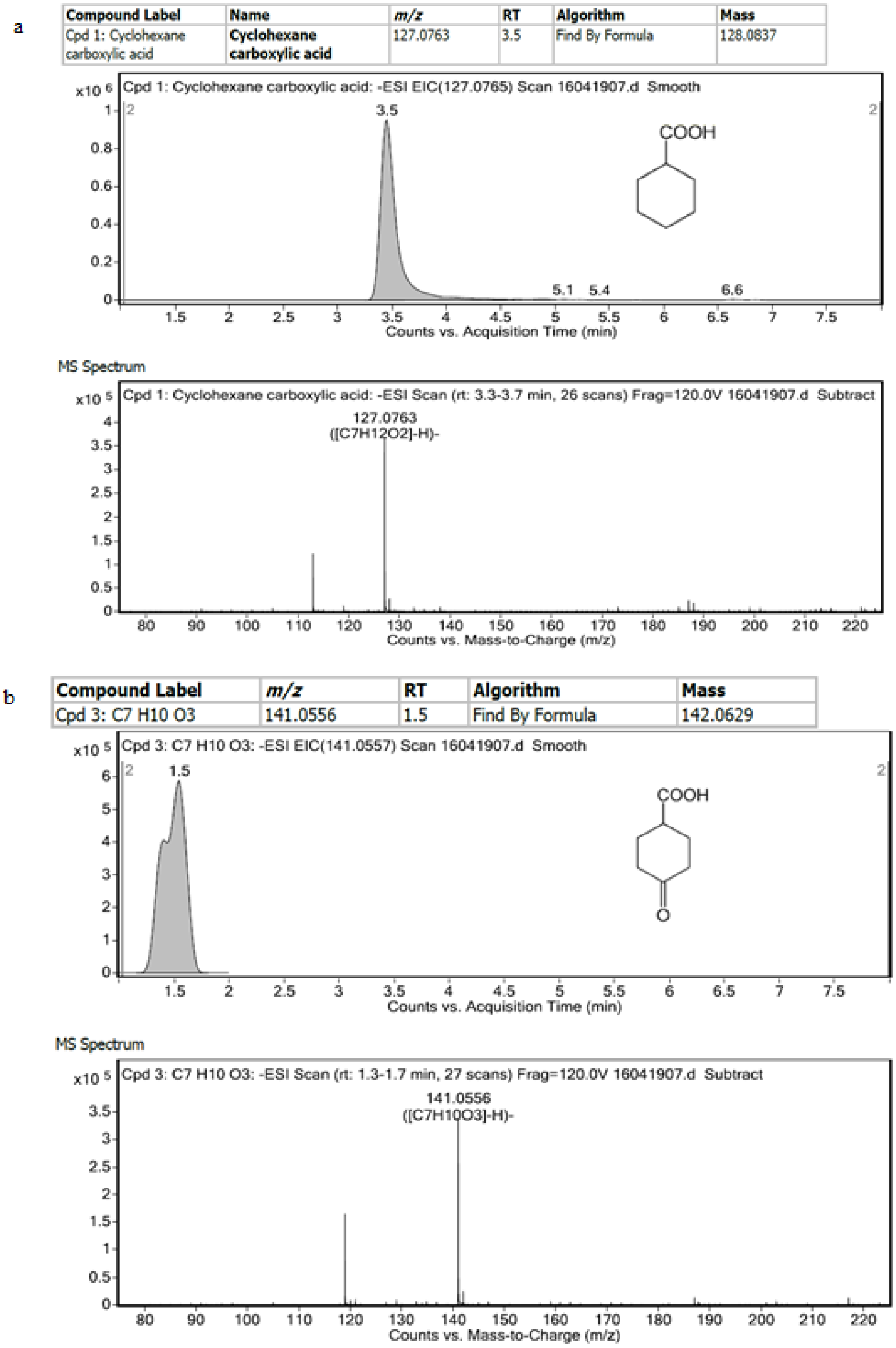


Figure 3-2. Time profiles of the species in the EDDS-Fenton process ($[CHA]_0$ = 0.39 mM, $[H_2O_2]_0$ = 2.94 mM, $[Fe(II)]_0$ = 0.45 mM, and $[EDDS:Fe]_0$ = 2:1).

The low degradation rate of CHA after 2 min could be attributed to the low amount of Fe(II) existing in the solution. CHA removal in the control experiments (not shown here) was less than 5%. The main CHA degradation products were detected as hydroxy-CHA (mass-to-charge ratio (m/z) = 143), dihydroxy-CHA (m/z = 159), and oxo-CHA (m/z = 141). The extracted-ion chromatograms of these species are provided in **Figure 3-3**a-d. The results were in coincidence with previous reports of the CHA oxidation products (Afzal et al., 2012; Drzewicz et al., 2010).



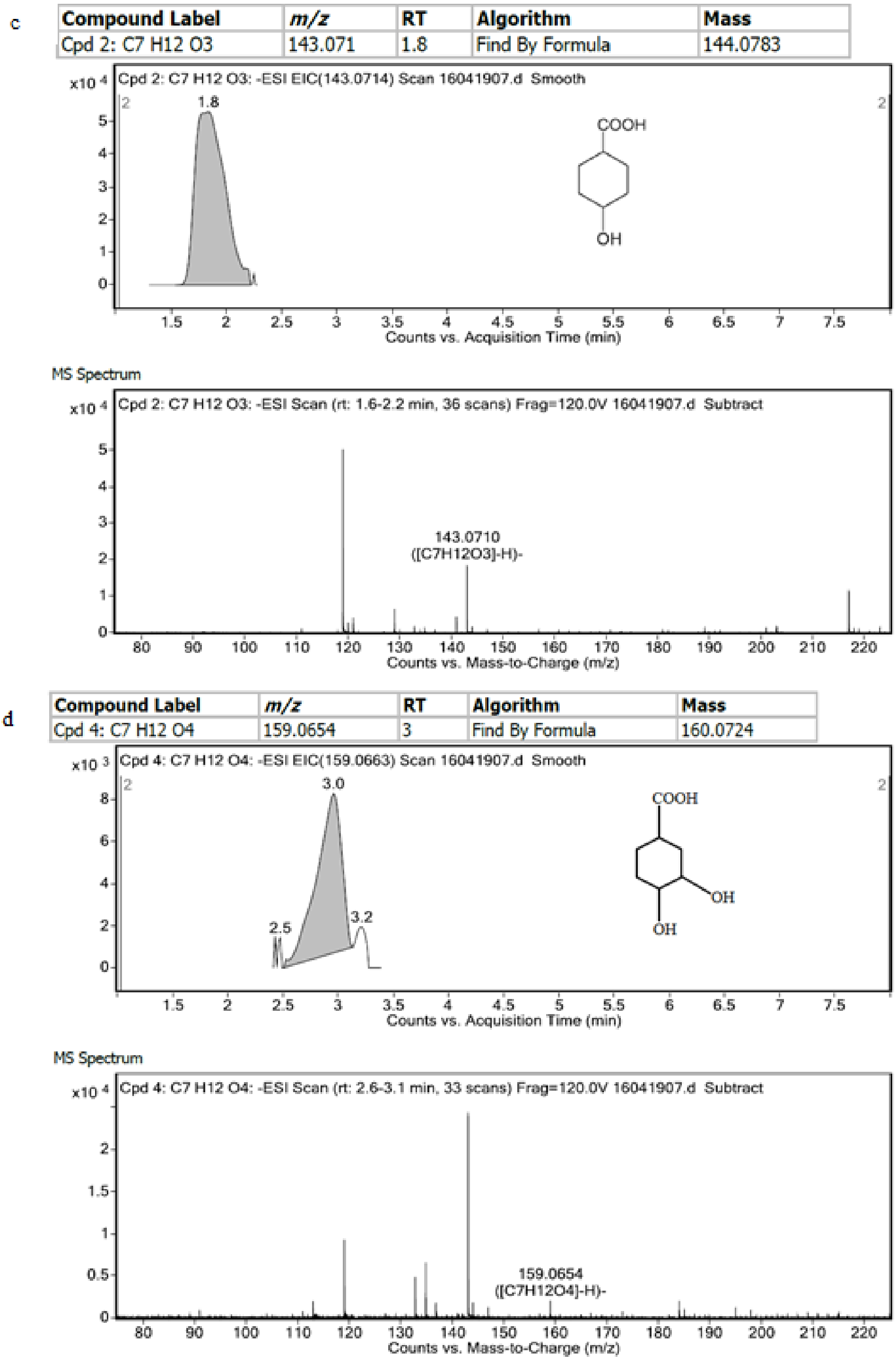
a

Compound Label	Name	*m/z*	RT	Algorithm	Mass
Cpd 1: Cyclohexane carboxylic acid	**Cyclohexane carboxylic acid**	127.0763	3.5	Find By Formula	128.0837

b

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 3: C7 H10 O3	141.0556	1.5	Find By Formula	142.0629

Figure 3-3. Extracted-ion chromatogram (EIC) of a) CHA and b) oxo-CHA in the CHA sample treated by EDDS-Fenton ($[CHA]_0$ = 0.39 mM, $[H_2O_2]_0$ = 2.94 mM, $[Fe(II)]_0$ = 0.45 mM, and $[EDDS:Fe]_0$ = 2:1).



c

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C7 H12 O3	143.071	1.8	Find By Formula	144.0783

d

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 4: C7 H12 O4	159.0654	3	Find By Formula	160.0724

Figure 3-3 (concluded). Extracted-ion chromatogram (EIC) of c) hydroxyl-CHA and d) dihydroxyl-CHA in the CHA sample treated by EDDS-Fenton ($[CHA]_0 = 0.39$ mM, $[H_2O_2]_0 = 2.94$ mM, $[Fe(II)]_0 = 0.45$ mM, and $[EDDS:Fe]_0 = 2:1$).

No COD removal was observed during the process, indicating that neither EDDS nor CHA was degraded into CO_2, and no change of the mean oxidation state of the treated substance occurred in the reaction.

The stability of the oxidation state of metal ions may change distinctly by being chelated by ligands (Kleinberg et al., 1960). The amount of Fe(II) in the EDDS-Fenton process decreased from 0.45 mM to 0.015 mM in the first 2 min, increased gradually as the reaction proceeded, reached 0.1 mM at 120 min, and kept stable for the rest of the reaction. Fe(II) in the solution came from the reduction of Fe(III) by H_2O_2 (Eq. 3-2) or by $HO_2^{\bullet}/O_2^{\bullet-}$ (Eq. 3-5) generated in the process.

The species in the process reacting with $^{\bullet}OH$ included primarily Fe-EDDS complex, EDDS, CHA, and H_2O_2, with second-order rate constants between EDDS and $^{\bullet}OH$ as 2.48×10^9 $M^{-1}s^{-1}$ obtained in this study (the rate constant between Fe-EDDS and $^{\bullet}OH$ was not found, so an assumption was taken as 2.48×10^9 $M^{-1}s^{-1}$), between H_2O_2 and $^{\bullet}OH$ as 2.7×10^7 $M^{-1}s^{-1}$ (De Laat & Gallard, 1999; Gallard & De Laat, 2000; Huang et al., 2013), and between CHA and $^{\bullet}OH$ as 4.09×10^9 $M^{-1}s^{-1}$ obtained in our previous study (Zhang et al., 2016). Huang et al. (2013) also used a same rate constant (2.0×10^8 $M^{-1}s^{-1}$ at pH 6.2) for the reactions of $^{\bullet}OH$ with EDDS and with Fe-EDDS. The percentage of $^{\bullet}OH$ consumed by those scavengers could be estimated using a scavenging term k_ic_i (k_i represents the second-order rate constant between $^{\bullet}OH$ and a solute i, and c_i is the concentration of i), as shown in Eq. 3-12 (Dao & De Laat, 2011). Under the experimental conditions, the percentage of $^{\bullet}OH$ consumed by H_2O_2, EDDS (including Fe-EDDS), and CHA was 2.0%, 56.9%, and 41.1%, respectively.

$$R = \frac{k_i c_i}{k_i c_i + \sum k_j c_j} \tag{3-12}$$

where R denotes the percentage of $^{\bullet}$OH consumed by a specific species i. j denotes the other scavengers except i in the system.

The CHA degradation can be used to predict the degradation of other NAs with similar and dissimilar structures based on the structure reactivity towards oxidation. Generally, the reactivity of NAs increases with increasing carbon number due to increasing overall number of H atoms available for $^{\bullet}$OH attack. Moreover, the reactivity increases with increasing number of rings in NAs due to the tertiary carbon atoms introduced to a structure by the presence of rings (Pérez-Estrada et al., 2011). The H atoms on tertiary carbons are more reactive towards hydrogen abstraction than the H atoms on secondary or primary carbons. This is owing to the fact that the stability of the resulting carbon centered radicals of the tertiary carbons after H atom abstraction is higher than those of the secondary or primary carbons (Anbar et al., 1966; Pérez-Estrada et al., 2011). Therefore, the investigation of CHA degradation would be a very useful tool for evaluating the efficiency of the process on the total NA removal.

3.3.2 Spectra of Fe-EDDS

The mixture of 0.89 mM EDDS and 0.39 mM CHA and 2.94 mM H_2O_2 had low absorbance below 240 nm and almost none above 240 nm (**Figure 3-4**a). The Fe-EDDS complex, on the other hand, displayed a significant absorbance below 400 nm. Li (2010) also reported high absorbance of Fe(III)EDDS from 200 nm to 400 nm with a molar absorption coefficient ε of 6530 $L\cdot mol^{-1}\cdot cm^{-1}$at 239 nm. Like EDTA, EDDS is known for forming stable complexes with many metals in a wide range of pH, and the complexes show good absorbance between 200 to 300 nm (Nagaraju et al., 2007). The absorbance of Fe-EDDS did not change significantly with increasing ratios of EDDS:Fe (from 1:1 to 10:1), indicating the same structure of the formed complexes. It was proposed that in the Fe-EDDS complex, $EDDS^{4-}$ acts as a pentadentate ligand and water occupies the sixth coordination site (Huang et al., 2013; Orama et al., 2002; Schneppensieper et al., 2001).

The spectra of the samples with 2.94 mM H_2O_2 were recorded after the total consumption of H_2O_2. For low ratios of EDDS to Fe (1:1 and 2:1), the addition of 2.94 mM H_2O_2 changed the absorbance of Fe-EDDS to lower values below 320 nm and to higher values above 320 nm, compared to the original absorbance of the samples. The changes of the spectra were due to the progressive oxidation of the ligands and subsequent polymerization of the ferric species (Rush & Koppenol, 1988). While, for high ratios of EDDS:Fe (4:1 and 10:1), with the addition of 2.94 mM H_2O_2, the absorbance of Fe-EDDS showed an increase above 230 nm with an obvious shoulder from 260 to 280 nm compared to the original absorbance. Time profile of the spectrum of Fe-EDDS (EDDS:Fe = 2:1) is shown in **Figure 3-4**b. As the reaction proceeded, the absorbance increased to higher values first and then decreased to lower values between 230 to 315 nm. The absorbance above 315 nm increased with time. No literature can be found for the Fe-EDDS spectrum change in the presence of excess EDDS. It may have something to do with the formation of peroxocomplexes, which is the first step of the decomposition of H_2O_2 by iron-aminopolycarboxylate complexes (De Laat et al., 2011; Francis et al., 1985; Tachiev et al., 2000; Walling et al., 1970). Purple intermediates were formed for the reaction of H_2O_2 with Fe(III)EDTA (De Laat et al., 2011; Francis et al., 1985; Walling et al., 1970). No literature has been reported yet on the formation of peroxocomplex in the Fe-EDDS/H_2O_2 system.

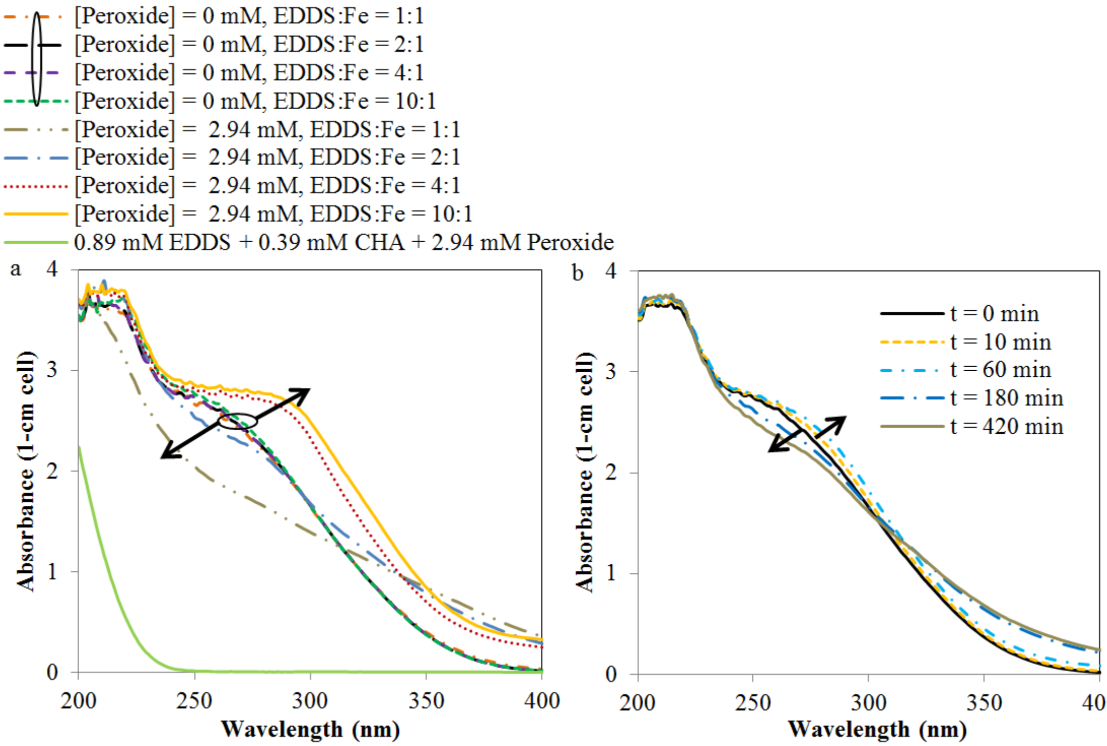


Figure 3-4. a) Absorption spectra of Fe-EDDS ($[Fe(II)]_0$ = 0.45 mM and $[EDDS:Fe]_0$ = 2:1) and b) time profile of the absorption spectra of Fe-EDDS ($[H_2O_2]_0$ = 2.94 mM, $[Fe(II)]_0$ = 0.45 mM, and $[EDDS:Fe]_0$ = 2:1).

3.3.3 Second-order rate constant between •OH and EDDS

The second-order rate constant between EDDS and •OH is very important for estimating the scavenging effect of EDDS on •OH. However, few papers have been published with the measurement of the second-order rate constant between EDDS and •OH. In this study, the rate constant was investigated using the competition-kinetic approach described in Section 3.2.3. pCBA was chosen as the reference compound because of its widely accepted second-order rate constant with •OH, 5.0×10^9 $M^{-1}s^{-1}$ (Buxton et al., 1988; Shu et al., 2013). The pseudo-first order degradation of pCBA and EDDS by •OH is shown in **Figure 3-5**.

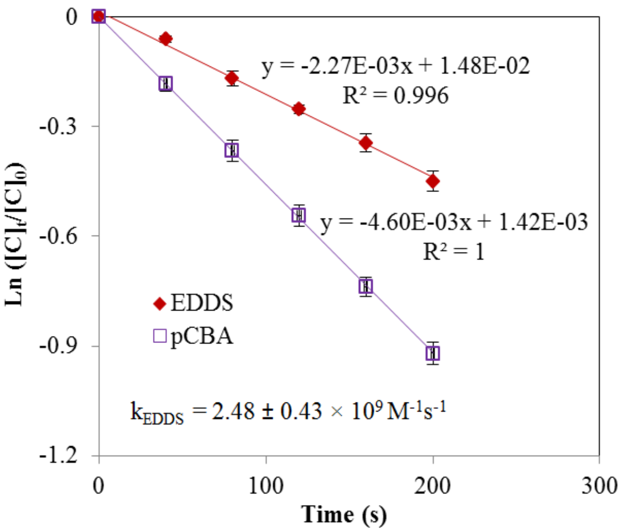


Figure 3-5. Pseudo-first order degradation of pCBA and EDDS by $^{\bullet}$OH ($[H_2O_2]_0$ = 50 mM and $[pCBA]_0$ = $[EDDS]_0$ = 0.2 mM).

The second-order rate constants between organics and $^{\bullet}$OH are in a range of 10^6 to 10^{10} $M^{-1}s^{-1}$ (Pereira et al., 2007; Shu et al., 2013). The rate constant between EDDS and $^{\bullet}$OH obtained in this study at pH 8 is $2.48\pm0.43\times10^9$ $M^{-1}s^{-1}$, in disagreement with a literature value of 2.0×10^8 $M^{-1}s^{-1}$ reported by Li (2010). Reasons for the discrepancy could be the different experimental conditions of two studies, such as different pH values (pH 3 in Li's study) and different source for the generation of $^{\bullet}$OH (UV irradiation of NO_3^- in Li's study), which might generate different accompanied oxidants. Moreover, reactor types, system geometry, and the concentration of reactants also could contribute to the difference in the rate constants.

By comparing the second-order rate constants of $^{\bullet}$OH with EDDS ($2.48\pm0.43\times10^9$ $M^{-1}s^{-1}$) and CHA (4.09×10^9 $M^{-1}s^{-1}$), it can be concluded that EDDS was almost as reactive towards $^{\bullet}$OH as CHA, in coincidence with the removal of EDDS (70%) and CHA (64%) in Section 3.3.1. Therefore, the degradation of EDDS by $^{\bullet}$OH is a main factor that needs to be considered in this modified Fenton process.

The reactions between $^{\bullet}$OH and organic matters usually take place by adding the radical to a C=C double bond (Eq. 3-13) or by abstracting a H-atom from an aliphatic chain (Eq. 3-14) (von Sonntag et al., 1997).

$$^{\bullet}OH + R_2C = CR_2 \rightarrow R_2(HO)C - CR_2^{\bullet} \tag{3-13}$$

$$^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet} \tag{3-14}$$

The addition of $^{\bullet}$OH to double bonds is generally faster than the hydrogen abstraction reaction (von Sonntag et al., 1997), which can explain the faster reaction between $^{\bullet}$OH and pCBA with double bonds than that between $^{\bullet}$OH and CHA without double bonds. The other cause for the faster former reaction is the high reactivity of the chlorinated carbon double bonds towards $^{\bullet}$OH in pCBA (von Sonntag et al., 1997). Based on the discussion of the NA reactivity in Section 3.3.1, the lower reactivity of EDDS towards $^{\bullet}$OH compared with that of CHA might be attributed to the deficiency of rings or tertiary carbons in the molecule.

The degradation of EDDS could be observed from the color change of the sample, yellowish at the beginning of the reaction to dark yellow at the end of the reaction. The oxidation products of EDDS could not be found in the literature. However, as a structural isomer of EDTA, the oxidation of EDDS might be referred to the oxidation of EDTA, which takes place at the C-N bond due to the electrophilic attack, where the acetic group of EDTA is substituted by a hydrogen atom (Colodette et al., 1988; Sillanpää et al., 2011). Similarly, we can also refer the degradation of EDDS to the $^{\bullet}$OH attack on another APCA, NTA, which takes place also at C-N bond and generates iminodiacetic acid (IDA), glycine, oxalic acid, ammonia, and CO_2 (Andrianirinaharivelo et al., 1993). Jones and Williams (2001) reported that the biodegradation of [S,S]-EDDS with the non-hydrolytic cleavage of the C-N bond between the ethylenediamine part of the molecule and one of the succinyl residues gave weak chelating agents N-(2-aminoethyl) aspartic acid (AEAA) and fumarate, and eventually CO_2. The cleavage of C-N bond might also be responsible for the further degradation of AEAA, however, the mechanism is still not clear (Bucheli-Witschel & Egli, 2001). Metal-EDDS is found to be low toxic (Fabbricino et al., 2013), and the toxicity of [S,S]-EDDS to fish and daphnia has an EC_{50} > 1000 mg/L (Bucheli-Witschel & Egli, 2001). Unfortunately, no literature has reported the toxicity of the oxidation products of EDDS so far.

3.3.4 Effect of dosing modes of H_2O_2 and Fe-EDDS

The effect of dosing mode of H_2O_2 and Fe-EDDS on the process performance was investigated. CHA removal at the end of the reaction was 64.4% at one dose of 2.94 mM H_2O_2 and 0.45 mM Fe-EDDS, 76.4% at four consecutive doses of 0.74 mM H_2O_2 and one dose of 0.45 mM Fe-EDDS, and 84.0% at four consecutive doses of 0.74 mM H_2O_2 and 0.11 mM Fe-EDDS (see **Figure 3-6**).

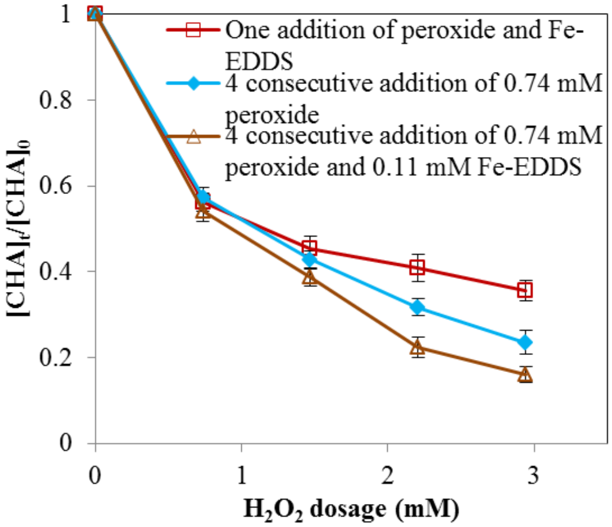


Figure 3-6. Effect of the dosing mode of H_2O_2 and Fe-EDDS on the CHA degradation ($[CHA]_0 = 0.39$ mM, $[H_2O_2]_0 = 2.94$ mM, $[Fe(II)]_0 = 0.45$ mM, and $[EDDS]_0 = 0.90$ mM).

Both H_2O_2 and EDDS as scavengers of $^{\bullet}OH$ have negative effect on the efficiency of the process. As discussed Section 3.3.1, the percentage of $^{\bullet}OH$ scavenged by 2.94 mM H_2O_2, 0.89 mM EDDS (including Fe-EDDS), and 0.39 mM CHA was 2.0%, 56.9%, and 41.1%, respectively. Most $^{\bullet}OH$ generated in the process was scavenged by EDDS. When H_2O_2 and Fe-EDDS were added consecutively into the samples, the percentage of $^{\bullet}OH$ scavenged by the reagents should be much lower compared to adding the reagents at a time, thus more radicals could be used for the CHA removal. Therefore, when EDDS is used as a chelating agent in the modified Fenton process, consecutive dosing mode of H_2O_2 and Fe-EDDS is recommended. Increase the dosing times (> 4) might further improve the CHA degradation. The actual dosing times for the application of the process *in situ* should be determined according to specific requirements.

3.3.5 Radicals responsible for the degradation of CHA

To investigate the role of $^{\bullet}OH$ in the degradation of CHA, TBA was used as a scavenger of $^{\bullet}OH$ in this study with a second-order rate constant of 6×10^{8} $M^{-1}s^{-1}$ (Dao & De Laat, 2011). The CHA degradation decreased from 64.4% to 6.0% with TBA concentration increasing from 0 mM to 200 mM (**Figure 3-7**a). No decrease of the CHA degradation was observed when TBA increased from 200 mM to 400 mM, indicating that all the $^{\bullet}OH$ was scavenged with TBA $\geq$ 200 mM. This result confirmed that the main species responsible for the CHA degradation in the EDDS-Fenton process was $^{\bullet}OH$, which agrees very well with the study conducted by Huang et al. (2013). The 6% degradation of CHA without the presence of $^{\bullet}OH$ indicated the generation of the other oxidant species. It is suggested that oxidant species other than $^{\bullet}OH$ could be yielded in the Fenton system at high pH (Dao & De Laat, 2011; De Laat & Legube, 1998; Hug & Leupin, 2003; Katsoyiannis et al., 2008; Keenan & Sedlak, 2008; Rivas et al., 2001). It was also reported that only $^{\bullet}OH$ is formed when H_2O_2 is excess, while, Fe(IV)=O species can be obtained with a large amount of Fe(II). In hydrophobic medium, the formation of the ferryl species predominates (Pierre & Fontecave, 1999). Moreover, iron complexes can react with molecular oxygen and its reduced species, leading to the production of very reactive high-valent iron-oxo species (Pierre & Fontecave, 1999).

$CHCl_3$ was used to investigate the role of $O_2^{\bullet -}$ in the CHA degradation. $HO_2^{\bullet}/O_2^{\bullet -}$ (with a pKa of 4.8) generated in the reaction between Fe(III) and H_2O_2 is mainly in the form of $O_2^{\bullet -}$ at high pH (Bielski et al., 1985; De Laat et al., 2011). $CHCl_3$ is highly reactive with $O_2^{\bullet -}$ with a second-order rate constant of 3×10^{10} $M^{-1}s^{-1}$ and much less reactive with $^{\bullet}OH$ with a second-order rate constant of 5×10^{6} $M^{-1}s^{-1}$ (Buxton et al., 1988; Huang et al., 2013). TBA, CHA, EDDS, and H_2O_2 have rate constants with $^{\bullet}OH$ of 6×10^{8} $M^{-1}s^{-1}$ (Dao & De Laat, 2011), 4.09×10^{9} $M^{-1}s^{-1}$, 2.48×10^{9} $M^{-1}s^{-1}$, and 2.7×10^{7} $M^{-1}s^{-1}$, respectively. In the presence of these species, the scavenging effect of $CHCl_3$ on $^{\bullet}OH$ was negligible. Therefore, $CHCl_3$ can be used as a scavenger of $O_2^{\bullet -}$. The solubility of $CHCl_3$ in water is very low. TBA (40 mM) was used to dissolve $CHCl_3$ in this study. 40 mM was chosen because a low concentration of TBA could not dissolve enough $CHCl_3$, while a high concentration of TBA introduced into the test solutions would scavenge all the $^{\bullet}OH$. Our previous results showed no reaction between TBA and $O_2^{\bullet -}$ produced in KO_2 solution (80% DMSO/20% water) (Zhang et al., 2016). Therefore, it is safe to use TBA to dissolve $CHCl_3$. The degradation of CHA decreased with increasing $CHCl_3$ concentration, from 17% at 0 mM $CHCl_3$ to 11% at 2.5 mM $CHCl_3$ (shown in **Figure 3-7**b), signifying that $O_2^{\bullet -}$ was produced and had some influence on the degradation of CHA. Statistical analysis of the data was performed using ANOVA: two-factor without replication. With p $(5.1\times10^{-8}) < 0.05$ at 95% level of confidence, it was reasonable to conclude that there was significant difference in the yields produced by the dose of $CHCl_3$.

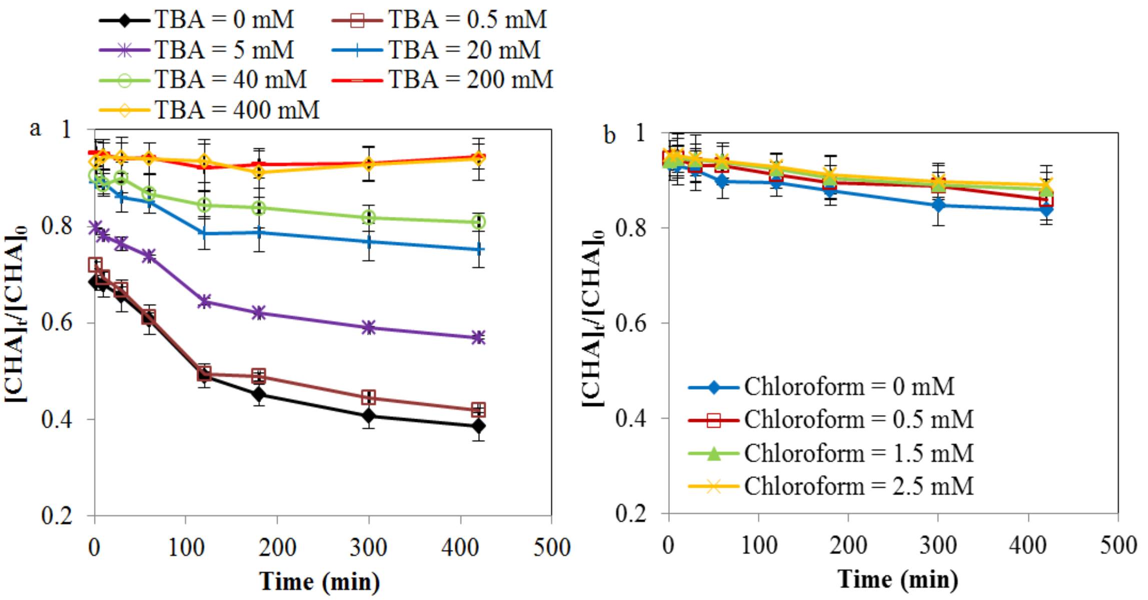


Figure 3-7. a) Effect of TBA on the CHA degradation ($[H_2O_2]_0$ = 2.94 mM, $[Fe(II)]_0$ = 0.45 mM, and $[EDDS:Fe]_0$ = 2:1) and b) effect of chloroform on the CHA degradation ($[H_2O_2]_0$ = 2.94 mM, $[Fe(II)]_0$ = 0.45 mM, $[EDDS:Fe]_0$= 2:1, and $[TBA]_0$ = 40 mM).

When all the $^{\bullet}OH$ was scavenged (TBA ≥ 200 mM), there was no difference in the CHA degradation at different $CHCl_3$ doses (**Figure 3-8**), indicating that no $O_2^{\bullet-}$ existed in the solution or $O_2^{\bullet-}$ alone couldn't degrade CHA under the experimental conditions. The main influence of $O_2^{\bullet-}$ on the degradation of CHA was probably through its influence on the generation of $^{\bullet}OH$. In the study conducted by Huang et al. (2013), it was demonstrated that 20% $^{\bullet}OH$ resulted from the reaction between Fe(II)EDDS and H_2O_2 directly, while, 80% $^{\bullet}OH$ generation depended on the production of $O_2^{\bullet-}$ in the reaction between Fe(III)EDDS and H_2O_2. The role of $O_2^{\bullet-}$ in the generation of $^{\bullet}OH$ and degradation of target compound needs further investigation.

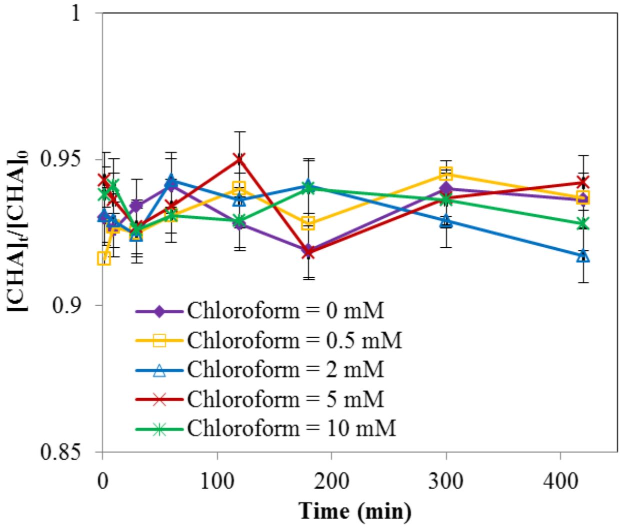


Figure 3-8. Effect of chloroform concentration on the CHA degradation in the EDDS-modified Fenton process ($[H_2O_2]_0$ = 2.94 mM, $[Fe]_0$ = 0.45 mM, $[EDDS:Fe]_0$ = 2:1, and $[TBA]_0$ = 200 mM).

3.3.6 Half-wave potential of Fe(III/II)EDDS and the influence of OSPW matrix

The cyclic voltammograms of Fe(III/II)EDDS at three pHs (7, 8, and 9) are shown in **Figure 3-9** with the oxidation and reduction peaks marked with red circles. Potential values at the oxidation peaks at pH 7, 8, and 9 were 650 mV, 270 mV, and 190 mV, respectively. The values at the reduction peaks at pH 7, 8, and 9 were -750 mV, -820 mV, and -840 mV, respectively. The half-wave potential ($E_{1/2}$) values were calculated by taking the average of the potentials at the oxidation and reduction peaks and referring them (by adding 236 mV to $E_{1/2}$) to the standard hydrogen electrode (SHE). The $E_{1/2}$ values were obtained as 186 mV, -39 mV, and -89 mV (vs SHE) at pH 7, 8, and 9, respectively, close to a value of 69 mV (vs SHE) at pH 6.2 reported by Huang et al. (2013). Different experimental conditions, such as pH, reference electrodes, and electrolytes (saturated calomel electrode and 0.05 M KCl electrolyte in Huang et al's study), might attribute to the difference of the $E_{1/2}$ values. Both oxidation and reduction peaks shifted to more negative potentials as pH increased from 7 to 9, which could be attributed to the fact that Fe-EDDS formed different species with hydroxide at different pH (Shimizu et al., 2007).

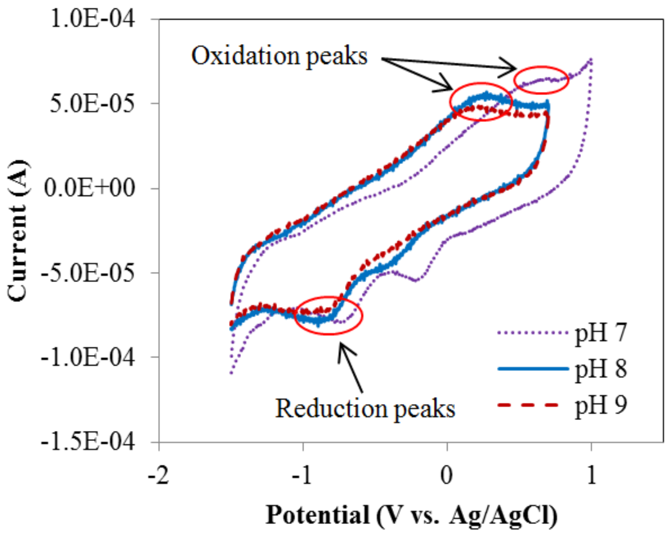


Figure 3-9. Cyclic voltammograms of Fe(III/II)EDDS at pH 7, 8, and 9 ($[Fe]_0$ = 1mM and $[EDDS:Fe]_0$= 2:1).

Relationship between $E_{1/2}$ and formal potential ($E^{0'}$) is shown in Eq. 3-15 (Ho et al., 2012; Schalley, 2007).

$$E_{1/2} = E^{0\prime} + \frac{RT}{2nF}\ln\left(\frac{D_{Red}}{D_{Ox}}\right) \tag{3-15}$$

where R is the gas constant (8.31 V·C/mol·K). T is the temperature (K). n denotes the number of electrons in an oxidation-reduction reaction. F is the Faraday constant (96485C·mol^{-1}). D denotes the diffusion coefficient (in cm^2/s).

$E_{1/2}$ is reported to be in coincidence with the formal potential because the diffusion coefficient of an oxidant can be considered as same as that of the corresponding reductant (Schalley, 2007). The diffusion coefficient is a physical constant dependent on the properties of the diffusing substance, such as molecule size, and also on temperature and pressure. The diffusion coefficient in liquids can be defined by the *Strokes-Einstein* equation, shown in Eq. 3-16 (Flury & Gimmi, 2002):

$$D = \frac{kT}{6\pi r_0 \mu} \tag{3-16}$$

where k is Boltzmann's constant (1.380×10^{-23} J·K^{-1}), and T denotes the absolute temperature (in K). r_0 is the particle (molecule) radius (in L), and μ denotes the liquid viscosity (in M·L^{-1}·T^{-1}).

The parameters k, T, and μ in Eq. 3-16 for the oxidant (Fe(III)EDDS) were as same as those for the reductant (Fe(II)EDDS). The particle radius of Fe(III)EDDS can be considered as same as that of Fe(II)EDDS. Therefore, we assumed the diffusion coefficient of Fe(III)EDDS was equal to that of Fe(II)EDDS. It was also reported in the literature that an oxidant and the corresponding reductant show very similar diffusion coefficients (Schalley, 2007).

The estimation of ΔG_0 based on the formal potential obtained in this study is provided in Eq. 3-17:

$$\Delta G_0 = -nFE^0 \tag{3-17}$$

where F is the Faraday constant (96485 C·mol^{-1}), E^0 is the standard potential (in V), and n denotes the number of electrons in a half reaction.

We can use the formal potential obtained in the study to estimate ΔG_0 (Eqs. 3-18 to 3-20).

$$\Delta G_0 = -1 \times 96485 \times 0.186 = -17946\, J = -17.9\, KJ \text{ at pH 7} \tag{3-18}$$

$$\Delta G_0 = -1 \times 96485 \times (-0.039) = 3763\, J = 3.8\, KJ \text{ at pH 8} \tag{3-19}$$

$$\Delta G_0 = -1 \times 96485 \times (-0.089) = 8587\, J = 8.6\, KJ \text{ at pH 9} \tag{3-20}$$

The electron transfer in modified Fenton processes is thermodynamically allowed when the redox potential of iron complexes is in a range of -324 to 460 mV (vs NHE) (Huang et al., 2013; Pierre & Fontecave, 1999). Therefore, the redox potential of Fe(III/II)EDDS thermodynamically enables the modified Fenton reactions at pH 7 to 9. The ΔG_0 values indicated that as the pH increased, the reduction of Fe(III)EDDS to Fe(II)EDDS became more difficult, resulting in lower H_2O_2 decomposition rate in the EDDS-Fenton process.

The iron concentration in OSPW (0.014-0.054 mM) (Allen, 2008) is much lower than the iron dose (0.45 mM) applied in this study. Therefore, additional iron might be needed for the application of this process in the treatment of OSPW. The high concentration of inorganic ions, including chloride (~75 to 550 mg/L), sulphate (~200 to 300 mg/L) (Allen, 2008), and bicarbonate (700 to 1000 mg/L) (Pourrezaei, 2013), would scavenge $^{\bullet}OH$ and decrease the degradation of NAs. The presence of heavy metal ions in OSPW may also interfere with the process by competing with iron for the chelating agent. The organic compounds in OSPW other than NAs, such as unrecovered bitumen (oil and grease), polyaromatic hydrocarbons (PAH), BTEX (benzene, toluene, ethyl benzene, and xylenes), as well as fulvic and humic acids (Allen, 2008; Madill et al., 2001; Mohamed et al., 2011; Pourrezaei, 2013; Rogers et al., 2002), might compete with NAs for $^{\bullet}OH$ (Afzal et al., 2012). Fulvic and humic acids might form co-complexes with Fe-EDDS, thus interfering with the reactivity of the complex. The influence of the OSPW water matrix on the behavior of Fe-EDDS and removal of organic contaminants in the process needs further research.

The tetraborate ion in the borate buffer solution exhibits co-complexing ability with various substances (Hitchcock & Puckett, 2013). The co-complexing effect of the buffer solution on Fe-EDDS might impose some influence on the efficiency of the process; therefore, further research is warranted.

3.4 Conclusions

EDDS-Fenton was applied for the degradation of CHA at pH 8 and proposed as a potential treatment process for OSPW remediation. The results showed that the process was very efficient in degrading CHA at pH 8 especially with four consecutive doses of 0.74 mM H_2O_2 and 0.11 mM Fe-EDDS (84% CHA removal). $^{\bullet}OH$ was found to be the main species responsible for the CHA degradation. The scavenging effect of EDDS on $^{\bullet}OH$ (rate constant at pH 8 was obtained as $2.48 \pm 0.43 \times 10^9$ $M^{-1}s^{-1}$) was a major concern in the application of this process. The half-wave potentials of Fe(III/II)EDDS at pH 7 to 9 were reported for the first time. The findings obtained in this study can further be applied to the planning and design of effective advanced oxidation processes for OSPW treatment. However, the species in OSPW, such as the organics, inorganic ions, and heavy metal ions, may interfere with the efficiency of the process. More studies need to be conducted for the further application of the process on the OSPW treatment.

3.5 References

Afzal, A., Drzewicz, P., Martin, J. W., & Gamal El-Din, M. (2012). Decomposition of cyclohexanoic acid by the UV/H_2O_2 process under various conditions. *Science of the Total Environment, 426*, 387-392.

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

Anbar, M., Meyerstein, D., & Neta, P. (1966). Reactivity of aliphatic compounds towards hydroxyl radicals. *Journal of the Chemical Society B: Physical Organic*, 742-747.

Andrianirinaharivelo, S. L., Pilichowski, J. F., & Bolte, M. (1993). Nitrilotriacetic acid transformation photo-induced by complexation with iron(III) in aqueous solution. *Transition Metal Chemistry, 18*(1), 37-41.

Basu, S., & Wei, I. W. (1998a). Advanced chemical oxidation of 2, 4, 6 trichlorophenol in aqueous phase by fenton's reagent-part i: effects of the amounts of oxidant and catalyst on the treatment reaction. *Chemical Engineering Communications, 164*(1), 111-137.

Basu, S., & Wei, I. W. (1998b). Advanced chemical oxidation of 2, 4, 6 trichlorophenol in aqueous phase by Fenton's Reagent-Part II: Effects of various reaction parameters on the treatment reaction. *Chemical Engineering Communications, 164*(1), 139-151.

Bielski, B. H. J., Cabelli, D. E., & Arudi, R. L. (1985). Reactivity of H_2O_2/O_2^- radicals in aqueous solution. *Journal of Physical and Chemical Reference Data, 4*, 1041-1100.

Bucheli - Witschel, M., & Egli, T. (2001). Environmental fate and microbial degradation of aminopolycarboxylic acids. *FEMS Microbiology Reviews, 25*(1), 69-106.

Buxton, G. V., Greenstock, C. L., Helman, W. P., & Ross, A. B. (1988). Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals. *Journal of Physical and Chemical Reference Data, 17*, 513-886.

Colodette, J., Rothenberg, S., & Dence, C. (1988). Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemimechanical pulps. I: hydrogen peroxide stability in the absence of stabilizing systems. *Journal of Pulp and Paper Science, 14*(6), J126-J132.

Dao, Y. H., & De Laat, J. (2011). Hydroxyl radical involvement in the decomposition of hydrogen peroxide by ferrous and ferric-nitrilotriacetate complexes at neutral pH. *Water Research, 45*(11), 3309-3317.

De Laat, J., Dao, Y. H., Hamdi El Najjar, N., & Daou, C. (2011). Effect of some parameters on the rate of the catalysed decomposition of hydrogen peroxide by iron(III)-nitrilotriacetate in water. *Water Research, 45*(17), 5654-5664.

De Laat, J., & Gallard, H. (1999). Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modeling. *Environmental Science & Technology, 33*(16), 2726-2732.

De Laat, J., & Legube, B. (1998). Influence du pH sur la vitesse d'oxydation de compose' s organiques par Fe^{II}/H_2O_2. Me' canismes re' actionnels et mode' lisation. *New Journal of Chemistry, 22*(3), 263-268.

Drzewicz, P., Afzal, A., Gamal El-Din, M., & Martin, J. W. (2010). 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, 114*(45), 12067-12074.

Fabbricino, M., Ferraro, A., Del Giudice, G., & d'Antonio, L. (2013). Current views on EDDS use for ex situ washing of potentially toxic metal contaminated soils. *Reviews in Environmental Science and Bio/Technology, 12*(4), 391-398.

Flury, M., & Gimmi, T. (2002). Solute diffusion, in Methods of Soil Analysis: Part 4 Physical Methods. Madison, WI: Soil Science Society of America.

Francis, K. C., Cummins, D., & Oakes, J. (1985). Kinetic and structural investigations of [Fe^{III} (edta)]-[edta = ethylenediaminetetra-acetate (4-)] catalysed decomposition of hydrogen peroxide. *Journal of the Chemical Society, Dalton Transactions*(3), 493-501.

Fu, H., Gamal El-Din, M., Smith, D. W., MacKinnon, M., & Zubot, W. (2008). Ozone treatment of naphthenic acids in Athabasca oil sands process-affected water. Paper presented at the First International Oil Sands Tailings Conference,, Edmonton, AB, Canda.

Gallard, H., & De Laat, J. (2000). Kinetic modelling of Fe(III)/H_2O_2 oxidation reactions in dilute aqueous solution using atrazine as a model organic compound. *Water Research, 34*(12), 3107-3116.

García Einschlag, F. S., Lopez, J., Carlos, L., Capparelli, A. L., Braun, A. M., & Oliveros, E. (2002). Evaluation of the efficiency of photodegradation of nitroaromatics applying the UV/H_2O_2 technique. *Environmental Science & Technology, 36*(18), 3936-3944.

Georgi, A., Schierz, A., Trommler, U., Horwitz, C. P., Collins, T. J., & Kopinke, F. D. (2007). Humic acid modified Fenton reagent for enhancement of the working pH range. *Applied Catalysis B: Environmental, 72*(1-2), 26-36.

He, Y. H., Wiseman, S. B., Hecker, M., Zhang, X. W., Wang, N., Perez, L. A., . . . Giesy, J. P. (2011). Effect of ozonation on the estrogenicity and androgenicity of oil sands process-affected water. *Environmental Science & Technology, 45*(15), 6268-6274.

Hitchcock, W. W., & Puckett, J. M. (2013). United States Patent.

Ho, J., Coote, M. L., Cramer, C. J., & Truhlar, D. G. (2012). Theoretical calculation of reduction potentials. *Organic electrochemistry, 5*.

Huang, W. Y., Brigante, M., Wu, F., Mousty, C., Hanna, K., & Mailhot, G. (2013). Assessment of the Fe(III)–EDDS complex in Fenton-like processes: from the radical formation to the degradation of bisphenol A. *Environmental Science & Technology, 47*(4), 1952-1959.

Hug, S. J., & Leupin, O. (2003). Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. *Environmental Science & Technology, 37*(12), 2734-2742.

Jaworska, J. S., Schowanek, D., & Feijtel, T. C. (1999). Environmental risk assessment for trisodium [S, S]-ethylene diamine disuccinate, a biodegradable chelator used in detergent applications. *Chemosphere, 38*(15), 3597-3625.

Jones, P. W., & Williams, D. R. (2001). Chemical speciation used to assess [S, S′]-ethylenediaminedisuccinic acid (EDDS) as a readily-biodegradable replacement for EDTA in radiochemical decontamination formulations. *Applied Radiation and Isotopes, 54*(4), 587-593.

Kannel, P. R., & Gan, T. Y. (2012). 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, 47*(1), 1-21.

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

Keenan, C. R., & Sedlak, D. L. (2008). Ligand-enhanced reactive oxidant generation by nanoparticulate zero-valent iron and oxygen. *Environmental Science & Technology, 42*(18), 6936-6941.

Klamerth, N., Malato, S., Aguera, A., Fernandez-Alba, A., & Mailhot, G. (2012). Treatment of municipal wastewater treatment plant effluents with modified photo-Fenton as a tertiary treatment for the degradation of micro pollutants and disinfection. *Environmental Science & Technology, 46*(5), 2885-2892.

Klamerth, N., Malato, S., Maldonado, M. I., Agüera, A., & Fernández-Alba, A. (2011). Modified photo-Fenton for degradation of emerging contaminants in municipal wastewater effluents. *Catalysis Today, 161*(1), 241-246.

Kleinberg, J., William, J., Argersinger, J. R., & Ernest, G. (1960). Inorganic Chemistry. Lexington, Massachusetts, United States: D.C. Heath and Company.

Kwan, W. P., & Voelker, B. M. (2003). Rates of hydroxyl radical generation and organic compound oxidation in mineral-catalyzed Fenton-like systems. *Environmental Science & Technology, 37*(6), 1150-1158.

Li, J. (2010). 17beta-estradiol degradation photoinduced by iron complex, clay and iron oxide minerals: effect of the iron complexing agent ethylenediamine-N, N'-disuccinic acid. (Docter of Philosophy), Université Blaise Pascal-Clermont-Ferrand II; Université de Wuhan.

Li, Y. C., Bachas, L. G., & Bhattacharyya, D. (2005). Kinetics studies of trichlorophenol destruction by chelate-based Fenton reaction. *Environmental Engineering Science, 22*(6), 756-771.

Lipczynska-Kochany, E., & Kochany, J. (2008). Effect of humic substances on the Fenton treatment of wastewater at acidic and neutral pH. *Chemosphere, 73*(5), 745-750.

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

Metsärinne, S., Tuhkanen, T., & Aksela, R. (2001). Photodegradation of ethylenediaminetetraacetic acid (EDTA) and ethylenediamine disuccinic acid (EDDS) within natural UV radiation range. *Chemosphere, 45*(6), 949-955.

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

Munoz, M., Alonso, J., Bartroli, J., & Valiente, M. (1990). Automated spectrophotometric determination of titanium(IV) in water and brines by flow injection based on its reaction with hydrogen peroxide. *Analyst, 115*(3), 315-318.

Nagaraju, V., Goje, T., & Crouch, A. M. (2007). Determination of Copper and Iron Using [S, S']-Ethylenediaminedisuccinic Acid as a Chelating Agent in Wood Pulp by Capillary Electrophoresis. *Analytical Sciences, 23*(4), 493-496.

OECD. (1996). OECD Guidelines for Testing of Chemicals *Degradation and Accumulation*. Paris.

Onstein, P., Stefan, M. I., & Bolton, J. R. (1999). Competition kinetics method for the determination of rate constants for the reaction of hydroxyl radicals with organic pollutants using the UV/H_2O_2 advanced oxidation technology: the rate constants for the tert-butyl formate ester and 2, 4-dinitrophenol. *Journal of Advanced Oxidation Technologies, 4*(2), 231-236.

Orama, M., Hyvönen, H., Saarinen, H., & Aksela, R. (2002). Complexation of [S, S] and mixed stereoisomers of N, N′ -ethylenediaminedisuccinic acid (EDDS) with Fe(III), Cu(II), Zn(II) and Mn(II) ions in aqueous solution. *Journal of the Chemical Society, Dalton Transactions* (24), 4644-4648.

Pavelčik, F., & Majer, J. (1978). New complexanes. XXXIV. Preparation and properties of the meso and rac forms of ethy! enediamine-iV, iV'-disuccinic acid. *Chemické Zvesti, 32*(1), 37-41.

Pereira, V. J., Weinberg, H. S., Linden, K. G., & Singer, P. C. (2007). UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm. *Environmental Science & Technology, 41*(5), 1682-1688.

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

Pierre, J., & Fontecave, M. (1999). Iron and activated oxygen species in biology: the basic chemistry. *Biometals, 12*(3), 195-199.

Pignatello, J. J., Oliveros, E., & MacKay, A. (2006). Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology, 36*(1), 1-84.

Pourrezaei, P. (2013). Physico-Chemical Processes for Oil Sands Process-Affected Water Treatment. (Doctor of Philosophy), University of Alberta, Edmonton, A.B.

Rivas, F. J., Beltran, F. J., Frades, J., & Buxeda, P. (2001). Oxidation of p-hydroxybenzoic acid by Fenton's reagent. *Water Research, 35*(2), 387-396.

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

Rush, J., & Koppenol, W. (1988). Reactions of iron(II) nitrilotriacetate and iron(II) ethylenediamine-N, N'-diacetate complexes with hydrogen peroxide. *Journal of the American Chemical Society, 110*(15), 4957-4963.

Schalley, C. A. (2007). Analytical methods in supramolecular chemistry. Winheim, Gemany: Wiley-VCH.

Schneppensieper, T., Seibig, S., Zahl, A., Tregloan, P., & van Eldik, R. (2001). Influence of chelate effects on the water-exchange mechanism of polyaminecarboxylate complexes of iron (III). *Inorganic Chemistry, 40*(15), 3670-3676.

Schowanek, D., Feijtel, T. C., Perkins, C. M., Hartman, F. A., Federle, T. W., & Larson, R. J. (1997). Biodegradation of [S, S], [R, R] and mixed stereoisomers of ethylene diamine disuccinic acid (EDDS), a transition metal chelator. *Chemosphere, 34*(11), 2375-2391.

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

Shimizu, K., Hutcheson, R., Engelmann, M. D., & Cheng, I. F. (2007). Cyclic voltammetric and aqueous equilibria model study of the pH dependant iron(II/III) ethylenediamminetetraacetate complex reduction potential. *Journal of Electroanalytical Chemistry, 603*(1), 44-50.

Shu, Z., Bolton, J. R., Belosevic, M., & Gamal El-Din, M. (2013). Photodegradation of emerging micropollutants using the medium-pressure UV/H_2O_2 Advanced Oxidation Process. *Water Research, 47*(8), 2881-2889.

Sillanpää, M. E., Kurniawan, T. A., & Lo, W.-h. (2011). Degradation of chelating agents in aqueous solution using advanced oxidation process (AOP). *Chemosphere, 83*(11), 1443-1460.

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

Tachiev, G., Roth, J., & Bowers, A. (2000). Kinetics of hydrogen peroxide decomposition with complexed and "free" iron catalysts. *International Journal of Chemical Kinetics, 32*(1), 24-35.

Teel, A. L., Warberg, C. R., Atkinson, D. A., & Watts, R. J. (2001). Comparison of mineral and soluble iron Fenton's catalysts for the treatment of trichloroethylene. *Water Research, 35*(4), 977-984.

von Sonntag, C., Dowideit, P., Fang, X., Mertens, R., Pan, X., Schuchmann, M. N., & Schuchmann, H.-P. (1997). The fate of peroxyl radicals in aqueous solution. *Water science and technology, 35*(4), 9-15.

Walling, C., Kurz, M., & Schugar, H. J. (1970). Iron(III)-ethylenediaminetetraacetic acid-peroxide system. *Inorganic Chemistry, 9*(4), 931-937.

Wang, Y. N. (2011). Application of Coagulation-Flocculation Process for Treating Oil Sands Process-Affected Water. (Master of Science), University of Alberta, Edmonton, AB, Canada.

Whitburn, J. S., Wilkinson, S. D., & Williams, D. R. (1999). Chemical speciation of ethylenediamine-N, N′ -disuccinic acid (EDDS) and its metal complexes in solution. *Chemical Speciation & Bioavailability, 11*(3), 85-93.

Willkinson, S. D. (1998). Chemical Speciation of a Biodegradable Replacement Ligand for EDTA. (Docter of Philosophy), University of Wales, Cardiff.

Zhang, Y., Klamerth, N., & Gamal El-Din, M. (2016). Degradation of a Model Naphthenic Acid by Nitrilotriacetic Acid-Modified Fenton Process. *Chemical Engineering Journal, 292*, 340-347.

4 COMPARISON OF FENTON, NTA-FENTON, UV-FENTON, UV-FE-NTA, UV-NTA-FENTON, AND UV-H_2O_2 FOR THE DEGRADATION OF CYCLOHEXANOIC ACID AT TWO PHS[3]

4.1 Introduction

The storage of oil sands process-affected waters (OSPW) in Alberta, Canada has brought several environmental concerns, such as possibilities of groundwater contamination by long time infiltration and the toxicity of OSPW to aquatic biota and mammals (Garcia-Garcia et al., 2011; Jones et al., 2011; Pourrezaei et al., 2014; Pourrezaei et al., 2011). Naphthenic acids (NAs), a group of aliphatic and alicyclic carboxylic acids, are considered to be mainly responsible for the OSPW toxicity (Allen, 2008a; Nelson et al., 1993). Ample literature has been published on the analysis, toxicity and possible treatment of OSPW (Allen, 2008a, 2008b; Gamal El-Din et al., 2011; Grewer et al., 2010; Pourrezaei, 2013; Pourrezaei et al., 2014; Scott et al., 2008; Tollefsen et al., 2012; Wang et al., 2016; Zhang et al., 2015; Zhou et al., 2008). However, up to date, no viable economical and practical treatment approach can be applied to treat OSPW efficiently (Pourrezaei, 2013).

Based on the production of hydroxyl radical ($^{\bullet}OH$), advanced oxidation processes (AOPs) are capable of degrading recalcitrant NAs and reducing the overall toxicity towards selected

---

[3] A version of this chapter has been submitted previously: Ying Zhang, Nikolaus Klamerth, Pamela Chelme-Ayala, & Mohamed Gamal El-Din. Comparison of Fenton, Nitrilotriacetic acid (NTA)-Fenton, UV-Fenton, UV-Fe-NTA, UV-NTA-Fenton, and UV-H_2O_2 for the Degradation of Cyclohexanoic Acid at Two pHs. *Journal of Hazardous Materials* (Submitted date: May 14, 2016).

organisms (Fu et al., 2008; Scott et al., 2008; Wang, 2011). Fenton and photo-Fenton as very common AOPs have not been applied on the OSPW treatment yet.

In the classical Fenton, the reduction of Fe(III) to Fe(II) by H_2O_2 (Eq. 4-2) is very slow compared to the oxidation of Fe(II) (Eq. 4-1), making the second reaction the rate-limiting step.

$$\text{Fe(II)} + H_2O_2 \rightarrow \text{Fe(III)} + {}^{\bullet}OH + OH^- \quad k = 70\ M^{-1}s^{-1} \tag{4-1}$$

$$\text{Fe(III)} + H_2O_2 \rightarrow \text{Fe(II)} + HO_2^{\bullet} + H^+ \quad k = 0.01\ M^{-1}s^{-1} \tag{4-2}$$

As Fe(III) precipitates at pH > 3 due to the formation of insoluble Fe-hydroxides, chelating agents have been adopted to enable Fenton at natural pH (Gutteridge et al., 1990; Huang et al., 2013; Li et al., 2010; Nam et al., 2001). Nitrilotriacetic acid (NTA) as a chelating agent can form complexes with divalent and trivalent metal cations. The complexing constant of Fe(III)NTA is $\log K_c = 15.9$ (Anderegg, 1986; Andrianirinaharivelo et al., 1993). The generation pathway of $^{\bullet}OH$ and the possible reduction pathways of Fe(III)NTA in NTA-Fenton are given in Eqs. 4-3 to 4-5 (De Laat et al., 2011).

$$\text{Fe(II)NTA} + H_2O_2 \rightarrow \text{Fe(III)NTA} + {}^{\bullet}OH + OH^- \quad k = 9.7 \times 10^3\ M^{-1}s^{-1} \tag{4-3}$$

$$\text{Fe(III)NTA} + H_2O_2 \rightarrow \text{Fe(II)NTA} + HO_2^{\bullet}/O_2^{\bullet -} \tag{4-4}$$

$$\text{Fe(III)NTA} + HO_2^{\bullet}/O_2^{\bullet -} \rightarrow \text{Fe(II)NTA} + O_2 \tag{4-5}$$

However, although possible in theory, no reduction of Fe(III)NTA to Fe(II)NTA by either H_2O_2 or $HO_2^{\bullet}/O_2^{\bullet -}$ was observed in the NTA-Fenton (Dao & De Laat, 2011; Zhang et al., 2016), which means that with the complete oxidation of Fe(II)NTA to Fe(III)NTA in Eq. 4-3, the cyclic reactions in the NTA-Fenton system almost come to an end.

The efficiency of Fenton can be significantly accelerated by the presence of natural sunlight (Klamerth et al., 2013; Klamerth et al., 2012; Vermilyea & Voelker, 2009) and UV light (De la Cruz et al., 2012; Kušić et al., 2006). The dominant monomeric Fe(III)-hydroxyl complex between pH 2.5 to 5 is $Fe(OH)^{2+}$ (Faust & Hoigné, 1990) with a charge transfer band from 290 nm to 400 nm (Faust & Hoigné, 1990; Feng & Nansheng, 2000; Weschler et al., 1986) and a quantum yield (Φ) of 0.21 for the $^{\bullet}$OH production at 347 nm (Eq. 4-6) (Nadtochenko & Kiwi, 1998). UV irradiation is also known to be able to reduce Fe(III)L to Fe(II)L at high pH through Eq. 4-7.

$$\mathrm{Fe(III)}(OH)^{2+} + hv \rightarrow \mathrm{Fe(II)} + {}^{\bullet}OH \tag{4-6}$$

$$\mathrm{Fe(III)L} + hv \rightarrow \mathrm{Fe(II)} + L^{\bullet} \tag{4-7}$$

In the case of NTA, Φ of the Fe(II) formation in Eq. 4-7 was reported as 0.46 at pH 4 and 0.16 at pH 6 at 313 nm (Abida et al., 2006). Therefore, UV irradiation can greatly accelerate the reduction of Fe(III) to Fe(II) and of Fe(III)NTA to Fe(II)NTA, leading to more $^{\bullet}$OH production in the UV-Fenton and UV-NTA-Fenton processes.

One important factor that needs to be considered under UV irradiation is the degradation of the chelating agent. Fe(III)NTA has been reported to undergo rapid photolysis and generate $^{\bullet}$OH at the same time (Stolzberg & Hume, 1975; Trott et al., 1972). The major degradation products of NTA are iminodiacetic acid (IDA), formaldehyde, and CO_2 (Bunescu et al., 2008). The general reaction of the photolysis occurs according to Eq. 4-8 (Langford et al., 1973; Trott et al., 1972).

$$2[\mathrm{Fe(III)NTA}] + hv \rightarrow [\mathrm{Fe(II)NTA}]^{-} + [\mathrm{Fe(II)IDA}] + CH_2O + CO_2 \tag{4-8}$$

UV-H_2O_2 as another common process with the adoption of UV irradiation is also very efficient in $^{\bullet}OH$ generation below 310 nm (Perez et al., 2002). Φ for the $^{\bullet}OH$ production in Eq. 4-9 was reported to be 1.1±0.07 in the wavelength range of 205-280 nm (Goldstein et al., 2007).

$$H_2O_2 + hv \rightarrow 2^{\bullet}OH \tag{4-9}$$

pH has a significant effect on the reactivity of compounds, the formation of by-products, and the efficiency of AOPs (Afzal et al., 2012; Bojanowska-Czajka et al., 2006; Homlok et al., 2010; Panadés et al., 2000). The reactivity of α carbon next to a carboxylic group is partly dependent on whether the group is protonated or dissociated (Afzal et al., 2012; Hewgill & Proudfoot, 1976). However, the information of pH influence on the decomposition of NAs in AOPs is very limited. Only one literature reported the decomposition of cyclohexanoic acid (CHA) as a model compound for NAs in the UV-H_2O_2 process at two different pHs (Afzal et al., 2012).

It would be very interesting to investigate and compare the degradation of the contaminants in OSPW with classical Fenton, UV-Fenton, NTA-Fenton, UV-NTA-Fenton, UV-Fe-NTA, and UV-H_2O_2 processes at two different pHs (3 and 8). Because of the complexity of the OSPW matrix, CHA was used to investigate the reaction mechanisms and kinetics before applying the processes on the OSPW remediation. The decomposition of CHA, NTA, and H_2O_2 under different conditions were recorded and compared for the first time. Fe precipitation at pH 8 in UV-Fe(III)NTA and UV-NTA-Fenton was also described and compared. The influence of borate buffer on the reactivity of Fe(III)NTA and efficiency of UV-NTA-Fenton was also investigated for the first time.

4.2 Materials and Methods

4.2.1 Chemicals and sample preparation

Cyclohexanoic acid (CHA) was purchased from TCI (Portland, OR, USA). NaOH, H_2O_2 (30%), $FeSO_4 \cdot 7H_2O$, 98% H_2SO_4, sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$), 1,10-phenanthroline, acetic acid, and sodium acetate were purchased from Fisher Scientific Co. Canada. Nitrilotriacetic acid (NTA) (99%), bovine catalase, and optima methanol and acetonitrile were purchased from Sigma Aldrich. Titanium (IV) oxysulfate and ammonium acetate were purchased from Fluka Analytical. Filters used were millex syringe-driven 0.2 μm nylon membrane filters provided by Thermo Scientific. 18 MΩ MilliQ water was provided with a system from Millipore Corporation.

A CHA test solution of 0.39 mM was prepared by diluting a CHA stock solution (15.6 mM in 18 MΩ MilliQ water). A 47.6 mM Fe(II) stock solution was prepared by dissolving $FeSO_4 \cdot 7H_2O$ in MilliQ water at pH 3 prior to Fenton reactions. A 0.18 M NTA stock solution was prepared by dissolving NTA in MilliQ water at pH 4 [45]. pH 8 borate buffer solution was prepared by mixing 0.05M sodium tetraborate and sulfuric acid at a ratio of 1.25:1.

4.2.2 Experimental design

UV irradiation experiments were conducted by placing a 100-mL beaker (5.4-cm diameter) with a 80 mL sample solution on a magnetic stirrer under a collimated beam UV apparatus (Model PSI-I-120, Calgon Carbon Corporation, USA) equipped with a 1-kw medium-pressure (MP) Hg-lamp (Calgon Carbon, Pittsburgh, PA, USA) (**Figure 8-1**). The emission of the lamp was from 200 nm to 530 nm (**Figure 4-1**). Samples were taken periodically. Bovine catalase (1g/L) was used to destroy excess H_2O_2. Control experiments were conducted under UV irradiation only. Experiments were carried out in duplicates.

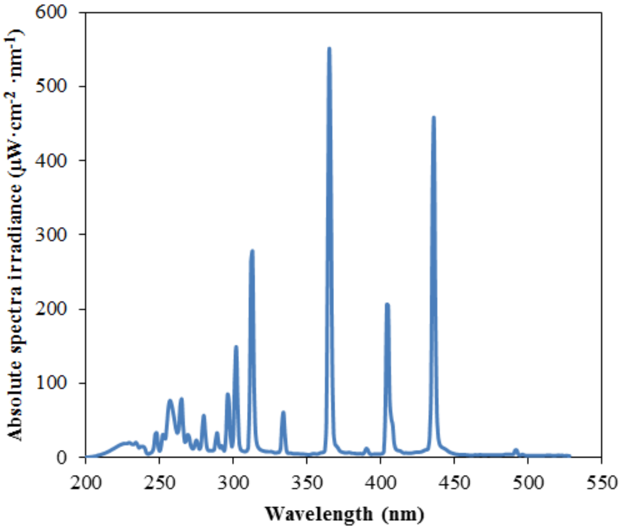


Figure 4-1. Absolute spectrum irradiance of the MP lamp.

4.2.3 Analytical methods

H_2O_2 was measured by titanium (IV) oxysulfate method (DIN 38402H15) at 410 nm (GENESYS™ 10S UV-Vis spectrophotometer) [31, 49]. Fe was measured by 1,10-phenanthroline (ISO 6332) method at 510 nm [21]. The pH was controlled with a pH meter (Fisher Scientific, AR 50) using 0.1 M NaOH and H_2SO_4. NTA as its chelate Fe-NTA was measured by HPLC-UV (Agilent Technologies, 1260 Infinity) at 254 nm with a C18 column of 5 μm, 150 mm×4.6 mm, from Phenomenex. The mobile phase consisted of 0.03 M sodium acetate, 0.002 M tetrabutylammonium bromide, and 5% methanol. pH of the solution was adjusted to 2.78 using acetic acid. Flow rate was 1 mL/min. HPLC-ion trap MS (Agilent Poroshell 120 SB) with a C18 column of 2.7 μm, 50 mm×2.1 mm was used for the analysis of CHA. The column temperature was set at 40°C. Solvents were: A, 4 mM ammonium acetate with 0.1% acetic acid, and B, 100% acetonitrile. Flow rate was 0.35 mL/min. Injection volume was 10 μL. The HPLC solvent gradient for the CHA analysis is given in **Table 4-1**.

Table 4-1. HPLC solvent gradient for the CHA detection.

Time (min)	The percentage of solvent B (%)	Flow (mL/min)
0	5	0.35
1	5	0.35
3	95	0.35
5.5	95	0.35
5.6	5	0.6
8	5	0.6

4.3 Results and Discussions

4.3.1 CHA degradation and H_2O_2 decomposition at pH 3 and 8

CHA (0.39 mM) and H_2O_2 (1.47 mM) decomposition were investigated at pH 3 and pH 8 under UV irradiation, in the UV-H_2O_2, Fenton, NTA-Fenton, UV-Fenton, UV-Fe-NTA, and UV-NTA-Fenton processes. The experimental conditions were: $[Fe]_0$ = 0.089 mM for all the processes except UV irradiation and UV-H_2O_2; $[NTA]_0$ = 0.18 mM for NTA-Fenton, UV-Fe-NTA, and UV-NTA-Fenton; and $[NTA]_0$ = 0.36 mM for UV-NTA-Fenton ($[NTA:Fe]_0$ = 4:1) at pH 8. The form of Fe-NTA without denoting the valence of the metal ion was used in most cases throughout the manuscript because that Fe existed primarily in Fe(II) at pH 3 and Fe(III) at pH 8 at the beginning of the reactions.

4.3.1.1 At pH 3

The CHA and H_2O_2 decomposition at pH 3 can be seen in **Figure 4-2**a-b and **Table 4-2**. The results showed 15.3% and 54.2% CHA degradation in 60 min under UV irradiation and in the UV-Fe-NTA, respectively. 12.7% CHA degradation and 3.1% H_2O_2 decomposition was achieved in the NTA-Fenton and Fenton in 60 min. UV-H_2O_2 decomposed 100% CHA and 14.5% H_2O_2 (from 1.47 mM to 1.26 mM) in 50 min. 12 min and 17 min were needed to completely degrade CHA in the UV-NTA-Fenton (70.0% H_2O_2 decomposition) and UV-Fenton (35.0% H_2O_2 decomposition) processes, respectively. Complete decomposition H_2O_2 occurred at 25 min for the former process and 40 min for the latter, respectively.

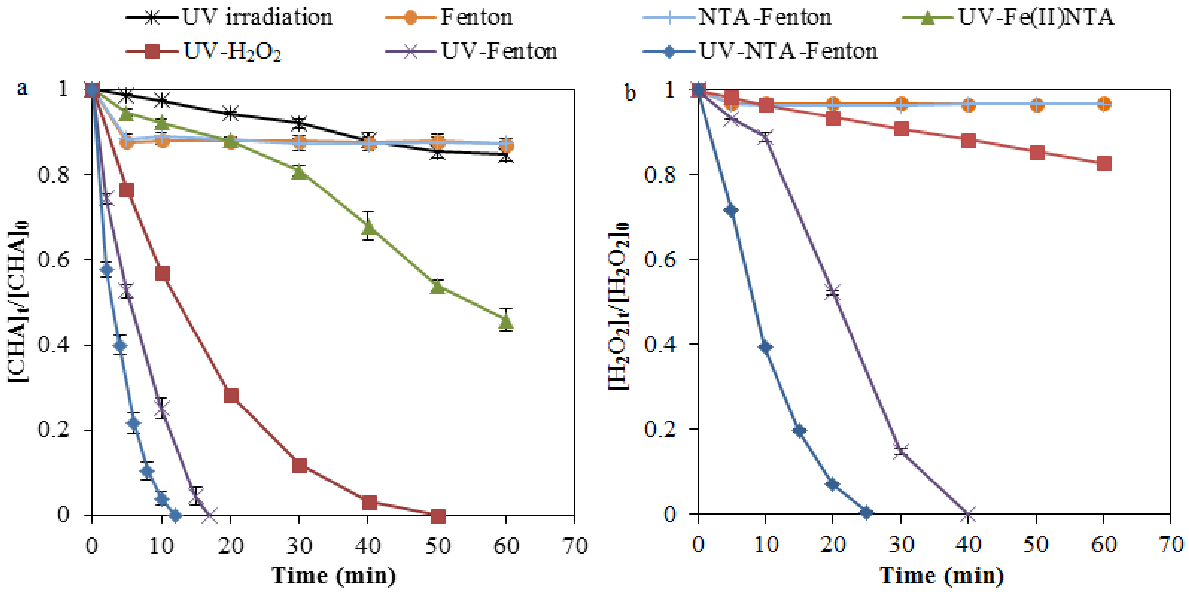


Figure 4-2. a) CHA and b) H_2O_2 decomposition at pH 3 ($[CHA]_0$ = 0.39 mM for all the processes. $[H_2O_2]_0$ = 1.47 mM for all the processes except UV irradiation and UV-Fe(II)NTA. $[Fe]_0$ = 0.089 mM for all the processes except UV irradiation and UV-H_2O_2. $[NTA]_0$ = 0.18 mM for NTA-Fenton, UV-Fe(II)NTA, and UV-NTA-Fenton).

The percentage of Fe-NTA in the total Fe was 41.6% at 0.089 mM Fe and 0.089 mM NTA, and 43.0% at 0.089 mM Fe and 0.18 mM NTA. Therefore, 58.4% Fe was in the form of free ion for the former case and 57.0% for the latter. Brown and Mazzarella (1987) reported 64% of uncomplexed Fe(II) ion at 10% excess ligand and 1/3 total iron in the reduced state at pH 3. The Fe-NTA percentage (41.6% in the presence of 0.089 mM Fe and 0.089 mM NTA) was taken into consideration in the calculation of the molar absorption coefficients of Fe-NTA at pH 3 (**Figure 4-3**).

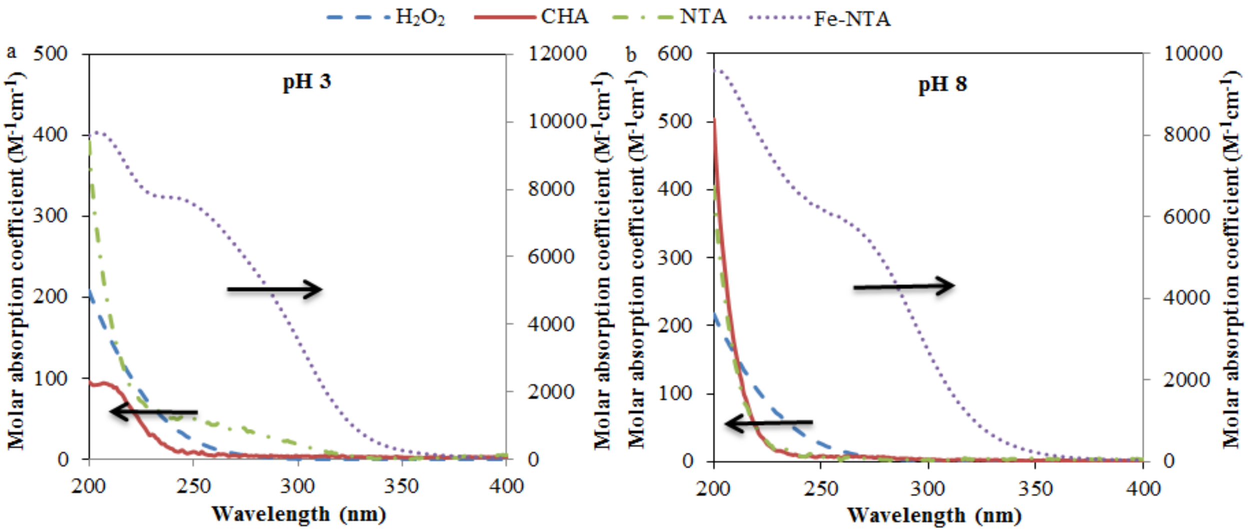


Figure 4-3. Molar absorption coefficients for different species at a) pH 3 and b) pH 8.

Fe-NTA can absorb UV light up to 400 nm, with a shoulder at about 260 nm (molar absorbance coefficient of 7058.77 $M^{-1}cm^{-1}$ at pH 3 and 5971.11 $M^{-1}cm^{-1}$ at pH 8). The high absorption of Fe-NTA from 200 nm to 400 nm indicated that the MP lamp is very efficient in the photolysis of the complex. The protonated form of Fe(NTA)·$2H_2O$ in acidic medium undergoes charge transfer either between Fe and carboxylate group at high wavelength (such as 365 nm) or between Fe and H_2O ligands at low wavelength (such as 254 nm) (Andrianirinaharivelo et al., 1993), which produces $^{\bullet}OH$ directly.

At acidic pH, UV-Fenton has higher efficiency than UV-H_2O_2 in degrading contaminants because of the high solubility of iron ion, the rapid reduction of Fe(III) to Fe(II) by UV, and the fast reaction between Fe(II) species and H_2O_2 (Hu et al., 2011). It is very interesting to notice that the addition of NTA can further improve the efficiency of UV-Fenton, indicating the faster reaction between H_2O_2 and Fe(II)NTA than Fe(II) alone. The Fe-NTA species can accelerate the light-induced Fenton reaction, in agreement with Fukushima and Tatsumi (1999). H_2O_2 reacts 10-1000 times faster with Fe(II)-polycarboxylates than with Fe(II) alone (Faust & Zepp, 1993; Rush et al., 1990), due to the fact that the photo-initiated charge transfer to iron from an organo-ligand is favored over the charge transfer from a hydroxide ligand (Sun & Pignatello, 1993). Similar results were obtained by Deng et al. (1997; 1998) that Fe-chelates were more efficient in the acceleration of the photodegradation of dyes than Fe-hydroxy complexes. The results showed that the most efficient process for degrading CHA at pH 3 was the UV-NTA-Fenton.

4.3.1.2 At pH 8

The results of CHA and H_2O_2 decomposition in different processes at pH 8 are provided in **Figure 4-4**a-b and **Table 4-2**. No CHA degradation occurred under UV irradiation at pH 8, in contrast with 15.3% degradation at pH 3. 19.0% CHA and 8.9% H_2O_2 decomposition in 60 min were observed in the NTA-Fenton process. The degradation of CHA in 60 min in the UV-Fe(III)NTA process was 19.8%. 100% CHA and 20.8% H_2O_2 decomposition were achieved in 60 min in UV-H_2O_2. In the UV-NTA-Fenton with 0.18 mM NTA, CHA degradation can be described in two phases: fast stage for the first 20 min (80.8% removal) and slow stage for the following 40 min (11.5% removal). The results coincided with the H_2O_2 decomposition in the same process, 57.5% decomposition in the first 20 min and 19.7% in the following 40 min. CHA removal reached 95.7% in 15 min in the UV-NTA-Fenton with 0.36 mM NTA. The negligible

CHA removal (2.2%) in the following 15 min in this process was attributed to the complete consumption of H_2O_2 at 17 min (**Figure 4-4**b).

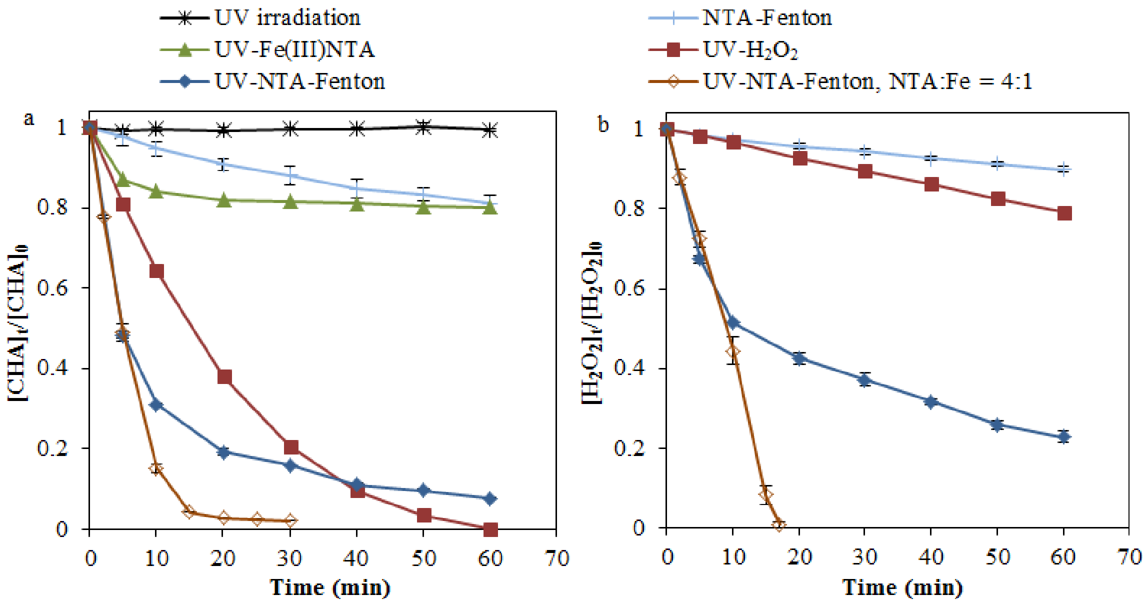


Figure 4-4. a) CHA and b) H_2O_2 decomposition at pH 8 ($[CHA]_0$ = 0.39 mM for all the processes. $[H_2O_2]_0$ = 1.47 mM for all the processes except UV irradiation and UV-Fe(III)NTA. $[Fe]_0$ = 0.089 mM for all the processes except UV irradiation and UV-H_2O_2. $[NTA]_0$ = 0.18 mM for NTA-Fenton, UV-Fe(III)NTA, and UV-NTA-Fenton. $[NTA]_0$ = 0.36 mM for UV-NTA-Fenton, $[NTA:Fe]_0$ = 4:1).

CHA with a pK_a of 4.9 (Perrin et al., 1981) exists mainly in the protonated form at pH 3 and unprotonated form at pH 8. The comparison of the results at two different pHs (**Table 4-2**) confirmed that the CHA degradation at pH 3 was primarily attributed to the direct photolysis of the protonated CHA. The results agree with Stefan and Bolton (2002), who reported a much faster photolysis of N-nitrosodimethylamine at pH 3 than that at pH 7. Song et al. (2013) also declared a faster photodegradation rate of metsulfuron-methyl at acidic pH than that at neutral or basic conditions. No CHA degradation by direct photolysis at 254 nm at pH 9 was reported by Afzal et al. (2012). The mechanisms of the direct photolysis of CHA are not clear yet. However, it was reported that one pathway for the direct photolysis of organics is the absorption of a photon by a molecule, R, producing an electronically-excited-state species, R*, which eventually transfers to final products via the production of reactive ground-state intermediates. The other possible pathway for the direct photolysis is the bond-breaking and bond-forming processes via a single transition state (Wardle, 2009).

Table 4-2. CHA and H_2O_2 decomposition at pH 3 and 8 ($[CHA]_0$ = 0.39 mM for all the processes. $[H_2O_2]_0$ = 1.47 mM for all the processes except UV irradiation and UV-Fe-NTA. $[Fe]_0$ = 0.089 mM for all the processes except UV irradiation and UV-H_2O_2. $[NTA]_0$ = 0.18 mM for NTA-Fenton, UV-Fe-NTA, and UV-NTA-Fenton).

	CHA/H_2O_2/ NTA/Fe Depletion	**UV photolysis**	**Fenton**	**NTA-Fenton**	**UV-Fe-NTA**	**UV-H_2O_2**	**UV-Fenton**	**UV-NTA-Fenton**
pH 3	CHA	15.3%	12.7%	12.7%	54.2%	100% in 50 min	100% in 17 min	100% in 12 min
	H_2O_2	-	3.1%	3.1%	-	17%	100% in 40 min	100% in 25 min
	NTA	1.0%	-	3.6%	100% in 15 min	29.2%	-	100% in 6 min
pH 8	CHA	0	-	19.0%	19.8%	100% in 60 min	-	92.3%
	H_2O_2	-	-	8.9%	-	20.8%	-	77.2%
	NTA	0	-	3.6%	100% in 20 min	8.6%	-	100% in 15 min
	Fe	-	-	0	71.1%	-	-	29.6%

Note: All the depletion was obtained at 60 min except these 100% depletion.

The efficiency of NTA-Fenton at pH 8 was higher than that of NTA-Fenton and Fenton at pH 3, indicating higher activity of Fe(III)NTA than Fe(II) toward H_2O_2, in coincidence with the discussion in Section 4.3.1.1. The higher reaction rate between $^{\bullet}OH$ and unprotonated CHA than protonated CHA also contributed to the higher efficiency at pH 8. Hofman-Caris et al. (2003) stated that the unprotonated forms of organic compounds have rate constants with $^{\bullet}OH$ one or two orders of magnitude larger than their protonated forms. Based on this theory, CHA removal in $^{\bullet}OH$-based processes at pH 8 should be higher than that at pH 3. However, our results of the processes with UV irradiation were the opposite of the hypothesis, which was primarily due to the significant direct photolysis of CHA at pH 3 (**Figure 4-2**a).

The low CHA degradation (19.8%) in UV-Fe(III)NTA at pH 8 can be attributed to the slow photolysis of the complex, which led to slow $^{\bullet}OH$ generation rate. Abida et al. (2006) suggested that the photodegradation of Fe(III)NTA decreased as pH increased. Higher pH is preferred for UV-H_2O_2 because that HO_2^- can absorb UV light more effectively than H_2O_2 (p*K*a = 11.6) (Hofman-Caris et al., 2003). However, the CHA degradation in this process was faster at pH 3 than at pH 8 due to the fast CHA photolysis at the former pH. The complete decomposition of NTA in 15 min in the UV-NTA-Fenton (0.18 mM NTA) at pH 8 (**Figure 4-6**b) led to a progressive decomplexation and precipitation of Fe, resulting in low CHA removal. Although most of Fe was kept soluble in the solution by the NTA degradation product IDA, Fe(III)IDA was much less active than Fe(III)NTA for the H_2O_2 decomposition (De Laat et al., 2011). Fe(III)NTA forms an oxo-bridged dimer at high pH (Gustafson & Martell, 1963; Trott et al., 1972), which would also impose some influence on the behavior of the complex. High dose of NTA (0.36 mM) at pH 8 benefited the CHA and H_2O_2 decomposition in the UV-NTA-Fenton because of the presence of large amounts of active Fe(III)NTA. The results suggested that in order to obtain high efficiency in the UV-NTA-Fenton process at high pH, a high ratio of NTA to Fe (≥ 4) should be applied.

The plots for the pseudo-first-order kinetics of CHA degradation in different processes are included in **Figure 4-5** and the rate constants are given in **Table 4-3**. The highest rate constant was obtained with the UV-NTA-Fenton (NTA:Fe = 2:1) at pH 3 (0.27±0.025 min^{-1}), followed by the same process (NTA:Fe = 4:1) at pH 8 (0.19±0.0085 min^{-1}). By comparing the rate constants obtained in this study (such as 0.058±0.0015 min^{-1} with 1.47 mM H_2O_2 at pH 8) using the MP UV lamp and those reported by Afzal et al. (2012) (such as 0.022±0.003 min^{-1} with 1.76 mM H_2O_2 at pH 9) using a LP UV lamp, it can be concluded that MP lamp was much more efficient than LP lamp in the $^{\bullet}OH$ generation in the H_2O_2 photolysis.

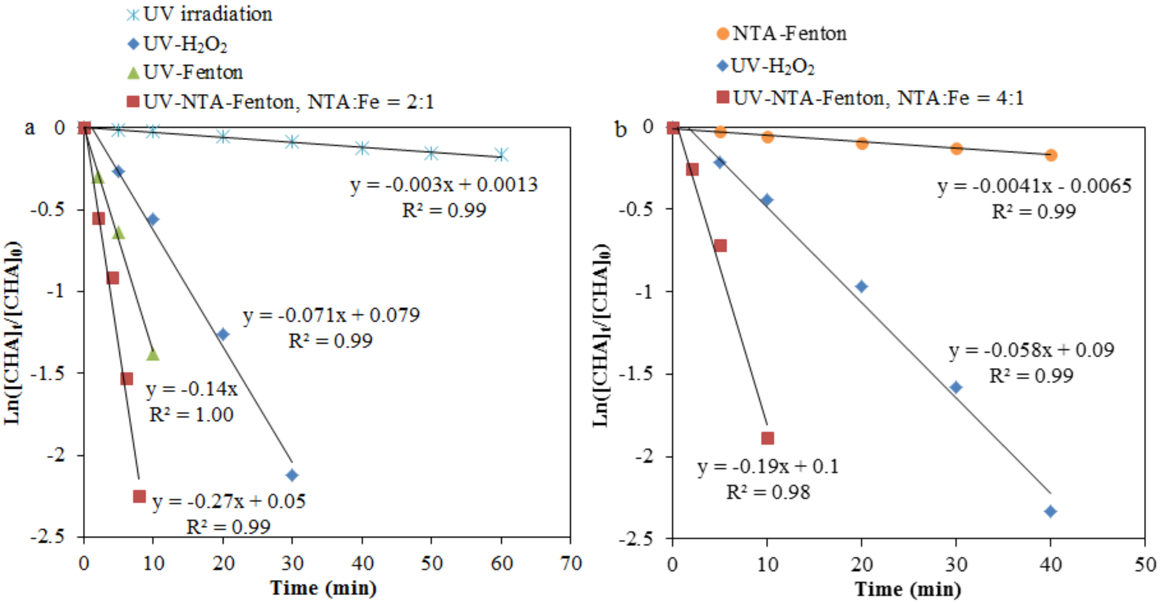


Figure 4-5. Pseudo-first-order degradation of CHA in different processes at a) pH 3 and b) pH 8 ($[CHA]_0$ = 0.39 mM for all the processes. $[H_2O_2]_0$ = 1.47 mM for all the processes except UV irradiation. $[Fe]_0$ = 0.089 mM for all the processes except UV irradiation and UV-H_2O_2. $[NTA]_0$ = 0.18 mM for NTA-Fenton, UV-Fe(II)NTA, and UV-NTA-Fenton ($[NTA:Fe]_0$ = 2:1). $[NTA]_0$ = 0.36 mM for UV-NTA-Fenton ($[NTA:Fe]_0$ = 4:1)).

Table 4-3. Pseudo-first-order rate constants of CHA degradation ($[CHA]_0$ = 0.39 mM for all the processes except the reference. $[H_2O_2]_0$ = 1.47 mM for all the processes except UV irradiation and the reference. $[Fe]_0$ = 0.089 mM for all the processes except UV irradiation and UV-H_2O_2).

Process	pH	Pseudo-first-order rate constant (min^{-1})
UV irradiation	3	0.003±0.00035
UV-H_2O_2	3	0.071±0.0011
UV-H_2O_2	8	0.058±0.0015
UV-H_2O_2 ($[CHA]_0$ = 0.078 mM and $[H_2O_2]_0$ = 0.59 mM)	9	0.0057±0.0009 (Afzal et al., 2012)
UV-H_2O_2 ($[CHA]_0$ = 0.078 mM and $[H_2O_2]_0$ = 1.18 mM)	9	0.013±0.001 (Afzal et al., 2012)
UV-H_2O_2 ($[CHA]_0$ = 0.078 mM and $[H_2O_2]_0$ = 1.76 mM)	9	0.022±0.003 (Afzal et al., 2012)
UV-H_2O_2 ($[CHA]_0$ = 0.078 mM and $[H_2O_2]_0$ = 2.35 mM)	9	0.025±0.001 (Afzal et al., 2012)
UV-Fenton	3	0.14±0.0096
NTA-Fenton, $[NTA:Fe]_0$ = 2:1	8	0.0041±0.00021
UV-NTA-Fenton, $[NTA:Fe]_0$ = 2:1	3	0.27±0.025
UV-NTA-Fenton, $[NTA:Fe]_0$ = 4:1	8	0.19±0.0085

4.3.2 NTA degradation at pH 3 and 8

The degradation of 0.18 mM NTA in different processes at pH 3 (**Figure 4-6**a) and 8 (**Figure 4-6**b) was investigated and compared. Negligible degradation of NTA under UV irradiation was observed and only 3.6% depletion of NTA was found in NTA-Fenton at pHs 3 and 8. UV-H_2O_2 was more efficient in degrading NTA at pH 3 (29.2% in 60 min) than at pH 8 (8.6% in 60 min). Complete degradation of NTA took place in 15 min and 20 min in UV-Fe-NTA at pH 3 and 8, respectively. In the UV-NTA-Fenton process, it took 6 min and 15 min to completely degrade NTA at pH 3 and 8, respectively.

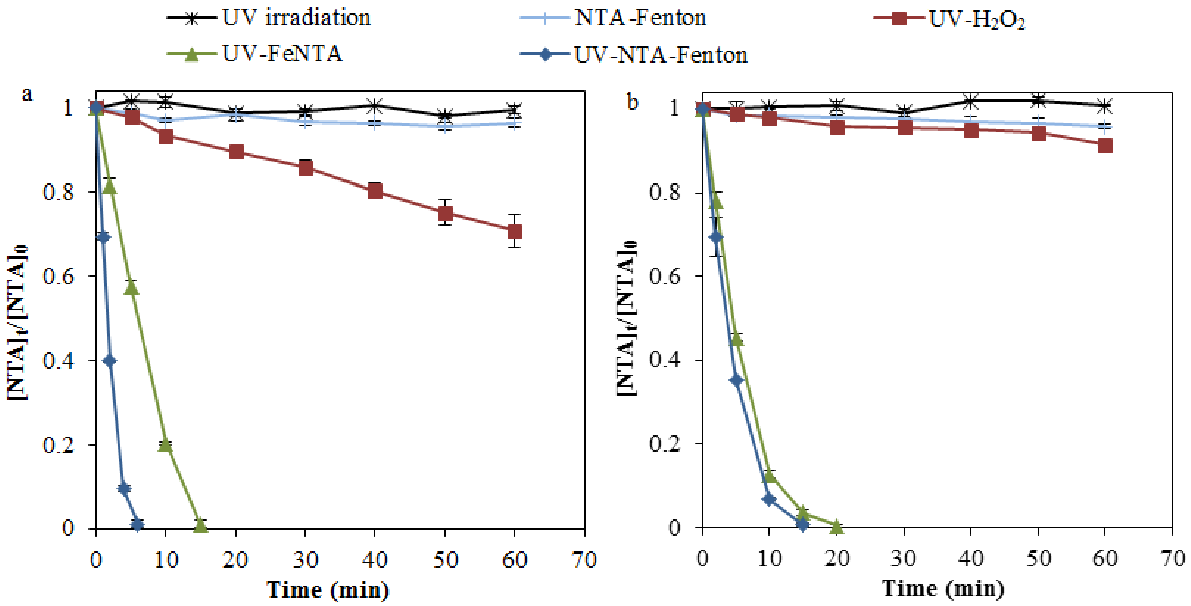


Figure 4-6. NTA degradation at a) pH 3 and b) pH 8 ($[H_2O_2]_0$ = 1.47 mM for all the processes except UV irradiation and UV-Fe-NTA. $[Fe]_0$ = 0.089 mM and $[NTA]_0$ = 0.18 mM for all the processes except UV irradiation and UV-H_2O_2).

The negligible direct photolysis of NTA at pH 3 and 8 was due to the low absorbance of NTA between 200 nm to 400 nm (**Figure 4-3**). The NTA degradation in the NTA-Fenton was caused by the reaction with $^{\bullet}OH$. The second-order rate constant between NTA and $^{\bullet}OH$ was reported as $4.77 \pm 0.24 \times 10^8$ $M^{-1}s^{-1}$ at pH 8 in our previous study, much lower than the rate constant between CHA and $^{\bullet}OH$ ($4.09 \pm 0.39 \times 10^9$ $M^{-1}s^{-1}$) (Zhang et al., 2016). Sahul and Sharma (1987) reported the rate constant between NTA and $^{\bullet}OH$ as 6.1×10^7 $M^{-1}s^{-1}$ at pH 2, 5.5×10^8 $M^{-1}s^{-1}$ at pH 6, and 4.2×10^9 $M^{-1}s^{-1}$ at pH 10. Lati and Meyerstein (1978) reported two constant values, 7.5×10^8 $M^{-1}s^{-1}$ at pH 4 and 2.5×10^9 $M^{-1}s^{-1}$ at pH 9. All these values suggested higher reaction rate of NTA with $^{\bullet}OH$ at high pH, which is inconsistent with our observations in the UV-H_2O_2. One major difference between our study and the literature is the different light sources used. Gamma radiolysis was used by Sahul and Sharma (1987) and pulse radiolysis was used by Lati and Meyerstein (1978), quite different from our MP UV lamp, which might impose different influence on the activity of NTA. NTA has pK_{a1} = 1.89, pK_{a2} = 2.49, and pK_{a3} = 9.73 (Yamasaki & Shibahara, 1992). The amount of the protonated form of NTA at pH 3 was much higher than that at pH 8. The results of this study suggest that UV irradiation imposed influence on the activity of the protonated form of NTA at low pH, thus affecting the reaction rate between NTA and $^{\bullet}$OH. The faster photodecomposition of Fe-NTA complex at pH 3 than pH 8 was in coincidence with Abida et al. (2006). Stolzberg and Hume (1975) also declared that the efficiency of the Fe(III)NTA photodegradation was a function of pH, with slower rates at higher pH.

4.3.3 Fe concentration at pH 8

Fe concentration in UV-Fe(III)NTA and UV-NTA-Fenton at pH 8 were recorded (**Figure 4-7**). In the UV-Fe(III)NTA, Fe decreased from 0.089 mM to 0.085 mM in the first 20 min and fell off quickly to 0.024 mM at 60 min. In the UV-NTA-Fenton, Fe concentration was stable at 0.086-0.089 mM in the first 20 min, and then decreased slowly to 0.063 mM in the following 40 min. In the first 20 min in the UV-Fe(III)NTA process, iron was kept in solution by the presence of NTA, and as NTA degraded completely within 20 min (**Figure 4-6**b), Fe concentration decreased dramatically. IDA, the primary product of NTA, was responsible for keeping Fe soluble after the complete degradation of NTA. Due to the low stability constant of Fe-IDA (6.3×10^{5} $M^{-1}s^{-1}$ at 20 °C) (Abida et al., 2006; Martell & Smith, 1974), the photodecomposition of the complex was slower than that of Fe-NTA (Stolzberg & Hume, 1975).

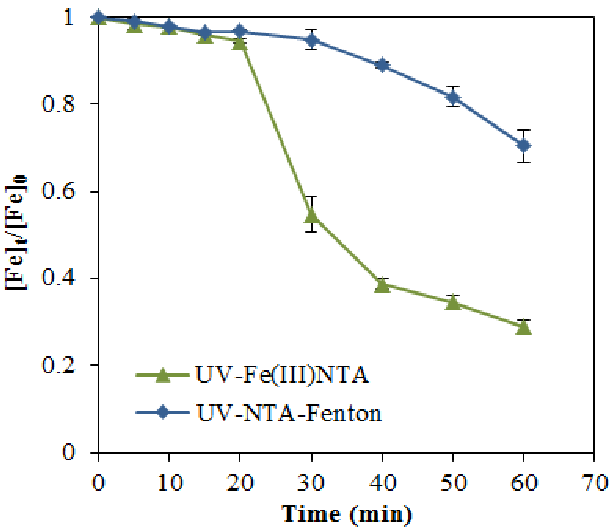
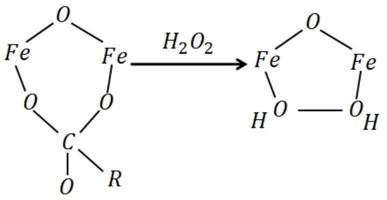


Figure 4-7. Total Fe concentration in UV-Fe(III)NTA and UV-NTA-Fenton at pH 8 ($[H_2O_2]_0$ = 1.47 mM for UV-NTA-Fenton. $[Fe]_0$ = 0.089 mM and $[NTA]_0$ = 0.18 mM for both processes).

For free Fe(III) ion, it was demonstrated that the first step in the reaction of Fe(III) and H_2O_2 is the formation of Fe(III)-peroxocomplexes (Gallard et al., 1999). In the case of the reaction of H_2O_2 with Fe(III)EDTA, the formation of purple intermediates has been reported by several researchers (De Laat et al., 2011; Francis et al., 1985; Walling et al., 1970). Fe(III)EDTA-H_2O_2 can catalyze both H_2O_2 decomposition and the oxidation of organic substrates, such as complexed and uncomplexed EDTA (Walling et al., 1975). The formation of peroxide adducts depends on the Fe-O (carbonate group) bonds. The stronger the bond, the harder of the formation of peroxide adducts (Nishida et al., 1994). Similar to EDTA, Nishida et al. (1994) proposed a peroxide adduct of Fe(III)NTA based on the formation of binuclear Fe(III)-H_2O_2 adduct and the peroxide adduct formed with Mo(VI). The formation of Fe(III)NTA-H_2O_2 was shown in **Scheme 4-1**.



Scheme 4-1.

Based on this hypothesis and the results obtained in our study, it can be concluded that the slow precipitation of Fe in the UV-NTA-Fenton was attributed to the formation of Fe(III)NTA-H_2O_2. H_2O_2 acted as a co-complexing agent helping NTA to prevent iron from precipitation. Similar to Fe(III)EDTA-H_2O_2, the Fe(III)NTA-H_2O_2 adduct exhibits different reactivity in contrast with Fe(III)NTA, such as absorbing light between 350-600 nm where Fe(III)NTA and H_2O_2 do not absorb (De Laat et al., 2011).

4.3.4 Effect of borate buffer

Borate buffer is a weak chelating agent. It was widely used in Fenton and photo-Fenton systems (Dubinina et al., 2002; Lee & Sedlak, 2009; Lee et al., 2008; White et al., 2003). However, none of these researchers studied the influence of borate buffer on Fe-ligand complexes. In this study, we compared the decomposition of CHA, NTA, and H_2O_2, and Fe precipitation in the UV-NTA-Fenton in borate buffer and in MilliQ water (**Figure 4-8**a-d). pH of the borate buffer was stable at 8. pH of MilliQ water decreased from 8 to 6.8 at the end of reaction. CHA degradation in 60 min in the borate buffer (67.8%) was slower than that in MilliQ water (92.3%). H_2O_2 decomposition in MilliQ water (57.5%) was faster than that in the borate buffer (52.1%) in the first 20 min, and became slower in the following 40 min (77.2% in MilliQ water and 90% in the borate buffer at the end of the reactions). There was no difference between the NTA degradation in the borate buffer and in MilliQ water, and over 97% NTA degradation in

15 min was observed in both solutions. No decrease of Fe and 29.2% Fe precipitation (from 0.089 mM to 0.063 mM) in 60 min were found in the borate buffer and in MilliQ water, respectively.

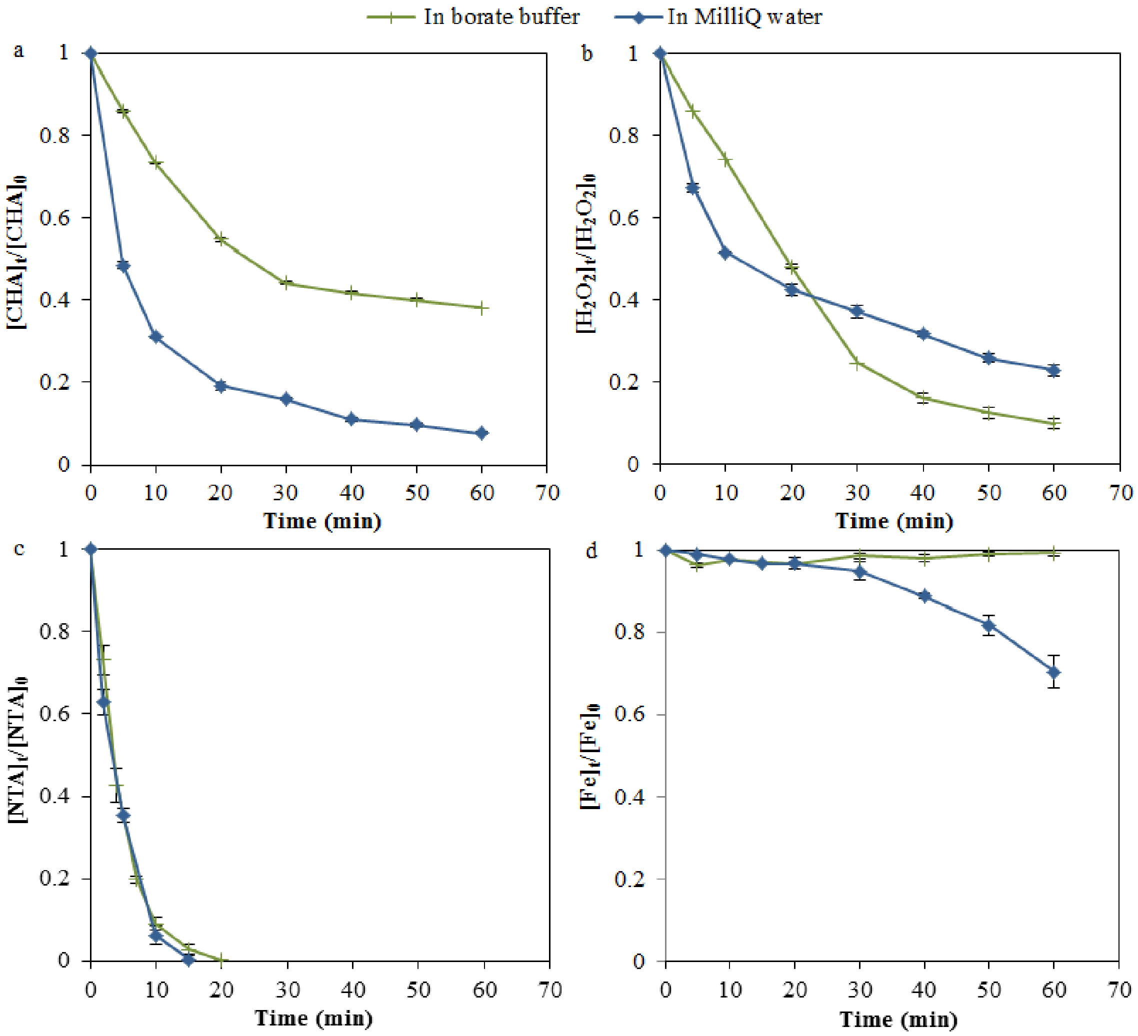


Figure 4-8. Comparison of the performance of UV-NTA-Fenton in borate buffer and MilliQ water at pH 8 in a) CHA, b) H_2O_2, and c) NTA decomposition, and d) total Fe concentration ($[CHA]_0 = 0.39$ mM, $[H_2O_2]_0 = 1.47$ mM, $[Fe]_0 = 0.089$ mM, and $[NTA]_0 = 0.18$ mM).

It was reported that tetraborate ion exhibits co-complexing ability with various substances and can be used as a deodorizing and sanitizing agent (Hitchcock & Puckett, 2013).

Studies of the borate complexation effect on selected lanthanides and actinides have been reported (Borkowski et al., 2010). Borate can also form inner-sphere complex with iron oxides (Su & Puls, 2001; Su & Suarez, 1995). Therefore, it is reasonable to assume the formation of borate-Fe(III)NTA complex based on the co-complexing ability of tetraborate ion.

No difference was found in the CHA removal in UV-H_2O_2 in the borate buffer and MilliQ water (data is not shown here), suggesting that borate ion does not consume $^\bullet OH$. The negative effect of the borate buffer on the CHA removal can be related to its effect on the release of $^\bullet OH$ from the metal center. It has been reported that $^\bullet OH$ generated in the Fenton reaction forms a bound with the iron center, either as $[Fe\cdots {}^\bullet OH]^{3+}$ or $[Fe{=}O]^{2+}$ (Lloyd et al., 1997). According to this theory, the co-complexing effect of borate buffer on Fe(III)NTA can hold back the release of $^\bullet OH$ from the central metal ion, thus reducing the $^\bullet OH$ amount for CHA degradation. Compared to MilliQ water, slower H_2O_2 decomposition in the borate buffer in the first 20 min was due to the H_2O_2 stabilization by tetraborate-Fe(III)NTA, similar to a previous report of Zuo and Hoigne (1992) in the Fe(III)-oxalate photolysis. High level of Fe in the buffer solution contributed to the faster H_2O_2 decomposition after the complete consumption of NTA at 20 min. The co-complexing effect of tetraborate did not affect the photolysis of Fe(III)NTA (**Figure 4-8**c). Borate ion alone does not have a high affinity for iron ion, as suggested by the low concentration of Fe trapped in the borate buffer only. The high concentration of Fe in the buffer solution can be attributed to the co-complexing effect of the tetraborate ion on Fe(III)NTA.

4.4 Conclusions

Compared to UV irradiation, UV-H_2O_2, Fenton, NTA-Fenton, UV-Fenton, and UV-Fe-NTA, UV-NTA-Fenton at pH 3 was much more efficient for the decomposition of H_2O_2, CHA, and NTA. MP UV lamp exhibited much higher efficiency in the generation of $^{\bullet}OH$ in H_2O_2 photolysis than LP UV lamp. The presence of Fe and UV irradiation was necessary for the fast degradation of NTA. Fe-NTA complex under UV irradiation was not a true catalyst because of its fast photodegradation. However, the degradation can eliminate the concerns of researchers about NTA contamination. The formation of H_2O_2 adduct with Fe(III)NTA attributed to the high concentration of Fe in the UV-NTA-Fenton at pH 8. Borate buffer as a co-complexing agent can help to keep iron soluble, however, it can also hinder the degradation of CHA by blocking the release of $^{\bullet}OH$ from the central metal ion. This research work indicated high possibility of the application of UV-NTA-Fenton with a high dose of NTA in the treatment of OSPW at natural pH, and the results can further be applied to the planning and design of the effective advanced oxidation processes for the treatment of other wastewaters.

4.5 References

Abida, O., Mailhot, G., Litter, M., & Bolte, M. (2006). Impact of iron-complex (Fe(III)-NTA) on photoinduced degradation of 4-chlorophenol in aqueous solution. *Photochemical & photobiological sciences : Official Journal of the European Photochemistry Association and the European Society for Photobiology, 5*(4), 395-402.

Afzal, A., Drzewicz, P., Martin, J. W., & Gamal El-Din, M. (2012). Decomposition of cyclohexanoic acid by the UV/H_2O_2 process under various conditions. *Science of the Total Environment, 426*, 387-392.

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

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

Anderegg, G. (1986). The stability of iron(III) complexes formed below pH = 3 with glycinate, iminodiacetate, β-hydroxyethyliminodiacetate, N, N-di-(Hydroxyethyl)-glycinate, nitrilotriacetate and triethanolamine. *Inorganica Chimica Acta, 121*(2), 229-231.

Andrianirinaharivelo, S. L., Pilichowski, J. F., & Bolte, M. (1993). Nitrilotriacetic acid transformation photo-induced by complexation with iron(III) in aqueous solution. *Transition Metal Chemistry, 18*(1), 37-41.

Bautista, P., Mohedano, A. F., Casas, J. A., Zazo, J. A., & Rodriguez, J. J. (2008). An overview of the application of Fenton oxidation to industrial wastewaters treatment. *Journal of Chemical Technology and Biotechnology, 83*(10), 1323-1338.

Bojanowska-Czajka, A., Drzewicz, P., Kozyra, C., Nałęcz-Jawecki, G., Sawicki, J., Szostek, B., & Trojanowicz, M. (2006). Radiolytic degradation of herbicide 4-chloro-2-methyl phenoxyacetic acid (MCPA) by γ-radiation for environmental protection. *Ecotoxicology and Environmental Safety, 65*(2), 265-277.

Borkowski, M., Richmann, M., Reed, D. T., & Xiong, Y. (2010). Complexation of Nd(III) with tetraborate ion and its effect on actinide(III) solubility in WIPP brine. *Radiochimica Acta, 98*(9-11), 577-582.

Brown, E., & Mazzarella, J. (1987). Mechanism of oxidation of ferrous polydentate complexes by dioxygen. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 222*(1), 173-192.

Bunescu, A., Besse-Hoggan, P., Sancelme, M., Mailhot, G., & Delort, A.-M. (2008). Fate of the nitrilotriacetic Acid-Fe(III) complex during photodegradation and biodegradation by Rhodococcus rhodochrous. *Applied and Environmental Microbiology, 74*(20), 6320-6326.

Dao, Y. H., & De Laat, J. (2011). Hydroxyl radical involvement in the decomposition of hydrogen peroxide by ferrous and ferric-nitrilotriacetate complexes at neutral pH. *Water Research, 45*(11), 3309-3317.

De la Cruz, N., Gimenez, J., Esplugas, S., Grandjean, D., de Alencastro, L. F., & Pulgarin, C. (2012). Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. *Water Research, 46*(6), 1947-1957.

De Laat, J., Dao, Y. H., Hamdi El Najjar, N., & Daou, C. (2011). Effect of some parameters on the rate of the catalysed decomposition of hydrogen peroxide by iron(III)-nitrilotriacetate in water. *Water Research, 45*(17), 5654-5664.

Deng, N., Wu, F., Luo, F., & Liu, Z. (1997). Photodegradation of dyes in aqueous solutions containing Fe(III)-oxalato complexes. *Chemosphere, 35*(11), 2697-2706.

Deng, N., Wu, F., Luo, F., & Xiao, M. (1998). Ferric citrate-induced photodegradation of dyes in aqueous solutions. *Chemosphere, 36*(15), 3101-3112.

Dubinina, E., Gavrovskaya, S., Kuzmich, E., Leonova, N., Morozova, M., Kovrugina, S., & Smirnova, T. (2002). Oxidative modification of proteins: oxidation of tryptophan and production of dityrosine in purified proteins using Fenton's system. *Biochemistry (Moscow), 67*(3), 343-350.

Faust, B. C., & Hoigné, J. (1990). Photolysis of Fe(III)-hydroxy complexes as sources of OH radicals in clouds, fog and rain. *Atmospheric Environment. Part A. General Topics, 24*(1), 79-89.

Faust, B. C., & Zepp, R. G. (1993). Photochemistry of aqueous iron(III)-polycarboxylate complexes: Roles in the chemistry of atmospheric and surface waters. *Environmental Science & Technology, 27*(12), 2517-2522.

Feng, W., & Nansheng, D. (2000). Photochemistry of hydrolytic iron(III) species and photoinduced degradation of organic compounds. A minireview. *Chemosphere, 41*(8), 1137-1147.

Francis, K. C., Cummins, D., & Oakes, J. (1985). Kinetic and structural investigations of [Fe^{III} (edta)]-[edta = ethylenediaminetetra-acetate (4-)] catalysed decomposition of hydrogen peroxide. *Journal of the Chemical Society, Dalton Transactions*(3), 493-501.

Fu, H., Gamal El-Din, M., Smith, D. W., MacKinnon, M., & Zubot, W. (2008). Ozone treatment of naphthenic acids in Athabasca oil sands process-affected water. Paper presented at the First International Oil Sands Tailings Conference,, Edmonton, AB, Canda.

Fukushima, M., & Tatsumi, K. (1999). Photocatalytic reaction by iron(III)-humate complex and its effect on the removal of organic pollutant. *Toxicological & Environmental Chemistry, 73*(1-2), 103-116.

Gallard, H., De Laat, J., & Legube, B. (1999). Spectrophotometric study of the formation of iron(III)-hydroperoxy complexes in homogeneous aqueous solutions. *Water Research, 33*(13), 2929-2936.

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

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

Goldstein, S., Aschengrau, D., Diamant, Y., & Rabani, J. (2007). Photolysis of aqueous H_2O_2: quantum yield and applications for polychromatic UV actinometry in photoreactors. *Environmental Science & Technology, 41*(21), 7486-7490.

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

Gustafson, R. L., & Martell, A. E. (1963). Hydrolytic Tendencies of Ferric Chelates[1]. *The Journal of Physical Chemistry, 67*(3), 576-582.

Gutteridge, J., Maidt, L., & Poyer, L. (1990). Superoxide dismutase and Fenton chemistry. Reaction of ferric-EDTA complex and ferric-bipyridyl complex with hydrogen peroxide without the apparent formation of iron(II). *Biochemical Journal, 269*, 169-174.

Hewgill, F., & Proudfoot, G. (1976). Regioselective oxidation of aliphatic acids by complexed hydroxyl radicals. *Australian Journal of Chemistry, 29*(3), 637-647.

Hitchcock, W. W., & Puckett, J. M. (2013). United States Patent.

Hofman-Caris, C., Harmsen, D., & Beerendonk, E. (2003). Degradation of priority compounds by UV and UV oxidation. *Advanced Oxidation Processes, TECHNEAU.*

Homlok, R., Takács, E., & Wojnárovits, L. (2010). Radiolytic degradation of 2, 4-dichlorophenoxyacetic acid in dilute aqueous solution: pH dependence. *Journal of Radioanalytical and Nuclear Chemistry, 284*(2), 415-419.

Hu, X., Wang, X., Ban, Y., & Ren, B. (2011). A comparative study of UV-Fenton, UV-H_2O_2 and Fenton reaction treatment of landfill leachate. *Environmental Technology, 32*(9), 945-951.

Huang, W. Y., Brigante, M., Wu, F., Mousty, C., Hanna, K., & Mailhot, G. (2013). Assessment of the Fe(III)-EDDS complex in Fenton-like processes: from the radical formation to the degradation of bisphenol A. *Environmental Science & Technology, 47*(4), 1952-1959.

Jones, D., Scarlett, A. G., West, C. E., & Rowland, S. J. (2011). Toxicity of individual naphthenic acids to Vibrio fischeri. *Environmental Science & Technology, 45*(22), 9776-9782.

Klamerth, N., Malato, S., Aguera, A., & Fernandez-Alba, A. (2013). Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: a comparison. *Water Research, 47*(2), 833-840.

Klamerth, N., Malato, S., Aguera, A., Fernandez-Alba, A., & Mailhot, G. (2012). Treatment of municipal wastewater treatment plant effluents with modified photo-Fenton as a tertiary treatment for the degradation of micro pollutants and disinfection. *Environmental Science & Technology, 46*(5), 2885-2892.

Kušić, H., Koprivanac, N., Božić, A. L., & Selanec, I. (2006). Photo-assisted Fenton type processes for the degradation of phenol: a kinetic study. *Journal of Hazardous Materials, 136*(3), 632-644.

Langford, C. H., Wingham, M., & Sastri, V. S. (1973). Ligand photooxidation in copper(II) complexes of nitrilotriacetic acid. Implications for natural waters. *Environmental Science & Technology, 7*(9), 820-822.

Lati, J., & Meyerstein, D. (1978). Oxidation of first-row bivalent transition-metal complexes containing ethylenediaminetetra-acetate and nitrilotriacetate ligands by free radicals: a pulse-radiolysis study. *Journal of the Chemical Society, Dalton Transactions*(9), 1105-1118.

Lee, C., & Sedlak, D. L. (2009). A novel homogeneous Fenton-like system with Fe(III)-phosphotungstate for oxidation of organic compounds at neutral pH values. *Journal of Molecular Catalysis A: Chemical, 311*(1), 1-6.

Lee, C. H., Keenan, C. R., & Sedlak, D. L. (2008). Polyoxometalate-enhanced oxidation of organic compounds by nanoparticulate zero-valent iron and ferrous ion in the presence of oxygen. *Environmental Science & Technology, 42*(13), 4921-4926.

Li, J., Mailhot, G., Wu, F., & Deng, N. S. (2010). Photochemical efficiency of Fe(III)-EDDS complex: OH radical production and 17β-estradiol degradation. *Journal of Photochemistry and Photobiology A: Chemistry, 212*(1), 1-7.

Lloyd, R. V., Hanna, P. M., & Mason, R. P. (1997). The origin of the hydroxyl radical oxygen in the Fenton reaction. *Free Radical Biology and Medicine, 22*(5), 885-888.

Martell, A. E., & Smith, R. M. (1974). Critical stability constants (Vol. 1). New York, Plenum Press: Springer.

Nadtochenko, V. A., & Kiwi, J. (1998). Photolysis of $FeOH^{2+}$ and $FeCl^{2+}$ in aqueous solution. Photodissociation kinetics and quantum yields. *Inorganic Chemistry, 37*(20), 5233-5238.

Nam, S., Renganathan, V., & Tratnyek, P. G. (2001). Substituent effects on azo dye oxidation by the Fe^{III}-EDTA-H_2O_2 system. *Chemosphere, 45*(1), 59-65.

Nelson, L. R., MacKinnon, M., & Gulley, J. R. (1993). Application of toxicity testing in the evaluation of reclamation options for oil sands fine tails. Paper presented at the Oil Sands-Our Petroleum Future Conference,, Edmonton, Alberta, Canada.

Neyens, E., & Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials, 98*(1-3), 33-50.

Nishida, Y., Goto, A., Akamatsu, T., Ohba, S., Fujita, T., Tokii, T., & Okada, S. (1994). Iron Chelates in Biological Systems. Its Relevance to Induction of Pathogenesis of Tissue Damage and Carcinogenesis. *Chemistry Letters*(3), 641-644.

Panadés, R., Ibarz, A., & Esplugas, S. (2000). Photodecomposition of carbendazim in aqueous solutions. *Water Research, 34*(11), 2951-2954.

Perez, M., Torrades, F., Domenech, X., & Peral, J. (2002). Fenton and photo-Fenton oxidation of textile effluents. *Water Research, 36*(11), 2703-2710.

Perrin, D. D., Dempsey, B., & Serjeant, E. P. (1981). pKa prediction for organic acids and bases (Vol. 1). London: Chapman and Hall: Springer.

Pourrezaei, P. (2013). Physico-Chemical Processes for Oil Sands Process-Affected Water Treatment. (Doctor of Philosophy), University of Alberta, Edmonton, A.B.

Pourrezaei, P., Alpatova, A., Khosravi, K., Drzewicz, P., Chen, Y., Chelme-Ayala, P., & Gamal El-Din, M. (2014). Removal of organic compounds and trace metals from oil sands process-affected water using zero valent iron enhanced by petroleum coke. *Journal of Environmental Management, 139*, 50-58.

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

Rigg, T., Taylor, W., & Weiss, J. (1954). The rate constant of the reaction between hydrogen peroxide and ferrous ions. *The Journal of Chemical Physics, 22*(4), 575-577.

Rush, J., Maskos, Z., & Koppenol, W. (1990). Distinction between hydroxyl radical and ferryl species. *Methods in Enzymology, 186*, 148-156.

Sahul, K., & Sharma, B. (1987). Gamma radiolysis of nitrilotriacetic acid (NTA) in aqueous solutions. *Journal of Radioanalytical and Nuclear Chemistry, 109*(2), 321-327.

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

Song, N., Wang, D., Shan, Z., & Shi, L. (2013). Influence of pH and dissolved organic matter on photolysis of metsulfuron-methyl. *Procedia Environmental Sciences, 18*, 585-591.

Stefan, M. I., & Bolton, J. R. (2002). UV direct photolysis of N-nitrosodimethylamine (NDMA): Kinetic and product study. *Helvetica Chimica Acta, 85*(5), 1416-1426.

Stolzberg, R. J., & Hume, D. N. (1975). Rapid formation of iminodiacetate from photochemical degradation of iron (III) nitrilotriacetate solutions. *Environmental Science & Technology, 9*(7), 654-656.

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

Su, C., & Suarez, D. L. (1995). Coordination of adsorbed boron: A FTIR spectroscopic study. *Environmental Science & Technology, 29*(2), 302-311.

Sun, Y., & Pignatello, J. J. (1993). Activation of hydrogen peroxide by iron(III) chelates for abiotic degradation of herbicides and insecticides in water. *Journal of Agricultural and Food Chemistry, 41*(2), 308-312.

Tollefsen, K. E., Petersen, K., & Rowland, S. J. (2012). Toxicity of synthetic naphthenic acids and mixtures of these to fish liver cells. *Environmental Science & Technology, 46*(9), 5143-5150.

Trott, T., Henwood, R. W., & Langford, C. H. (1972). Sunlight photochemistry of ferric nitrilotriacetate complexes. *Environmental Science & Technology, 6*(4), 367-368.

Vermilyea, A. W., & Voelker, B. M. (2009). Photo-Fenton reaction at near neutral pH. *Environmental Science & Technology, 43*(18), 6927-6933.

Walling, C., Kurz, M., & Schugar, H. J. (1970). Iron(III)-ethylenediaminetetraacetic acid-peroxide system. *Inorganic Chemistry, 9*(4), 931-937.

Walling, C., Partch, R. E., & Weil, T. (1975). Kinetics of the decomposition of hydrogen peroxide catalyzed by ferric ethylenediaminetetraacetate complex. *Proceedings of the National Academy of Sciences, 72*(1), 140-142.

Wang, C., Klamerth, N., Huang, R., Elnakar, H., & Gamal El-Din, M. (2016). Oxidation of Oil Sand Process-affected Water by Potassium Ferrate(VI). *Environmental Science & Technology*.

Wang, Y. N. (2011). Application of Coagulation-Flocculation Process for Treating Oil Sands Process-Affected Water. (Master of Science), University of Alberta, Edmonton, AB, Canada.

Wardle, B. (2009). Principles and applications of photochemistry. Chichester, West Sussex, United Kingdom: John Wiley & Sons.

Weschler, C., Mandich, M., & Graedel, T. (1986). Speciation, photosensitivity, and reactions of transition metal ions in atmospheric droplets. *Journal of Geophysical Research, D: Atmospheres, 91*(D4), 5189-5204.

White, E. M., Vaughan, P. P., & Zepp, R. G. (2003). Role of the photo-Fenton reaction in the production of hydroxyl radicals and photobleaching of colored dissolved organic matter in a coastal river of the southeastern United States. *Aquatic Sciences, 65*(4), 402-414.

Yamasaki, M., & Shibahara, T. (1992). Structure of Incomplete Cubane-Type Sulfur-Bridged Molybdenum Cluster Compound, $Na_2[Mo_3S_4(Hnta)_3]\cdot 5H_2O$ (H_3NTA= nitrilotriacetic acid). *Analytical sciences, 8*(5), 727-729.

Zhang, Y., Klamerth, N., & Gamal El-Din, M. (2016). Degradation of a Model Naphthenic Acid by Nitrilotriacetic Acid-Modified Fenton Process. *Chemical Engineering Journal, 292*, 340-347.

Zhang, Y., McPhedran, K. N., & Gamal El-Din, M. (2015). Pseudomonads biodegradation of aromatic compounds in oil sands process-affected water. *Science of the Total Environment, 521*, 59-67.

Zhou, S. Q., Huang, H. P., & Liu, Y. M. (2008). Biodegradation and origin of oil sands in the Western Canada sedimentary basin. *Petroleum Science, 5*(2), 87-94.

Zuo, Y., & Hoigne, J. (1992). Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III)-oxalato complexes. *Environmental Science & Technology, 26*(5), 1014-1022.

5 KINETICS STUDY OF FE(III)-TETRAPOLYPHOSPHATE AS A CATALYST FOR THE OXIDATION OF HYDROGEN SULFIDE[4]

5.1 Introduction

Wastewater from petroleum refinery contains both organic and inorganic compounds such as sulfide, phenol, and ammonia with concentrations ranging from 10 to 5000, 5 to 300, and 10 to 3000 mg/L, respectively (Alcántara et al., 2004). As a common toxic contaminant, phenol at high concentrations in wastewater can lead to toxicity towards aquatic organisms (Yan et al., 2008). The maximum inlet phenol concentration for biological wastewater treatment plants is 1-2 mg/L (Arana et al., 2001). Moreover, the presence of 1-10 µg/L phenol in freshwater produces unpleasant odour/taste during chlorination (Arana et al., 2001). The Canadian guideline value of phenol in freshwater for the protection of aquatic life is 4 µg/L (Environment Canada, 1998; Marine, 1999). Hydrogen sulfide (H_2S) is extremely toxic and irritating. H_2S ($pKa_1 = 6.9$ and $pKa_2 = 19$) exists mainly as HS^- in water at pH > 7 (DeLeon et al., 2012; Olson, 2005). H_2S has a permissible exposure limit of 20 parts per million (ppm), regulated by the Occupational Safety & Health Administration (OSHA, USA). Inhalation of 500-1000 (ppm) of H_2S will cause rapid unconsciousness and death through respiratory paralysis and asphyxiation (Doujaiji & Al-Tawfiq, 2010). Therefore, the amount of phenol and H_2S must be reduced to acceptable levels before discharge due to safety and environmental concerns.

---

[4] A version of this chapter will be submitted: Ying Zhang, Ali Safarzadeh-Amiri, Nikolaus Klamerth, Pamela Chelme-Ayala, & Mohamed Gamal El-Din. Kinetics Study of Fe(III)-Tetrapolyphosphate as a Catalyst for the Oxidation of Hydrogen Sulfide. *Applied Catalysis B: Environmental*.

Desulfurization by liquid redox sulfur recovery (LRSR) with iron(III)-chelates as catalysts (DeBerry, 1997; Demmink & Beenackers, 1997) have attracted a lot of attentions from both industry and academic researchers for the last several decades. In this process, H_2S is oxidized to elemental sulfur through the reduction of a Fe(III)-complex to Fe(II)-complex (Eq. 5-1). The reoxidation of the Fe(II)-complex to Fe(III)-complex occurs by contacting with O_2 (Eq. 5-2) (Deshmukh et al., 2013).

$$H_2S + 2Fe(III)L^{n-} \rightarrow S_{(S)} \downarrow + 2Fe(II)L^{n-} + 2H^+ \tag{5-1}$$

$$4Fe(II)L^{n-} + O_2 + 2H_2O \rightarrow 4Fe(III)L^{n-} + 2OH^- + 2H_2O_2 \tag{5-2}$$

where n denotes the charge of organic ligand L. The ligands employed are generally polyaminocarboxylic acids, such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) (Demmink & Beenackers, 1997). The oxidation of Fe(II) by O_2 can be accelerated by the presence of chelating agents (Harris & Aisen, 1973; Stumm & Lee, 1961). However, the regeneration of Fe(III)L complex by O_2 is still slow compared to its reduction in step one (Eq. 5-1), making the second step (Eq. 5-2) the rate limiting step in the desulfurization process (Demmink & Beenackers, 1997). For the oxidation of Fe(II)L by O_2, Brown and Mazarella (1987) proposed a four-step reaction mechanism illustrated in the following equations (Eqs. 5-3 to 5-5):

$$Fe(II)L + O_2 \xleftrightarrow{k_{-1}, k_1} Fe(III)L + {O_2}^{\bullet -} \tag{5-3}$$

$$Fe(II)L + {O_2}^{\bullet -} \overset{k_2}{\rightarrow} Fe(III)L + O_2^{2-} \tag{5-4}$$

$$2H_2O + 2Fe(II)L + O_2^{2-} \xrightarrow{fast} 2Fe(III)L + 4OH^- \tag{5-5}$$

The decrease of the concentration of Fe(II)L is expressed in the following equation (Eq. 5-6) by assuming the steady-state of the concentration of superoxide radical ($O_2^{\bullet -}$).

$$-\frac{d[Fe(II)L]}{dt} = \frac{4k_1k_2[O_2(soln)][Fe(II)L]^2}{k_{-1}[Fe(III)L]+k_2[Fe(II)L]} \tag{5-6}$$

The expression of the integrated rate is given in Eq. 5-7.

$$\frac{(k_{-1}-k_2)}{k_{-1}(1+R)} ln \frac{[Fe(II)L]}{[Fe(II)L]_0} + \frac{[Fe(II)L]_0-[Fe(II)L]}{[Fe(II)L]} = \frac{4k_2k_{eq}[O_2(soln)]}{(1+R)} t \tag{5-7}$$

The use of Fe(III)NTA as the best catalyst in the desulfurization process (Martell et al., 1996; Nassar et al., 2010; Ying et al., 2014) is limited by the degradation of the complex, which occurs through the reaction with hydroxyl radical ($^{\bullet}$OH) produced via the reaction of H_2O_2 (generated in Eq. 5-2) with Fe(II)L. This assumption was proven by McManus and Martell (1997), who added catalase to destroy H_2O_2 and significantly reduced the degradation rate of the ligand. Additional evidence of the generation of $^{\bullet}$OH was presented by Chen et al. (1995) based on the formation of *o*-, *m*-, and *p*-hydroxybenzoates from the reaction of benzoate and $^{\bullet}$OH. It is, therefore, of great significance to find a stable chelate towards $^{\bullet}$OH for the desulfurization process. It would be also very interesting to investigate the degradation of phenol in the desulfurization process based on the generation of $^{\bullet}$OH.

Polyphosphate chelating agents such as tripolyphosphate and tetrapolyphosphate (TPP) are capable of enhancing the production of $^{\bullet}$OH (Kachur et al., 1998; Wang et al., 2013). Biaglow and Kachur (1997) also demonstrated that for the polyphosphates, the most efficient chelation of Fe and generation of $^{\bullet}$OH occurred with TPP, which changed the reaction kinetics and stoichiometry of the maximal production of $^{\bullet}$OH. As a common food additive, TPP is safe and economically efficient for environmental applications (Wang et al., 2013). The research done by Safarzadeh-Amiria et al. (2016) showed that TPP was more stable than NTA in the desulfurization processes. For the purpose of this project, TPP was used to form complex with Fe(III) to catalyze the oxidation of H_2S.

Wang et al. (2013) demonstrated that the decrease of the redox potential of Fe(III/II) by combination with TPP was even more significant than EDTA. In the present study, the half-wave potential ($E_{1/2}$) of Fe(III/II)TPP was measured at different pHs. The relationship between $E_{1/2}$ and formal potential ($E^{0'}$) is shown in Eq. 5-8 (Ho et al., 2012; Schalley, 2007).

$$E_{1/2} = E^{0\prime} + \frac{RT}{2nF}\ln(\frac{D_{Red}}{D_{Ox}}) \tag{5-8}$$

where R is the gas constant (8.31 V·C/mol·K). T is the temperature (K). n denotes the number of electrons in an oxidation-reduction reaction. F is the Faraday constant (96485C·mol^{-1}). D denotes the diffusion coefficient (cm^2/s). $E_{1/2}$ is reported to be in coincidence with the formal potential because that the diffusion coefficients of oxidants can be considered as same as these of corresponding reductants (Schalley, 2007).

This is the first paper applying Fe(III)TPP as a catalyst for the oxidation of H_2S. Several parameters were studied, including 1) the formation of Fe(III)TPP-HS$^-$ by spectrophotometry; 2) the oxidation kinetics of Fe(II)TPP by O_2 at different pHs; 3) the values of $E_{1/2}$ of Fe(III/II)TPP; 4) the oxidation of HS$^-$ by Fe(III)TPP at pH 9 and the generation of Fe(II); 5) the rate constant of the direct reaction of Fe(III)TPP and HS$^-$; and 6) the degradation of phenol.

5.2 Materials and Methods

5.2.1 Reagents and solution preparation

All of the following chemicals were reagent grade and used as received. Sodium sulfide nonahydrate, iron(III) sulfate hydrate, iron(II) sulfate hydrate, sodium tetraborate decahydrate, sodium bicarbonate, hydrochloric acid, and potassium phosphate monobasic were purchased from Sigma Aldrich. Hydrogen sulfide measurement reagents 1 and 2 were purchased from HACH (Hach Company). Sodium tetrapolyphosphate was purchased from Zhong Ya Chemical (USA) Ltd. Sodium chloride was purchased from ACROS Organics. Potassium hydrogen phthalate and tris(hydroxymethyl)aminomethane were purchased from Alfa Aesar. Ammonium acetate was purchased from MP Biomedicals, LLC. 1,10-phenanthroline and sulfuric acid were purchased from Fisher Scientific Co. Canada. Acetic acid was purchased from Anachemia Canada Co.

A 0.1 M Fe(III)TPP (TPP:Fe = 2:1 mol ratio) stock solution was prepared by dissolving 0.01 mol TPP in 50 mL 18 MΩ MilliQ water (Millipore Corporation) and then slowly adding 0.0025 mol of $Fe_2(SO_4)_3$ into the solution. A 0.1 M Fe(III)NTA stock solution was prepared in the same way as Fe(III)TPP. A 0.5 M HS^- stock solution was prepared by dissolving 0.05 mol of sodium sulfide nonahydrate in 100 mL N_2-saturated MilliQ water. The pH of solutions was adjusted using 0.1 M NaOH and 0.1 M HCl.

The buffer solutions used were phthalate buffers at pHs 4.2, 5 and 5.9 (a mixture of 0.1 M potassium hydrogen phthalate and 0.1 M NaOH), Tris buffer at pH 7 (a mixture of 0.1 M Tris solution and 0.1 M HCl), and borate buffers at pHs 8 and 9 (a mixture of 0.05 M sodium tetraborate and 0.1 M HCl).

5.2.2 Analytical methods

Spectrophotometric measurements of sample spectra were done using a Varian Cary® 50 UV-Visible spectrophotometer. The spectrum of the mixture of Fe(III)L (L stands for TPP or NTA) with HS^- was obtained by adding HS^- stock solution into the Fe(III)L solution and scanning the mixture immediately. HACH DR 5000TM UV-Vis Spectrophotometer was used to measure the iron concentration using the 1.10-phenanthroline method at 510 nm (Standard Method for Examination of Water and Wastewater). HS^- was measured using the Methylene Blue Method 8131 with two specific sulfide measurement reagents from HACH. Phenol measurement was carried out using HPLC-UV at 270 nm (WatersTM 717 plus Autosampler, Waters 600-MS System Controller, and WatersTM 996 photodiode Array Detector). The column used for phenol analysis was Supelcosil LC-18, 5 μm, 250 mm×4.6 mm. The mobile phase was 40% acetonitrile and 60% 0.05% phosphoric acid (0.5 mL phosphoric acid in 1000 mL water). The injection volume was 50 uL. The total run time was 7.5 min.

Cyclic voltammetry was conducted with a Metrohm Autolab electrochemical workstation using a three-electrode system. Platinum, silver chloride and glass carbon electrodes were used as counter, reference and working electrodes, respectively. The electrolyte used in this study was 0.1 M NaCl. Scan rate was set at 1.2 V/s.

5.2.3 Measurement of the oxidation rate of Fe(II)TPP by O_2

The oxidation of Fe(II)TPP by O_2 was performed in 150 mL buffer solution in a 400-mL beaker on a magnetic stirrer (Thermo Scientific Stir S131125) at room temperature (21±0.5 °C). The mixing speed was set at 700 rpm. O_2 was supplied by a gas cylinder from Alphagaz™ and the test solutions were maintained O_2-saturated during the reaction. The reaction was initiated by adding 0.5 mM Fe(II)TPP (TPP:Fe = 2:1) into the test solution. Samples were taken at different time intervals (0.5 min, 1 min, 2 min, and 4 min) and analyzed for Fe(II).

5.2.4 HS^- oxidation and phenol degradation

The oxidation of HS^- (2 mM, 4 mM, 6 mM, and 8 mM) catalyzed by Fe(III)TPP was conducted in pH 9 borate buffer in a 125-mL Erlenmeyer flask under constant stirring (500 rpm). 0.5 mM Fe(III)TPP (TPP:Fe = 2:1) was added into the solution first and the reaction was initiated by the addition of HS^- (as NaHS) stock solution. Samples were taken at different time intervals (1, 2, 3, and 5 min) and analyzed for HS^- and Fe(II).

Phenol degradation experiments were conducted with 0.5 mM Fe(III)TPP (TPP:Fe = 2:1) and 0.1 mM phenol, and the reaction was initiated by the addition of 2, 4 and 8 mM HS^-. Samples were taken at 1, 5 min, then in 5 minute-intervals up to 50 minutes, and analyzed for phenol.

5.3 Results and Discussions

5.3.1 Formation of the Fe(III)L-HS^- intermediate

The absorbance of Fe(III)L and HS^- mixtures between 200-500 nm were measured and the results are given in **Figure 5-1**. Fe(III)TPP exhibited high absorbance below 230 nm, a plateau between 230 and 275 nm, a sharp falloff at 285 nm, and no absorbance above 350 nm. Fe(III)NTA had a high absorbance below 300 nm, a graduate decline between 300 to 400 nm, and no absorbance above 400 nm. The absorbance of the HS^- solution had sharp decrease between 260 and 280 nm with practically no absorbance above 290 nm. Adding HS^- to both Fe(III)TPP and Fe(III)NTA solutions changed their absorbance significantly, especially above

300 nm where the original solutions showed no absorption. Similar results were obtained by Safarzadeh-Amiria et al. (2016).

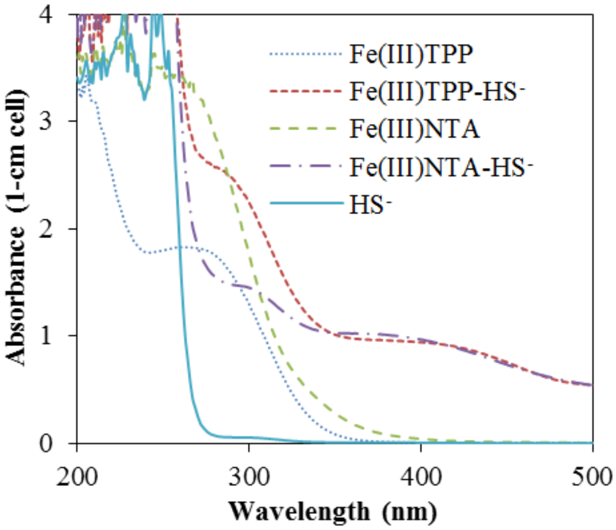


Figure 5-1. Spectra of the mixture of Fe(III)L and 1 mM HS^- at pH 9 ($[Fe(III)]_0$ = 0.5 mM, $[L:Fe]_0$ = 2:1, and L stands for TPP or NTA).

Research done by previous researchers (Demmink & Beenackers, 1998; Koch et al., 1986; Lonergan et al., 1995; Neyaglov et al., 1991; Philip & Brooks, 1974) indicated the generation of a meta stable ferric sulfide complex $Fe(III)L^{n-}(HS^-)$ in the direct reaction of $Fe(III)L^{n-}$ and HS^-, whose formation follows Eq. 5-9.

$$Fe(III)L^{n-} + \mathrm{HS}^- \leftrightarrow Fe(III)L^{n-}(HS^-) \tag{5-9}$$

According to Eq. 5-9, the direct reaction of Fe(III)TPP or Fe(III)NTA and HS^- (predominant at pH > 7) formed the Fe(III)L-HS^- complex, which explained the high absorbance above 300 nm. Similar intermediates were reported for the reaction of sulfide and $Fe(OH)_3$ precipitates by Dos Santos Afonso and Stumm (1992) and Yao and Millero (1996). The formation of the intermediates was also proposed for the ferric chelates of EDTA, hydroxyethylenediaminetriacetic aicd (HEDTA), diethylenetriaminepentaacetic acid (DTPA) and ethylene bis(oxyethyleneitrilo)tetraacetate (EGTA) (DeBerry et al., 1991; Wubs & Beenackers, 1994).

5.3.2 Half-wave potential of Fe(III/II)TPP

The efficiency of the desulfurization process depends mainly on the electron transfer capability of the iron-complexes, which is closely related to their reduction potential (also known as redox potential) (DeBerry, 1997; DeBerry, 1993). In the desulfurization process, iron complexes should have high enough redox potential to oxidize H_2S and low enough potential to be oxidized by oxygen, i.e., $E_{S/H_2S} < E_{Fe(III/II)L} < E_{O_2/H_2O}$, which is -0.21 V < $E_{Fe(III/II)L}$ < 0.59 V according to the study done by Ying et al. (2014).

The cyclic voltammograms of the $E_{1/2}$ of Fe(III/II)TPP in pH 4 to pH 9 buffer solutions are shown in **Figure 5-2**. The values of $E_{1/2}$ were calculated by taking the average of the potentials at the oxidation and reduction peaks marked with red circles, then referring them (by adding 236 mV to $E_{1/2}$) to standard hydrogen electrode (SHE). The $E_{1/2}$ value was 0.061 V, -0.014 V, -0.039 V, -0.064 V, -0.089 V, and -0.139 V (vs. SHE) at pH 4, 5, 6, 7, 8, and 9, respectively. Wang et al. (2013) reported a redox potential value of Fe(III/II)TPP as -0.099 V (vs. SHE) without pH adjustment.

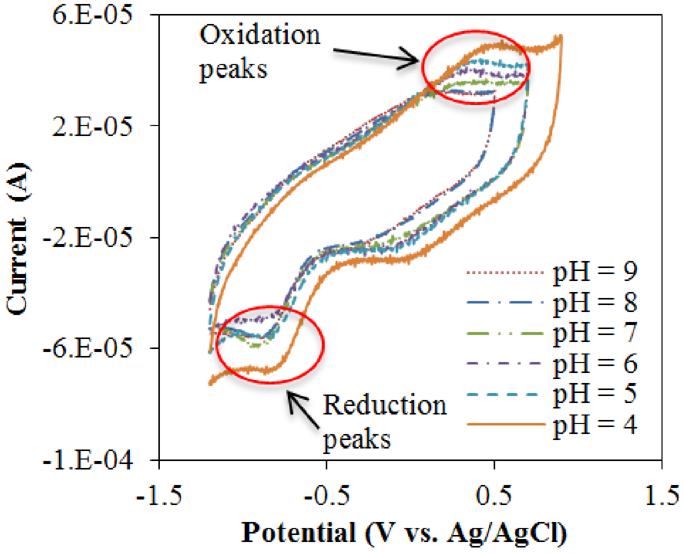


Figure 5-2. Cyclic voltammograms of Fe(III)TPP at pH 4-9 (V vs. Ag/AgCl) ($[Fe(III)]_0$ = 1 mM and $[TPP:Fe]_0$ = 2:1).

The $E_{1/2}$ value of Fe(III/II)TPP decreased with the increase of pH, which agrees well with the observation in a Fe(III/II)EDTA system reported previously (Shimizu et al., 2007). The dependence of the $E_{1/2}$ value on pH was due to the different iron hydroxide complexes formed at different pH (Shimizu et al., 2007), as well as due to the electrochemical reduction of Fe(III)(OH)L, shown in Eq. 5-10 (Bard & Faulkner, 1980; Shimizu et al., 2007).

$$Fe(III)(OH)L + e^- \rightarrow Fe(II)L + OH^- \tag{5-10}$$

The chelation of iron by TPP decreased the redox potential of Fe(III/II), making the oxidation of Fe(II) by O_2 more thermodynamically favorable compared to the free ion (Biaglow & Kachur, 1997). With the redox potential in a range of -0.139V to 0.061V, the chelation of iron by TPP makes the complex suitable for the oxidation of HS^-.

5.3.3 Oxidation of Fe(II)TPP by O_2

The oxidation rate of Fe(II)TPP in O_2-saturated solutions at different pHs was determined by measuring the rate of disappearance of Fe(II) (**Figure 5-3**a-f). The reaction rates between Fe(II)TPP and O_2 were calculated using time, concentrations of ferrous and ferric ion, the redox potential of the species, and the results are given in **Table 5-1**. Details of the calculation method and the reaction mechanism were described by Brown and Mazzarella (1987). The R-squared values (R^2) of the trend lines in **Figure 5-3**a-f were between 98.9% and 99.9%, indicating that the data followed a linear regression, which agrees very well with the linear relationship described in the literature (Brown & Mazzarella, 1987).

The parameters calculated were: k_{eq} (equilibrium constant), first-order constant k_{obs} (observed rate constant), and the second-order rate constants k_1, k_{-1}, and k_2 in Eqs. 5-3 and 5-4.

k_{eq} was calculated according to Eq. 5-11.

$$log k_{eq} = \frac{nF(E_{Ox} - E_{Red})}{RT} \tag{5-11}$$

where n denotes the number of electrons in an oxidation-reduction reaction; E_{Ox} and E_{Red} are the redox potentials of the oxidant ($O_2^{\bullet -}$ in this case) and reductant (Fe(II)TPP), respectively.

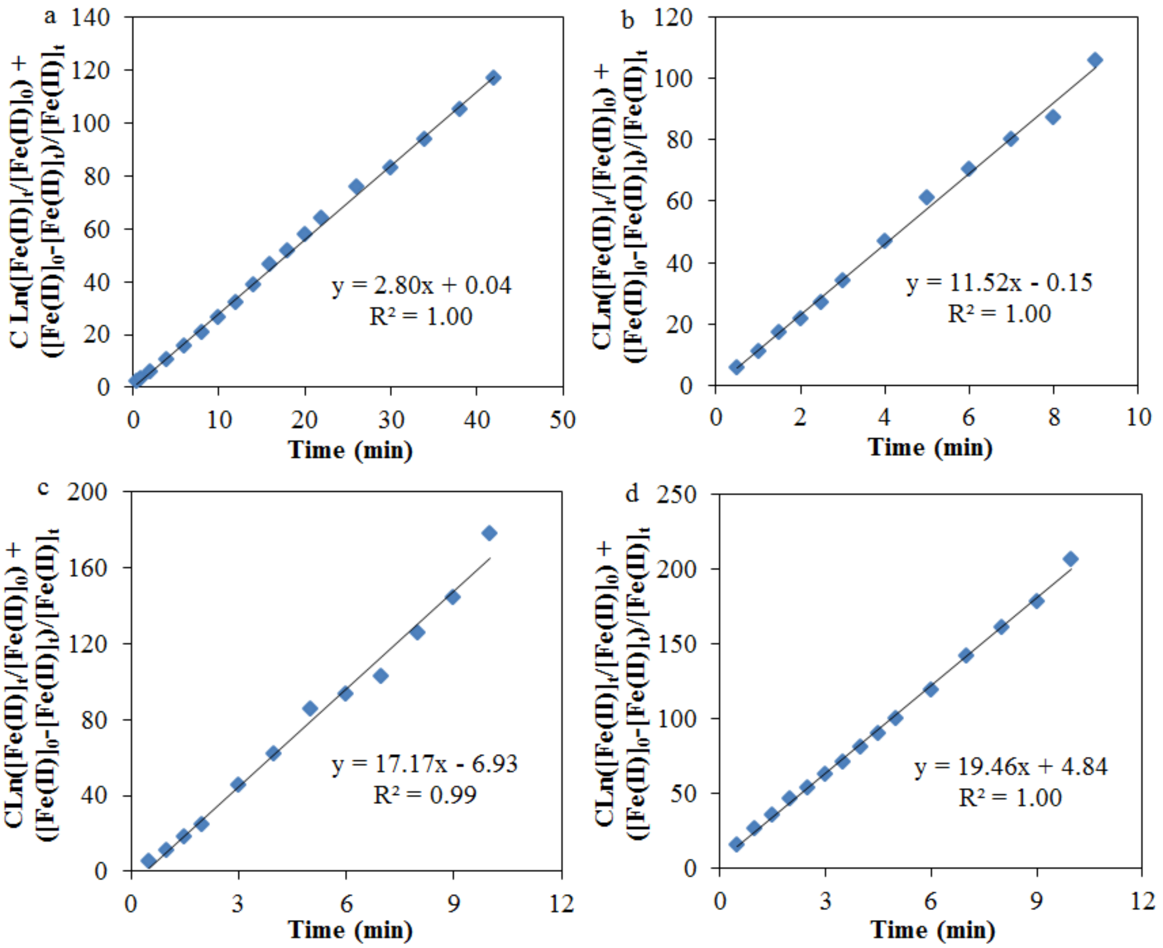


Figure 5-3. Kinetics of Fe(II)TPP oxidation by O_2 in a) pH 4.2 phthalate buffer, b) pH 5 phthalate buffer, c) pH 5.9 phthalate buffer, and d) pH 7 Tris buffer ($[Fe(II)]_0 = 0.5$ mM and $[TPP:Fe]_0 = 2:1$). C denotes the in-term coefficient $(k_{-1}-k_2)/k_{-1}(1+R)$ in Eq. 5-7.

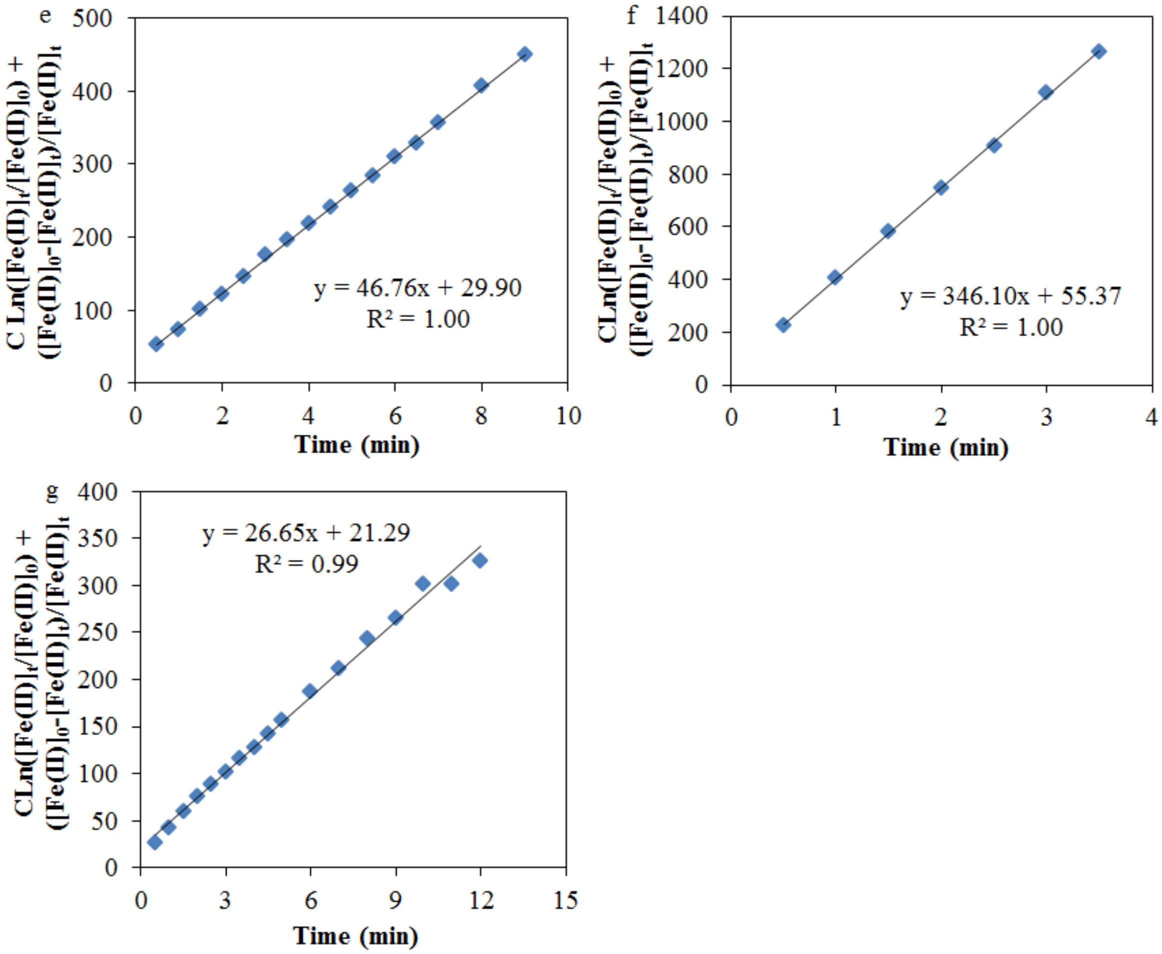


Figure 5-3 (concluded). Kinetics of Fe(II)TPP oxidation by O_2 in e) pH 8 borate buffer, f) pH 9 borate buffer ($[Fe(II)]_0 = 0.5$ mM and $[TPP{:}Fe]_0 = 2{:}1$), and g) pH 7 Tris buffer with the addition of extra Fe(III)TPP ($[Fe(II)]_0 = [Fe(III)]_0 = 0.5$ mM and $[TPP{:}Fe]_0 = 2{:}1$). C denotes the in-term coefficient $(k_{-1}-k_2)/k_{-1}(1+R)$ in Eq. 5-7.

Table 5-1. Kinetic parameters for the oxidation of Fe(II)TPP by O_2 at different pH ($[Fe(II)TPP]_0$ = 0.5 mM and $[TPP:Fe]_0$ = 2:1).

Buffers	**pH**	**10^2 K_{eq}**	**k_{obs} (s^{-1})**	**10^{-4} k_2 ($M^{-1}s^{-1}$)**	**10^{-3} k_{-1} ($M^{-1}s^{-1}$)**	**k_1 ($M^{-1}s^{-1}$)**
Phthalate	4.2	0.11	0.036±0.007	0.71±0.14	2.77±0.25	2.91±0.26
	5	0.48	0.17±0.013	0.76±0.056	2.50±0.032	12.02±0.15
	5.9	0.90	0.31±0.004	0.75±0.010	1.49±0.050	13.37±4.45
Tris	7	2.37	0.41±0.035	0.38±0.043	0.11±0.0005	2.72±0.012
Borate	8	6.29	0.67±0.068	0.22±0.023	0.031±0.001	1.92±0.08
	9	44.12	5.68±0.049	0.27±0.007	0.022±0.002	9.82±1.03

Notes: $K_{eq} = k_1/k_{-1}$, $k_{obs} = \frac{4k_2K_{eq}[O_2(soln)]}{(1+R)}t$.

The results showed that k_{obs} increased with increasing pH, indicating the promoting effect of high pH values on the reaction between Fe(II)TPP and O_2. Stumm and Lee (1961) reported a 100-fold increase in the oxidation rate of Fe(II) for an increase of one pH unit. The k_1 value was independent of pH, which agrees with the study about Fe(II)PDTA conducted by Brown and Mazzarella (1987). The decrease of $E_{1/2}$ of Fe(III/II)TPP with increasing pH made the reduction of Fe(III)TPP to Fe(II)TPP by $O_2^{\bullet-}$ more difficult at high pH, and that explained the decrease of k_{-1} value with increasing pH. The value of k_2 slightly decreased with increasing pH, which was in coincidence with Brown and Mazzarella (1987) about the oxidation of Fe(II)PDTA. The addition of Fe(III)TPP (or TPP) into the Fe(II)TPP solution did not affect the oxidation rate of Fe(II)TPP by O_2, as shown in **Figure 5-3**g, which lies in agreement with the study conducted by Sada et al. (1987).

5.3.4 Oxidation of HS^- by Fe(III)TPP and generation of Fe(II)

The oxidation rate of HS^- by Fe(III)TPP was investigated under O_2-saturated conditions in the borate buffer solution at pH 9. H_2S exists in the main form of HS^- at this pH. The time profile of the blank sample (HS^- at 8 mM) confirmed that the evaporation and oxidation of HS^-

by O_2 with a rate constant of 1.5×10^{-3} $M^{-1}s^{-1}$ (Resch et al., 1989) were negligible under these conditions (see the blank in **Figure 5-4**a). Four different doses of HS^- (2, 4, 6, and 8 mM) were investigated in the presence of 0.5 mM Fe(III)TPP. For 2 and 4 mM HS^-, the removal of HS^- by Fe(III)TPP was very fast in the first 20 min. The HS^- concentration decreased to 0.24 mM and to 0.76 mM for 2 mM and 4 mM HS^-, respectively. The HS^- removal became slower as the reaction proceeded, and its concentration decreased from 0.24 to 0.16 mM for 2 mM HS^- and from 0.76 to 0.40 mM for 4 mM HS^- in the following 30 min. For 6 and 8 mM HS^-, the removal of HS^- was in the first-order dependency of HS^- during the reaction period. Explanations for the dependency can be found in the following discussion in this Section and Section 5.3.5. At 50 minutes, 91.8%, 90.2%, 88.5% and 85.7% of HS^- were removed for the initial doses of 2, 4, 6, and 8 mM, respectively (**Figure 5-4**a). The generation of Fe(II) in this process is shown in **Figure 5-4**b. For 2 mM HS^-, the generation of Fe(II) increased from 0 mM at 0 min to 0.31 mM at 7 min, and then decreased in the following 20 min to 0.05 mM and to 0.018mM at 50 min. For 4 mM HS^-, the Fe(II) concentration increased from 0 mM at 0 min to 0.33 mM at 9 min, and this concentration was stable for the following 20 min, and then decreased quickly to 0.11 mM at 50 min. For 6 and 8 mM HS^-, the Fe(II) concentration was stable at 0.33 mM over 50 min. A more detailed plot of **Figure 5-4**b for the first 10 min of the reaction is given in **Figure 5-5**. The constant Fe(II) concentration indicated that the reduction rate of Fe(III) to Fe(II) by HS^- and the oxidation rate of Fe(II) to Fe(III) by O_2 were equivalent. While, the decrease of Fe(II) concentration indicated that the reduction rate of Fe(III) was slower than the oxidation rate of Fe(II).

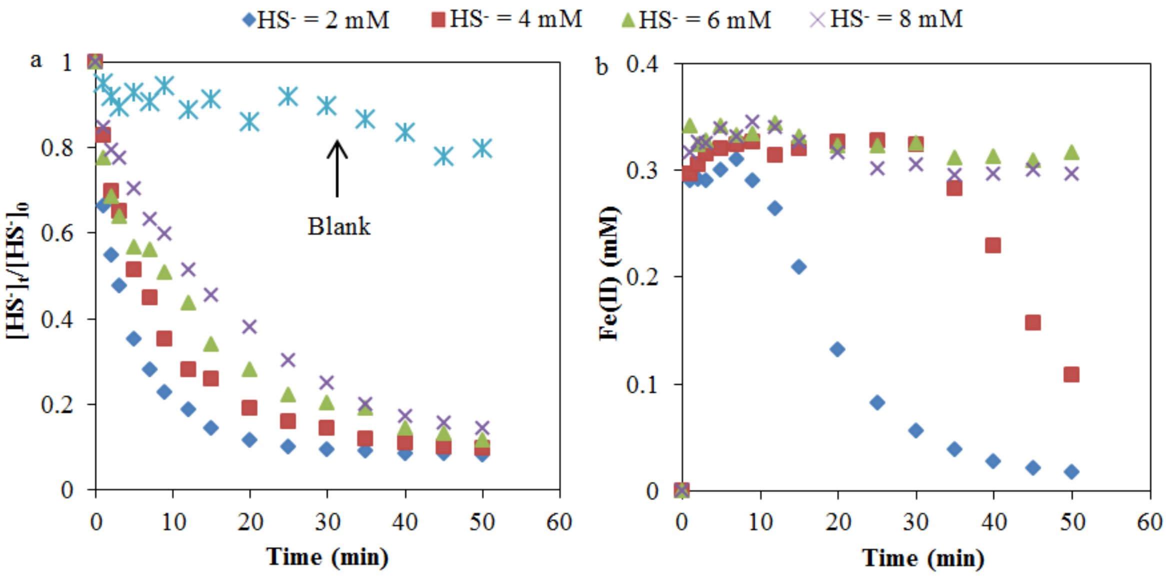


Figure 5-4. a) Oxidation of HS^- by Fe(III)TPP (HS^- dose for the blank was 8 mM) and b) Fe(II) generated in the reaction at pH 9 ($[Fe(III)]_0$ = 0.5 mM and $[TPP:Fe]_0$ = 2:1).

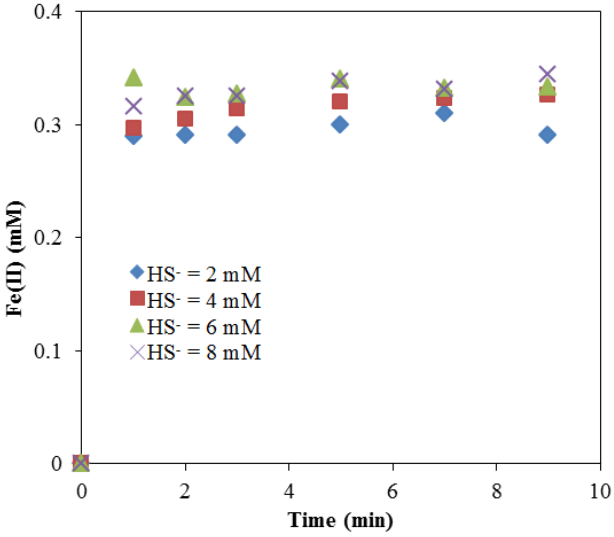


Figure 5-5. A detailed plot of **Figure 5-4**b for the first 10 minutes of the reaction.

Polysulfides (S_n^{2-}, n ≥ 2) are the main intermediates in the oxidation of HS^- by both O_2 (Chen & Morris, 1972; Petre & Larachi, 2007; Steudel, 1996) and ferric ion (Petre & Larachi, 2006; Petre & Larachi, 2007; Steudel, 1996) at neutral to alkaline pH. Therefore, polysulfides are expected to be the main intermediates in the reaction of HS^- and Fe(III)TPP. Due to the stronger nucleophility of polysulfides than HS^-, the substitution of HS^- by polysulfides in the reaction with Fe(III) (Petre & Larachi, 2007; Steudel, 1996) was considered as one reason for the gradually decreasing reaction rate. As mentioned in Section 5.3.1, the first step for the oxidation of H_2S was the generation of the Fe(III)TPP-HS^- complex through the reaction between Fe(III)TPP and H_2S expressed in Eq. 5-9. It was also the rate-limiting step, indicating the first-order dependency of the reaction rate on ferric chelate and HS^- (Philip & Brooks, 1974; Wubs & Beenackers, 1994). Thus, the degradation of HS^- by Fe(III)TPP can be described by Eq. 5-12.

$$-\frac{d[HS^-]}{dt} = k[Fe(III)TPP][HS^-] \tag{5-12}$$

Therefore, the decrease of the concentration of HS^- also accounted for the diminishing removal rate of HS^-.

5.3.5 Rate constant of the reaction between HS^- and Fe(III)TPP

As discussed in Section 5.3.4, the HS^- removal rate was in the first-order dependency of ferric chelate and HS^-, shown in Eq. 5-12, with k as the direct reaction rate between Fe(III)TPP and HS^-. For the HS^- dose of 6 mM and 8 mM, the concentration of Fe(II)TPP was constant at 0.33 mM throughout the whole reaction period, as shown in **Figure 5-4**b. As total iron concentration was 0.5 mM and Fe(II)TPP was 0.33 mM, the Fe(III)TPP concentration was 0.17 mM.

So, Eq. 5-12 was converted to Eq. 5-13.

$$-\frac{d[HS^-]}{dt} = 0.17k[HS^-] \tag{5-13}$$

Therefore, with a constant Fe(III)TPP concentration, the oxidation rate of HS$^-$ was in the first-order dependency on HS$^-$ concentration, with a slope of 0.17k. For HS$^-$ initial doses of 6 mM and 8 mM, the pseudo-first-order plots of HS$^-$ decomposition at pH 9 as a function of time are shown in **Figure 5-6**.

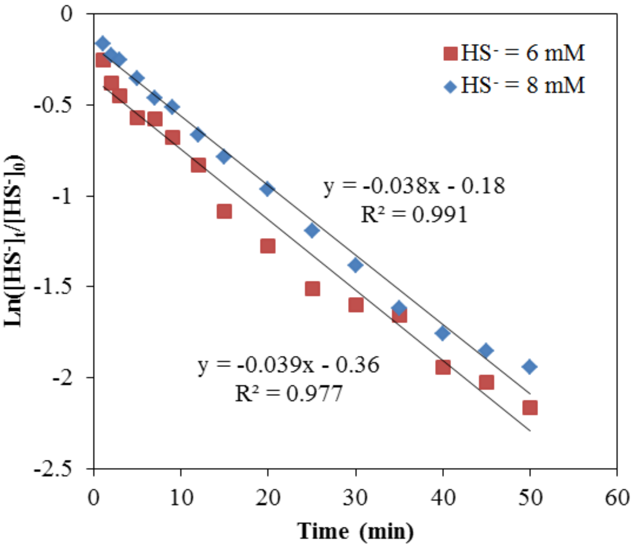


Figure 5-6. Pseudo-first-order plots of HS$^-$ decomposition as a function of time ($[Fe(III)]_0$ = 0.5 mM and $[TPP:Fe]_0$ = 2:1).

The rate constant k of the reaction between HS$^-$ and Fe(III)TPP was calculated by dividing the slope with -0.17. In the case of 6 mM HS$^-$, the slop of the line in **Figure 5-6** was -0.039; therefore, -0.17k = -0.039. Including the unit, the equation was converted to -0.17 mM·k = -0.039 min^{-1}, so k = 0.23 mM^{-1}min^{-1} = 3.83 M^{-1}s^{-1}. For 8 mM HS$^-$, k was calculated in the same way as for 6 mM HS$^-$, and obtained as 3.73 M^{-1}s^{-1}. By taking the average of the values at 6 mM HS$^-$ (3.83 M^{-1}s^{-1}) and 8 mM HS$^-$ (3.73 M^{-1}s^{-1}), the final rate constant k was 3.78 ± 0.032 M^{-1}s^{-1}. Therefore, the direct reaction rate between Fe(III)TPP and HS$^-$ was 3.78 ± 0.032 M^{-1}s^{-1} under the experimental conditions.

5.3.6 Degradation of phenol

To investigate the degradation of phenol (0.1 mM) in the oxidation of HS^- by Fe(III)TPP, a dose of Fe(III)TPP (Fe:TPP = 2:1) of 0.5 mM, and 3 different HS^- doses of 2 mM, 4 mM and 8 mM were applied. For 2 mM, 4 mM and 8 mM HS^-, phenol removal increased from 0 to 10%, 15% ,and 12% in the first 1 minute, respectively, and then the removal was constant for the rest of the reactions, indicating no further reaction, as shown in **Figure 5-7**.

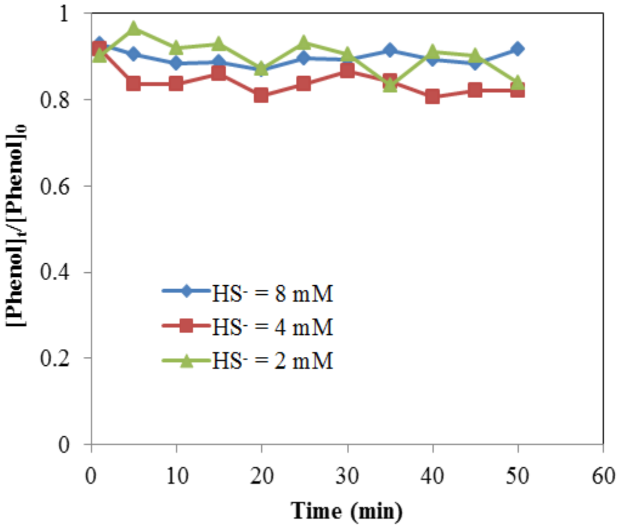


Figure 5-7. Phenol degradation in the desulfurization Fenton process ($[Fe(III)]_0$ = 0.5 mM and $[TPP:Fe]_0$ = 2:1).

The generation of $^{\bullet}OH$ in the reaction of Fe(II)TPP and H_2O_2 is given in Eq. 5-14.

$$Fe(II)TPP + H_2O_2 \rightarrow Fe(III)TPP + OH^- + {}^{\bullet}OH \tag{5-14}$$

Therefore, the degradation of phenol by $^{\bullet}OH$ in the oxidation of HS^- by Fe(III)TPP was expected. However, all three doses of HS^- delivered low removal of phenol (10% for 2mM, 15% for 4 mM, and 12% for 8mM). The low degradation of phenol can be explained by: 1) the low generation rate of $^{\bullet}OH$ due to the low production rate of H_2O_2; 2) competition of $^{\bullet}OH$ between phenol (1.4×10^{10} $M^{-1}s^{-1}$ (De et al., 1999; Land & Ebert, 1967)) and the other species, such as HS^- and H_2O_2. The reactions of $^{\bullet}OH$ with HS^- and H_2O_2 are given in Eqs. 5-15 and 5-16, with a second-order constant of 5.4×10^{9} $M^{-1}s^{-1}$ (Mills et al., 1987; Resch et al., 1989) and 2.7×10^{7} $M^{-1}s^{-1}$ (De Laat & Gallard, 1999; Gallard & De Laat, 2000; Huang et al., 2013), respectively; and 3) the consumption of H_2O_2 by HS^- (0.25 $M^{-1}s^{-1}$ (Resch et al., 1989)), given in Eq. 5-17.

$$HS^- + {}^{\bullet}OH \rightarrow \mathrm{HS}^{\bullet} + OH^- \tag{5-15}$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \tag{5-16}$$

$$H_2O_2 + 2HS^- \rightarrow 2\mathrm{HS}^{\bullet} + 2OH^- \tag{5-17}$$

The results showed that, although possible in theory, this process has low efficiency in the phenol degradation. It would be useful for phenol removal if some H_2O_2 was added to increase the amount of $^{\bullet}OH$.

5.4 Conclusions

Fe(III)TPP was applied as a catalyst for the oxidation of HS^- for the first time. The formation of an intermediate complex of Fe(III)TPP-HS^- in the reaction of Fe(III)TPP and HS^- was confirmed by spectrophotometry. Half-wave potentials of Fe(III/II)TPP at different pHs were measured in a three-electrode system, and the potential values confirmed that the complex is suitable for the desulfurization process. It was proved that the oxidation of Fe(II)TPP by O_2 follows a four-step mechanism proposed by previous researchers, and the reaction kinetic parameters at different pHs were calculated and provided. The oxidation of HS^- by Fe(III)TPP was investigated at pH 9 and the rate constant was reported for the first time. The degradation of phenol in the process was studied, and no significant phenol removal was observed. This study provided valuable information about the application of TPP as a potential chelating agent for the oxidation of HS^-. More studies need to be conducted on the reaction mechanisms and kinetics, especially on the generation of radicals in the process.

5.5 References

Alcántara, S., Velasco, A., Muñoz, A., Cid, J., Revah, S., & Razo-Flores, E. (2004). Hydrogen sulfide oxidation by a microbial consortium in a recirculation reactor system: sulfur formation under oxygen limitation and removal of phenols. *Environmental Science & Technology, 38*(3), 918-923.

Arana, J., Rendón, E. T., Rodrıguez, J. D., Melián, J. H., Dıaz, O. G., & Pena, J. P. (2001). Highly concentrated phenolic wastewater treatment by the Photo-Fenton reaction, mechanism study by FTIR-ATR. *Chemosphere, 44*(5), 1017-1023.

Bard, A. J., & Faulkner, L. R. (1980). Electrochemical methods: fundamentals and applications (Vol. 2): Wiley, New York.

Biaglow, J. E., & Kachur, A. V. (1997). The generation of hydroxyl radicals in the reaction of molecular oxygen with polyphosphate complexes of ferrous ion. *Radiation Research, 148*(2), 181-187.

Brown, E., & Mazzarella, J. (1987). Mechanism of oxidation of ferrous polydentate complexes by dioxygen. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 222*(1), 173-192.

Chen, D., Martell, A. E., & McManus, D. (1995). Studies on the mechanism of chelate degradation in iron-based, liquid redox H_2S removal processes. *Canadian Journal of Chemistry, 73*(2), 264-274.

Chen, K. Y., & Morris, J. C. (1972). Kinetics of oxidation of aqueous sulfide by oxygen. *Environmental Science & Technology, 6*(6), 529-537.

De, A. K., Chaudhuri, B., Bhattacharjee, S., & Dutta, B. K. (1999). Estimation of OH radical reaction rate constants for phenol and chlorinated phenols using UV/H_2O_2 photo-oxidation. *Journal of Hazardous Materials, 64*(1), 91-104.

De Laat, J., & Gallard, H. (1999). Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modeling. *Environmental Science & Technology, 33*(16), 2726-2732.

DeBerry, D. (1997). Chemical evolution of liquid redox processes. *Environmental Progress, 16*(3), 193-199.

DeBerry, D. W. (1993). Rates and mechanisms of reaction of hydrogen sulfide with Iron chelates. *Topical Report. Gas Research Institute.*

DeBerry, D. W., Petrinec, B., & Trofe, T. (1991). New insights from investigation of fundamental mechanism of liquid redox chemistry. Paper presented at the Liquid Redox Sulfur Recovery Conference, Texas.

DeLeon, E. R., Stoy, G. F., & Olson, K. R. (2012). Passive loss of hydrogen sulfide in biological experiments. *Analytical Biochemistry, 421*(1), 203-207.

Demmink, J., & Beenackers, A. (1997). Oxidation of ferrous nitrilotriacetic acid with oxygen: A model for oxygen mass transfer parallel to reaction kinetics. *Industrial & Engineering Chemistry Research, 36*(6), 1989-2005.

Demmink, J., & Beenackers, A. (1998). Gas desulfurization with ferric chelates of EDTA and HEDTA: new model for the oxidative absorption of hydrogen sulfide. *Industrial & Engineering Chemistry Research, 37*(4), 1444-1453.

Deshmukh, G. M., Shete, A., & Pawar, D. M. (2013). Oxidative absorption of hydrogen sulfide using an iron-chelate based process: chelate degradation. *Journal of Chemical Technology And Biotechnology, 88*(3), 432-436.

Dos Santos Afonso, M., & Stumm, W. (1992). Reductive dissolution of iron(III)(hydr) oxides by hydrogen sulfide. *Langmuir, 8*(6), 1671-1675.

Doujaiji, B., & Al-Tawfiq, J. A. (2010). Hydrogen sulfide exposure in an adult male. *Annals of Saudi Medicine, 30*(1), 76-80.

Environment Canada. (1998). Canadian water quality guidelines for phenols. Ottawa, Canada: Unpub.

Gallard, H., & De Laat, J. (2000). Kinetic modelling of Fe(III)/H_2O_2 oxidation reactions in dilute aqueous solution using atrazine as a model organic compound. *Water Research, 34*(12), 3107-3116.

Harris, D. C., & Aisen, P. (1973). Facilitation of Fe(II) antoxidation by Fe(III) complexing agents. *Biochimica et Biophysica Acta (BBA)-General Subjects, 329*(1), 156-158.

Ho, J., Coote, M. L., Cramer, C. J., & Truhlar, D. G. (2012). Theoretical calculation of reduction potentials. *Organic Electrochemistry, 5*.

Huang, W. Y., Brigante, M., Wu, F., Mousty, C., Hanna, K., & Mailhot, G. (2013). Assessment of the Fe(III)–EDDS complex in Fenton-like processes: from the radical formation to the degradation of bisphenol A. *Environmental Science & Technology, 47*(4), 1952-1959.

Kachur, A. V., Tuttle, S. W., & Biaglow, J. E. (1998). Autoxidation of ferrous ion complexes: a method for the generation of hydroxyl radicals. *Radiation Research, 150*(4), 475-482.

Koch, S., Ackermann, G., & Schülller, K. (1986). Über ternäre komplexe mit aminopolycarbonsäuren and sulfid. *Zeitschrift Für Chemie, 26*, 339.

Land, E., & Ebert, M. (1967). Pulse radiolysis studies of aqueous phenol. Water elimination from dihydroxycyclohexadienyl radicals to form phenoxyl. *Transactions of the Faraday Society, 63*, 1181-1190.

Lonergan, M., Lieberman, M., & Lewis, N. (1995). Mechanistic studies of redox sensors for the liquid redox process. Paper presented at the GRI Sulfur Recovery Conference, Austin, Texas.

Marine, N. (1999). Canadian Water Quality Guidelines for the Protection of Aquatic Life. *Canadian Council of Ministers of the Environment, Winnipeg*, 1-5.

Martell, A. E., Motekaitis, R. J., Chen, D., Hancock, R. D., & McManus, D. (1996). Selection of new Fe(III)/Fe(II) chelating agents as catalysts for the oxidation of hydrogen sulfide to sulfur by air. *Canadian Journal of Chemistry, 74*(10), 1872-1879.

McManus, D., & Martell, A. E. (1997). The evolution, chemistry and applications of chelated iron hydrogen sulfide removal and oxidation processes. *Journal of Molecular Catalysis A: Chemical, 117*(1), 289-297.

Mills, G., Schmidt, K., Matheson, M., & Meisel, D. (1987). Thermal and photochemical reactions of sulfhydryl radicals. Implications for colloid photocorrosion. *Journal of Physical Chemistry, 91*(6), 1590-1596.

Nassar, N. N., Husein, M. M., & Pereira-Almao, P. (2010). Ultradispersed particles in heavy oil: Part II, sorption of H 2 S (g). *Fuel Processing Technology, 91*(2), 169-174.

Neyaglov, A., Digurov, N., Bukharkina, T., Mazgarov, A., & Fakhriev, A. (1991). Kinetics and reaction mechanism of the liquid-phase oxidation of hydrogen sulfide by a chelate complex of trivalent iron (Fe^{3+} $EDTA^-$). *Kinetics and Catalysis, 32*(3), 485-489.

Olson, K. R. (2005). Vascular actions of hydrogen sulfide in nonmammalian vertebrates. *Antioxidants & Redox Signaling, 7*(5-6), 804-812.

Petre, C. F., & Larachi, F. (2006). Reaction between hydrosulfide and iron/cerium (hydr) oxide: Hydrosulfide oxidation and iron dissolution kinetics. *Topics in Catalysis, 37*(2-4), 97-106.

Petre, C. F., & Larachi, F. (2007). Anoxic alkaline oxidation of bisulfide by Fe/Ce oxides: Reaction pathway. *AI Ch. E. Journal, 53*(8), 2170-2187.

Philip, C., & Brooks, D. W. (1974). Iron(III) chelate complexes of hydrogen sulfide and mercaptans in aqueous solution. *Inorganic Chemistry, 13*(2), 384-386.

Resch, P., Field, R. J., Schneider, F., & Burger, M. (1989). Reduction of methylene blue by sulfide ion in the presence and absence of oxygen: simulation of the methylene blue-O_2-HS^- CSTR oscillations. *The Journal of Physical Chemistry, 93*(25), 8181-8186.

Sada, E., Kumazawa, H., & Machida, H. (1987). Oxidation kinetics of Fe^{II}-EDTA and Fe^{II}-NTA chelates by dissolved oxygen. *Industrial & Engineering Chemistry Research, 26*(7), 1468-1472.

Safarzadeh-Amiria, A., Waltonb, J., Mahmouda, I., & Sharifia, N. (2016). Iron(III)-Polyphosphate Chelates, True Catalysts for the Liquid Redox Sulfur Recover Process. Trojan Technologies.

Schalley, C. A. (2007). Analytical methods in supramolecular chemistry. Winheim, Gemany: Wiley-VCH.

Shimizu, K., Hutcheson, R., Engelmann, M. D., & Cheng, I. F. (2007). Cyclic voltammetric and aqueous equilibria model study of the pH dependant iron(II/III) ethylenediamminetetraacetate complex reduction potential. *Journal of Electroanalytical Chemistry, 603*(1), 44-50.

Steudel, R. (1996). Mechanism for the formation of elemental sulfur from aqueous sulfide in chemical and microbiological desulfurization processes. *Industrial & Engineering Chemistry Research, 35*(4), 1417-1423.

Stumm, W., & Lee, G. F. (1961). Oxygenation of ferrous iron. *Industrial & Engineering Chemistry, 53*(2), 143-146.

Wang, L., Wang, F., Li, P., & Zhang, L. (2013). Ferrous-tetrapolyphosphate complex induced dioxygen activation for toxic organic pollutants degradation. *Separation and Purification Technology, 120*, 148-155.

Wubs, H. J., & Beenackers, A. (1994). Kinetics of absorption of hydrogen sulfide into aqueous ferric solutions of EDTA and HEDTA. *AI Ch. E. Journal, 40*(3), 433-444.

Yan, Q., Yu, D., Wang, Z., Zou, H., & Ruan, W. (2008). Phenol inhibition and restoration of the bioactivity of anaerobic granular sludge. *Applied Biochemistry and Biotechnology, 150*(3), 259-265.

Yao, W., & Millero, F. J. (1996). Oxidation of hydrogen sulfide by hydrous Fe(III) oxides in seawater. *Marine Chemistry, 52*(1), 1-16.

Ying, L., Youzhi, L., Guisheng, Q., Huidong, G., & Zhengfeng, Z. (2014). Selection of Chelated Fe(III)/Fe(II) Catalytic Oxidation Agents for Desulfurization Based on Iron Complexation Method. *China Petroleum Processing and Petrochemical Technology, 16*(2), 50-58.

6 COMPARISON OF NITRILOTRIACETIC ACID AND [S,S]-ETHYLENEDIAMINE-N,N'-DISUCCINIC ACID IN UV-CHELATES-MODIFIED FENTON PROCESSES ON THE TREATMENT OF OIL SANDS PROCESS-AFFECTED WATER AT NATURAL PH[5]

6.1 Introduction

Canada's oil sands deposits are one of the largest oil resources, with around 174 billion barrels of recoverable oil in form of bitumen (Alberta Energy and Utilities Board, 2005; Drzewicz et al., 2010). For the production of one m^3 of oil, between 2-4 m^3 of fresh water are used in the caustic hot water extraction and the subsequent upgrading process (Drzewicz et al., 2010; Moschopedis et al., 1977). The whole process leads to the generation of oil sands process-affected water (OSPW), which is highly saline and acutely toxic to aquatic organisms. Organic compounds in OSPW include unrecovered bitumen (oil and grease), naphthenic acids (NAs), polyaromatic hydrocarbons (PAH), BTEX (benzene, toluene, ethyl benzene, and xylenes), and other organic compounds such as fulvic and humic acids (Allen, 2008; Madill et al., 2001; Mohamed et al., 2011; Pourrezaei, 2013; Rogers et al., 2002). The toxicity of OSPW is primarily attributed to the presence of NAs, which have biological half-lives exceeding 13 years (Han et al., 2009). NAs are a group of aliphatic and alicyclic carboxylic acids with a general formula of $C_nH_{2n+z}O_x$, where n is the carbon number, x is equal to two for classical NAs (c-NAs) and three

---

[5] A version of this chapter will be submitted: Ying Zhang, Nikolaus Klamerth, Pamela Chelme-Ayala, & Mohamed Gamal El-Din. Comparison of nitrilotriacetic acid and [S,S]-ethylenediamine-N,N'-disuccinic acid in UV-chelates-modified Fenton processes on the treatment of oil sands process-affected water at natural pH. *Environmental Sicence & Technology*.

or more for oxidized NAs (oxy-NAs) formed after the oxidation of c-NAs (Kannel & Gan, 2012), and z (zero or a negative even integer) indicates the hydrogen deficiency due to the presence of rings or double bonds (Rogers et al., 2002). Advanced oxidation processes (AOPs) have been proposed as a complementary approach to the biological treatment of OSPW due to their ability to degrade recalcitrant NAs and reduce the overall toxicity of OSPW towards selected organisms (Fu et al., 2008; Scott et al., 2008b; Wang, 2011). Although Fenton and photo-Fenton processes are very common AOPs and have been applied to treat wastewaters (De la Cruz et al., 2012; Kušić et al., 2006), they have not been applied in the OSPW treatment, as a low pH is needed to prevent the precipitation of Fe.

Chelating agents have been employed to form complexes with iron to enable Fenton reaction at high pH (Klamerth et al., 2011; Lipczynska-Kochany & Kochany, 2008; Pignatello et al., 2006; Rastogi et al., 2009; Sun & Pignatello, 1992; Wang et al., 2013b; Xue et al., 2009). Aminopolycarboxylic acids (APCAs) are comprised of several carboxylate groups bound to one or more nitrogen atoms, and they can form very stable complexes with many di- or trivalent metallic ions (Bunescu et al., 2008). Nitrilotriacetic acid (NTA) and [S,S]-ethylenediamine-N,N'-disuccinic acid ([S,S]-EDDS) are the most common aminopolycarboxylic acids used in the modified Fenton processes nowadays. NTA has been reported by Sun and Pignatello (1992) as one of the most active chelates among 50 chelating agents for the decomposition of H_2O_2 and the degradation of 2,4-dichlorophenoxyactic acid. [S,S]-EDDS (for simplification, the abbreviation EDDS was used) as a structural isomer of ethylenediaminetetraacetic acid (EDTA) is biodegradable and environmentally safe compared to EDTA (Subramanian et al., 2011; Wu et al., 2014; Zhang et al., 2008). Its performance is equal to EDTA in most cases and even much better under specific conditions (Jones & Williams, 2001; Whitburn et al., 1999; Willkinson, 1998).

UV irradiation has been widely applied to increase the efficiency of the modified Fenton processes (Huang et al., 2012; Klamerth et al., 2013; Spuhler et al., 2010; Vermilyea & Voelker, 2009; Wei et al., 2014), due to its ability to reduce Fe(III)L to Fe(II)L (L denotes NTA or EDDS in this case) at high pH through Eq. 6-1. The main pathways of the radical generation in the UV-chelate-modified Fenton processes are shown in Eq. 6-2 and Eq. 6-3 (De Laat et al., 2011; Huang et al., 2013).

$$\mathrm{Fe(III)L} + hv \rightarrow \mathrm{Fe(II)} + L^{\bullet} \qquad (6\text{-}1)$$

$$\mathrm{Fe(II)L} + H_2O_2 \rightarrow \mathrm{Fe(III)L} + {}^{\bullet}OH + OH^{-} \qquad (6\text{-}2)$$

$$H_2O_2 + hv \rightarrow 2{}^{\bullet}OH \qquad (6\text{-}3)$$

APCAs alone do not absorb solar light above 250 nm, and their photolysis is negligible. The complexes APCAs form with iron have been reported to exist as monomeric or dimeric species in aqueous solution, absorb light up to 400 nm, and present rapid photochemical degradation under UV irradiation (Andrianirinaharivelo et al., 1993; Bunescu et al., 2008; Natarajan & Endicott, 1973). The photolysis of Fe(III)NTA was described in several previous articles (Abida et al., 2006; Bunescu et al., 2008; Trott et al., 1972). Fe(III)EDDS was also reported to be easily photolyzed at neutral pH and hydroxyl radical (${}^{\bullet}$OH) was produced during the photolysis (Huang et al., 2012; Wu et al., 2014). Therefore, the degradation of chelating agents is a major factor that needs to be considered in the application of UV-chelate-modified Fenton processes. To date, no research has compared NTA and EDDS in their physicochemical characteristics or the efficiency of the modified Fenton processes using these two agents.

In this study, the UV-NTA/EDDS-modified Fenton processes were applied on the treatment of OSPW for the first time. We investigated the half-wave potentials ($E_{1/2}$) of

Fe(III/II)NTA and Fe(III/II)EDDS at three different pH values (7, 8, and 9), the degradation of Fe(III)NTA and Fe(III)EDDS under UV irradiation in MilliQ water and in OSPW, and the efficiency of the UV-NTA/EDDS-Fenton processes on the removal of acid extractable organic fraction (AEF), aromatics and the overall toxicity of OSPW towards *Vibrio fischeri*. The removal of c-NAs and oxy-NAs in the UV-NTA-Fenton, UV-H_2O_2 and NTA-Fenton processes was also presented and compared.

6.2 Materials and Methods

6.2.1 Chemicals and stock solutions

NaOH, H_2O_2 (30%), $FeSO_4{\cdot}7H_2O$, 98% H_2SO_4, 1,10-phenanthroline, acetic acid, methylene chloride (DCM), and sodium acetate were purchased from Fisher Scientific Co. Canada. Nitrilotriacetic acid (99%) (NTA), ethylenediamine-N,N'-disuccinic acid (35% in water) (EDDS), bovine catalase, sodium tetraborate decahydrate, hydrochloric acid, dimethyl sulfoxide (DMSO), and optima methanol and acetonitrile were purchased from Sigma Aldrich. Tris(hydroxymethyl)aminomethane was purchased from Alfa Aesar. Titanium (IV) oxysulfate was purchased from Fluka Analytical. Filters used were 0.45 μm nylon membrane filters (GE Healthcare Life Sciences).

Raw OSPW with pH of 8.3 was collected from an active oil sands tailings pond in Fort McMurray, Alberta, Canada, and was stored at 4˚C prior to use. 0.048 M Fe(II) stock solution was prepared by dissolving $FeSO_4{\cdot}7H_2O$ in MilliQ water (Millipore Corporation) at pH 3 prior to Fenton reactions. 0.18 M NTA stock solution was prepared by dissolving NTA in MilliQ water at pH 4 (Abida et al., 2006). 0.18 M EDDS stock solution was prepared by diluting 35% EDDS solution.

6.2.2 UV irradiation test

UV irradiation experiments were conducted by placing a 100-mL beaker (5.4-cm diameter) with a 80 mL sample solution on a magnetic stirrer under a collimated beam UV apparatus (Model PSI-I-120, Calgon Carbon Corporation, Pittsburgh, PA, USA) equipped with a 1-kw medium-pressure (MP) Hg-lamp (Calgon Carbon, Pittsburgh, PA, USA) (**Figure 8-1**). The emission of the lamp was from 200 nm to 530 nm (**Figure 6-1**). NTA (or EDDS) and Fe(II) stock solution were added to form Fe-NTA (or Fe-EDDS) complex, afterwards H_2O_2 was added, and then the shutter of the warmed-up UV lamp was opened immediately. For the measurement of Fourier transform infrared (FT-IR) spectrum, ^{1}H nuclear magnetic resonance (NMR) spectrum, synchronous fluorescence spectrum (SFS), and toxicity towards *Vibrio fischeri*, samples were taken at 30 min and added drops of bovine catalase (1g/L) to destroy the excess of H_2O_2. Control experiments were conducted under UV irradiation only. Experiments were carried out in duplicates.

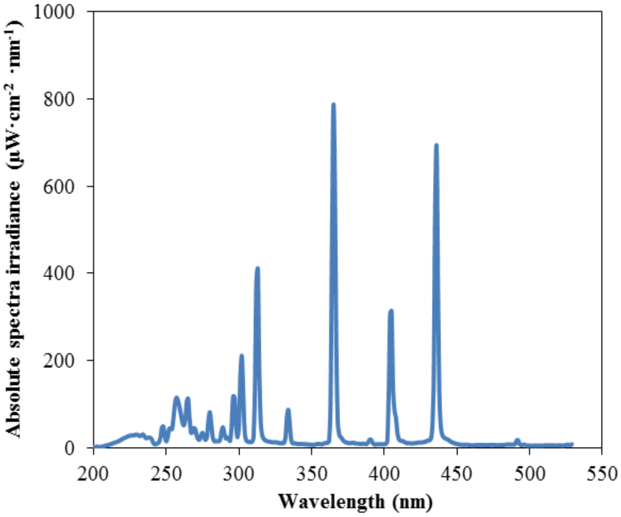


Figure 6-1. Absolute spectrum irradiance of the MP lamp.

6.2.3 Analytical methods

H_2O_2 was measured with titanium (IV) oxysulfate (DIN 38402H15) at 410 nm (Klamerth et al., 2011; Munoz et al., 1990) and Fe was measured with 1.10-phenanthroline (ISO 6332) at 510 nm (Klamerth et al., 2012) with photospectrometrical methods (GENESYS™ 10S UV-Vis spectrophotometer). pH was controlled with 0.1 M NaOH and 0.1 M H_2SO_4 using a pH meter (Fisher Scientific, AR 50). NTA and EDDS in the form of Fe(III)-complexes were analyzed by HPLC-UV (Agilent Technologies, 1260 Infinity) at 270 nm and 240 nm, respectively, with a column from Phenomenex (C18, 5 µm, 150 mm×4.6 mm). The mobile phase for NTA analysis consisted of 0.03 M sodium acetate, 0.002 M tetrabutylammonium bromide, and 5% methanol. The pH of the solution was adjusted to 2.78 using acetic acid. Flow rate was 0.8 mL/min. The EDDS analysis was performed with a mobile phase of a 10%/90% mixture of methanol and formate buffer (2 mM tetrabutylammonium hydrogen sulfate and 15 mM sodium formate) at a flow rate of 0.8 mL/min. The pH of the sodium formate solution was adjusted to 4 using formic acid.

Cyclic voltammetry was conducted with a Metrohm Autolab electrochemical workstation using a three-electrode system. Platinum electrode, silver chloride electrode, and glassy carbon electrode were used as counter, reference, and working electrodes, respectively. The electrolyte used in this study was 0.1 M NaCl. Scan rate was 1.2 V/s. The buffer solutions used were Tris buffer at pH 7 (a mixture of 0.1 M Tris solution and 0.1 M HCl), and borate buffers at pH 8 and pH 9 (a mixture of 0.05 M sodium tetraborate and 0.1 M HCl).

The measurement of metal ions in the OSPW was carried out in Perkin Elmer's Elan 6000. The instrument conditions were set at: ICP RF power of 1300 W; dual detector mode; subtract blank after internal standard correction; measurement units in cps (counts per second);

auto lens on; and Bi, Sc and In used as internal standards. The running conditions were: flow rate of 1 mL/min; and 35 sweeps/reading, 1 reading/replicate and 3 replicates, dwell times were 10 ms for Na, Al, K, Cu, Zn and Sr, and the others were 20 ms except Se (150 ms). The integration time was dwell time timing number sweeps (35 in this case), i.e. 350 ms for Al, K, Cu, Zn and Sr, 5250 ms for Se, and 700 ms for the others. The final results were the average of 3 replicates. Instrument conditions were: 4 points calibration curves (0, 0.25, 0.50, 1.00 ppm for Na, Ca, Mg, Fe, K and P, and 0, 0.005. 0.010, 0.020 ppm for rest elements); and typical count rates for 10 ppb Pb were 150000 cps to 200000 cps.

FT-IR spectra were obtained by using a PerkinElmer Spectrum 100 FT-IR Spectrometer (PerkinElmer Life and Analytical Sciences, Woodbridge, ON, CA). The protocol was described by Gamal El-Din et al. (2011) and Zhang et al. (2015). The 25 mL samples for FT-IR analysis were filtered with 0.45 μm nylon membrane filters. The pH of the samples was adjusted to 2.2. Then, the samples were extracted twice with 25 mL HPLC grade DCM and the extract was transferred to 50-mL glass tubes and evaporated to dryness. The residual in the tubes was reconstituted in 7 mL Optima grade DCM and injected into a KBr cell for analysis.

SFS were recorded in a Varian Cary Eclipse fluorescence spectrometer (Mississauga, ON, Canada). Excitation wavelengths were from 200 to 600 nm. Scanning speed was 600 nm/min. Photomultiplier (PMT) voltage was set at 800 mV.

NMR analysis was carried out in a 3-channel Agilent/Varian Unity Inova Spectrometer (Agilent Technologies, Santa Clara, CA, USA). The organic matters in the samples were extracted by HPLC grade DCM and the extract was evaporated overnight to dryness. Details of the preparation can be referred to the sample preparation for FT-IR analysis. The extract was reconstituted in 1 mL deuterated DMSO and transferred into NMR tubes with 5 mm outside diameter for analysis. Parameters for the analysis were: ^{1}H resonance frequency: 399.950 MHz; pw30 (i.e., 30 degree pulse): 3.3 ms; acquisition time: 5s; spectral width: 10000Hz or 25 ppm; transmitter offset: 989.9; and relaxation delay: 0.1 s. Data analysis was done in VNMRJ 4.2A software (Wang et al., 2016).

The analysis of NAs in an ultra-performance liquid chromatography (UPLC) can be referred to Wang et al. (2016). The column used for the chromatographic separation was a Waters UPLC Phenyl BEH column (1.7 µm, 150 mm×1 mm). Mobile phases were 10 mM ammonium acetate in water (A) and 10 mM ammonium acetate in 50/50 methanol/acetonitrile (B). Typically, the raw OSPW was injected and analyzed for quality control. The injection solution (1 mL) contained 0.5 mL sample, 0.1 mL of 4.0 mg/L internal standard (myristic acid-1-^{13}C) in methanol, and 0.4 mL methanol. A high-resolution time-of-flight mass spectrometer (TOF-MS, Synapt G2, Waters, Miford, MA, USA) was used to analyze samples with the electrospray ionization (ESI) at negative ion mode and TOF analyzer at high-resolution mode. Masslynx (Waters) and Targetlynx (Waters, Milford, MA, USA) were used to process data acquisition and data extraction from spectra, respectively. The quantification of each NA species based on its empirical formula $C_nH_{2n+z}O_x$ (x=2, 3, 4) was done by comparing its peak area with that of the internal standard. The chromatographic conditions were: 0-2 min, 1% B; 2-3 min, B increased from 1% to 60%; 3-7 min, B increased to 70%; 7-13 min, 95% B; 13-14 min, B decreased to 1% and was maintained at 1% to 20 min to equilibrate the column with a flow rate of 100 µL/min. The temperature of the column was set at 50 ºC and the sample was kept at 10 ºC.

The acute toxicity of the samples towards *Vibrio fischeri* was processed using Microtox® 81.9% screening test in a Microtox® 500 Analyzer by following the manufacturer's instructions. The toxicity (% inhibition effect) of the samples was calculated based on the change of the luminescence intensity. Reagent without inhibitors was used as a negative control to acquire the correction factor.

6.3 Results and Discussions

6.3.1 Half-wave potentials

Cyclic voltammograms of Fe(III/II)NTA and Fe(III/II)EDDS and the half-wave potentials ($E_{1/2}$) of these two complexes at pHs 7, 8 and 9 are included in **Figure 6-2**a and **Figure 6-2**b, respectively. These pH values were chosen due to fact that these are the most common pH values in modified Fenton processes. Potential values of Fe(III/II)NTA at pHs 7, 8, and 9 at the oxidation peaks were 200, 200, and 150 mV, respectively, and at the reduction peaks were -792, -900, and -1050 mV, respectively. Potential values of Fe(III/II)EDDS at pHs 7, 8, and 9 at the oxidation peaks were 650, 270, and 190 mV, respectively, and at the reduction peaks were -750, -820, and -840 mV, respectively. $E_{1/2}$ values were calculated by taking the average of the potentials at the oxidation and reduction peaks and referring the average potentials (by adding 236 mV to $E_{1/2}$) to the standard hydrogen electrode (SHE). The $E_{1/2}$ of Fe(III/II)NTA at pHs 7, 8 and 9 were -64, -114, and -214 mV (vs SHE), respectively, and the $E_{1/2}$ of Fe(III/II)EDDS at the same pH values were 186, -39, and -89 mV (vs SHE), respectively. A potential value of Fe(III/II)NTA at pH 8 was reported as -154 mV by Cuculić et al. (2005). Huang et al. (2013) reported a $E_{1/2}$ of Fe(III/II)EDDS of 69 mV at pH 6.2. Different experimental conditions, such as reference electrodes and electrolytes (static mercury drop electrode and 0.1 M $NaClO_4$ electrolyte in Cuculić et al's study and saturated calomel electrode and 0.05 M KCl electrolyte in Huang et al's study), might attribute to the difference of the potential values.

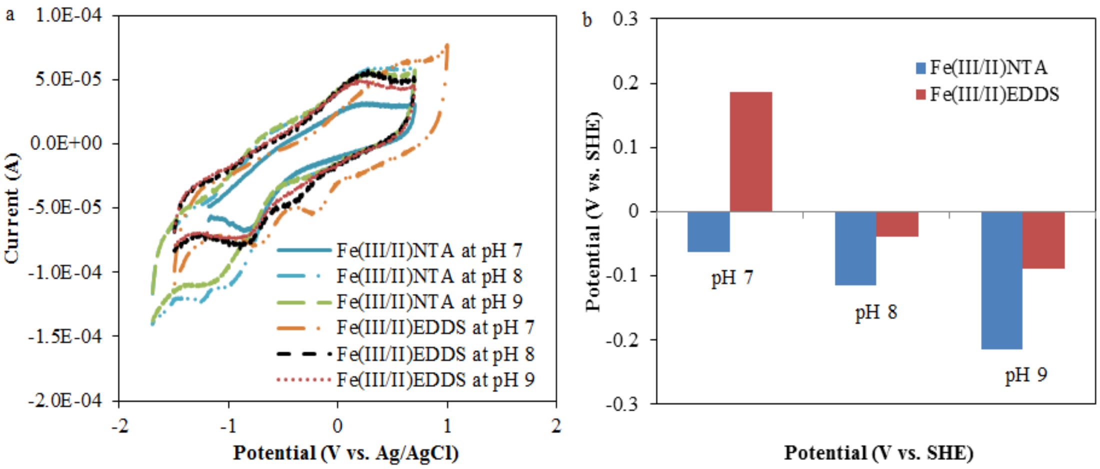


Figure 6-2. a) Cyclic voltammograms of Fe(III/II)NTA and Fe(III/II)EDDS and b) half-wave potentials of Fe(III/II)NTA and Fe(III/II)EDDS at pH 7, 8 and 9 ($[Fe]_0$ = 1mM and $[NTA]_0 = [EDDS]_0$ = 2 mM).

$HO_2^{\bullet}/O_2^{\bullet-}$ (with a pKa of 4.8) is mainly in the form of $O_2^{\bullet-}$ at high pH (Bielski et al., 1985; De Laat et al., 2011). Redox potentials of $O_2/O_2^{\bullet-}$ and $H_2O_2/O_2^{\bullet-}$ at pH 7 were reported as 70 and 360 mV, respectively (Rao & Hayon, 1975). Unfortunately, the redox potentials of these species at higher pHs (such as 8 and 9) are not available in the literature. By comparing the redox potentials of Fe(III/II)NTA (-64 mV) and Fe(III/II)EDDS (186 mV) at pH 7 with that of $H_2O_2/O_2^{\bullet-}$ (360 mV), it can be concluded that it is impossible for H_2O_2 to reduce Fe(III)NTA to Fe(II)NTA or Fe(III)EDDS to Fe(II)EDDS in the way shown in Eq. 6-4.

$$Fe(III)\mathrm{L} + H_2O_2 \rightarrow Fe(II)\mathrm{L} + HO_2^{\bullet}/O_2^{\bullet-} + H^+ \qquad (6\text{-}4)$$

This conclusion is in agreement with a previous report that H_2O_2 could not reduce complexed iron (Gutteridge et al., 1990; Melnyk et al., 1981; Wood, 1988), and the reduction of Fe(III)L is $O_2^{\bullet-}$-dependent not H_2O_2-dependent (Gutteridge et al., 1990). The redox potential of $O_2/O_2^{\bullet-}$ at pH 7 (70 mV) makes the radical capable of reducing Fe(III)EDDS to Fe(II)EDDS; however, incapable of reducing Fe(III)NTA to Fe(II)NTA in the way shown in Eq. 6-5.

$$Fe(III)L + HO_2^{\bullet}/O_2^{\bullet-} \rightarrow Fe(II)L + O_2 \qquad (6\text{-}5)$$

This hypothesis coincides with previous observation that no Fe(II) was detected in the NTA-Fenton process at pHs 7 and 8 (Dao & De Laat, 2011; Zhang et al., 2016b). Nonetheless, the regeneration of Fe(II) was observed in the EDDS-Fenton process at pH 8 (Zhang et al., 2016a). Therefore, with the presence of abundant chelates, the decomposition of H_2O_2 in the EDDS-Fenton system should be faster than that in the NTA-Fenton system due to the fast reaction between Fe(II)EDDS and H_2O_2, indicating a higher generation rate of $^{\bullet}OH$ in the former system. However, for the employment of the chelating agents in the modified Fenton process, the scavenging effect of the agents on $^{\bullet}OH$ also needs to be considered.

6.3.2 Photodegradation of NTA and EDDS

Metal ion concentration in the raw OSPW and the stability constants of metal-NTA/EDDS complexes are included in **Table 6-1**. The most concentrated metal ions were Na (600 mg/L), Mg (25 mg/L), K (29 mg/L), and Ca (41 mg/L). Li, B, Si, Sr, and Ba were in a range of 0.1-4 mg/L. Most transition metal ions existed in trace amounts (< 0.05 mg/L), such as Ni (0.009 mg/L) and Cu (0.010 mg/L), and the total Fe concentration was below the detection limit.

The stability constants of metal-chelates increase with increasing charge and decreasing radius of the metal ions, and also increase with the number of coordinating groups in the ligands (Smith & Martell, 1987). Generally, the stability constants of metal-NTA complexes are smaller than these of metal-EDDS complexes, such as 15.9 (Anderegg, 1986; Andrianirinaharivelo et al., 1993; Cuculić et al., 2005) for Fe(III)NTA and 20.6 (Orama et al., 2002) for Fe(III)EDDS, 18.45 (Gorelova et al., 1971; Martell & Smith, 1974-1989; Whitburn et al., 1999) for Cu(II)NTA and 14.20 (Bolton et al., 1996) or 13.1 (Smith & Martell, 1987) for Cu(II)EDDS, and 7.4 (Smith &

Martell, 1987) for Mn(II)NTA and 8.95 (Majer et al., 1968; Martell & Smith, 1974-1989; Whitburn et al., 1999) for Mn(II)EDDS (ignoring the temperature (20 or 25 ºC) difference for these values), indicating a higher strength of the interaction of metal ions in OSPW with EDDS than that with NTA. EDDS with six coordinating sites (two N donors and four O donors) forms both five- and six-membered chelate rings with metal ions with a ratio of 1:1 (Pavelčík & Majer, 1978), while NTA as a tetradentate ligand with four coordinating sites (one N donor and three O donors) can form not only 1:1 but also 2:1 complexes with metal ions (Anderegg, 1982). The lower number of coordinating sites in NTA compared to EDDS attributes to the smaller stability constants of metal-NTA complexes.

Table 6-1. Metal ions in the OSPW and the stability constants (log K) of metal-NTA/EDDS.

Metal ion	Conc. (mg/L)	log K of metal-EDDS	log K of metal-NTA
Li	0.18	-	2.5* (Smith & Martell, 1987)
B	1.78	-	-
Na	600	-	1.2* (Smith & Martell, 1987)
Mg	25.10	6.09 (Majer et al., 1968; Martell & Smith, 1974-1989; Whitburn et al., 1999)	5.24 (Tomita et al., 1965), 5.41 (Sunda et al., 1978)
Al	0.0076	16.27 for Al(III) (Tolkacheva et al.)	13.7* for Al(III) (Bolton et al., 1996)
Si	3.38	-	-
K	29.00	-	-
Ca	41.4	4.72 (Majer et al., 1968; Martell & Smith, 1974-1989; Whitburn et al., 1999)	6.4* (Smith & Martell, 1987; Sunda et al., 1978)
Ti	0.010	-	-
V	0.0089	-	-
Cr	0.014	-	7.1* (Smith & Martell, 1987)
Fe	< Detection limit	20.6 for Fe(III) (Orama et al., 2002)	15.9* for Fe(III) (Anderegg, 1986; Andrianirinaharivelo et al., 1993; Cuculić et al., 2005), 8.8* for Fe(II) (Smith & Martell, 1987)
Mn	0.0015	8.95 (Majer et al., 1968; Martell & Smith, 1974-1989; Whitburn et al., 1999)	7.4* (Smith & Martell, 1987)
Co	0.0017	14.02 (Majer et al., 1966; Martell & Smith, 1974-1989; Whitburn et al., 1999)	11.7* (Bolton et al., 1996), 10.3* (Smith & Martell, 1987)
Nb	0.00038	-	-
Mo	0.088	-	-
Zr	0.0019	-	-

Table 6-1 (concluded).

Metal ion	Conc. (mg/L)	log K of metal-EDDS	log K of metal-NTA
Ni	0.0089	18.02 (Majer et al., 1966; Martell & Smith, 1974-1989; Whitburn et al., 1999)	12.8* (Bolton et al., 1996), 11.5* (Smith & Martell, 1987)
Rb	0.036	-	0.1* (Smith & Martell, 1987)
Sr	1.09	3.37 (Majer et al., 1968; Martell & Smith, 1974-1989; Whitburn et al., 1999)	6.16* (Chowdhury & Blust, 2002)
Ru	0.00006	-	-
Cd	0.00014	10.80 (Majer et al., 1968; Martell & Smith, 1974-1989; Whitburn et al., 1999)	9.83 (Sunda et al., 1978)
Ba	0.14	3.10 (Majer et al., 1968; Martell & Smith, 1974-1989; Whitburn et al., 1999)	4.8* (Smith & Martell, 1987)
Hf	0.0011	-	-
Ta	0.00058	-	-
W	0.0070	-	-
Pb	0.0001	12.70* (Majer et al., 1968; Martell & Smith, 1974-1989; Whitburn et al., 1999)	12.1 (Krishnan et al., 2003)
Sn	0.00085	-	-
Sb	0.0032	-	-
Cs	0.00022	-	-
Th	0.0024	-	16.9* for Th(IV) (Smith & Martell, 1987)
U	0.010	-	-

Note: values refer to 20 ºC except values marked*, which are at 25 ºC. Values without valence notification are for divalent metal ions.

The degradation of 0.72 mM NTA and EDDS, respectively, under UV irradiation and in the UV photolysis of Fe(III)-L (Fe = 0.089 mM) in MilliQ water and in the OSPW showed no significant difference (**Figure 6-3**). No NTA degradation and negligible EDDS degradation (< 4.0%) were achieved under UV irradiation, which is consistent with the literature (Andrianirinaharivelo et al., 1993; Bunescu et al., 2008; Natarajan & Endicott, 1973). 81.0% and 84.6% degradation of Fe(III)NTA and Fe(III)EDDS, respectively, occurred in the UV photolysis of Fe(III)-L within 30 min due to the fast photolysis of metal-APCA complexes (Andrianirinaharivelo et al., 1993; Bunescu et al., 2008; Natarajan & Endicott, 1973). The decomposition of NTA takes place at C-N bond and generates iminodiacetic acid (IDA), glycine, oxalic acid, ammonia and carbon dioxide (Andrianirinaharivelo et al., 1993). No oxidation products of EDDS can be found in the literature; however, the biodegradation of EDDS takes place with a C-N cleavage and gives weak chelating agents N-(2-aminoethyl) aspartic acid (AEAA) and fumarate, and eventually CO_2 (Schowanek et al., 1997).

The degradation of Fe(III)NTA and Fe(III)EDDS under UV irradiation in MilliQ water was significantly accelerated by the addition of 5.88 mM H_2O_2, with a slightly higher degradation rate of the former complex (97.5% degradation in 7 min) than that of the latter complex (97.8% degradation in 10 min).

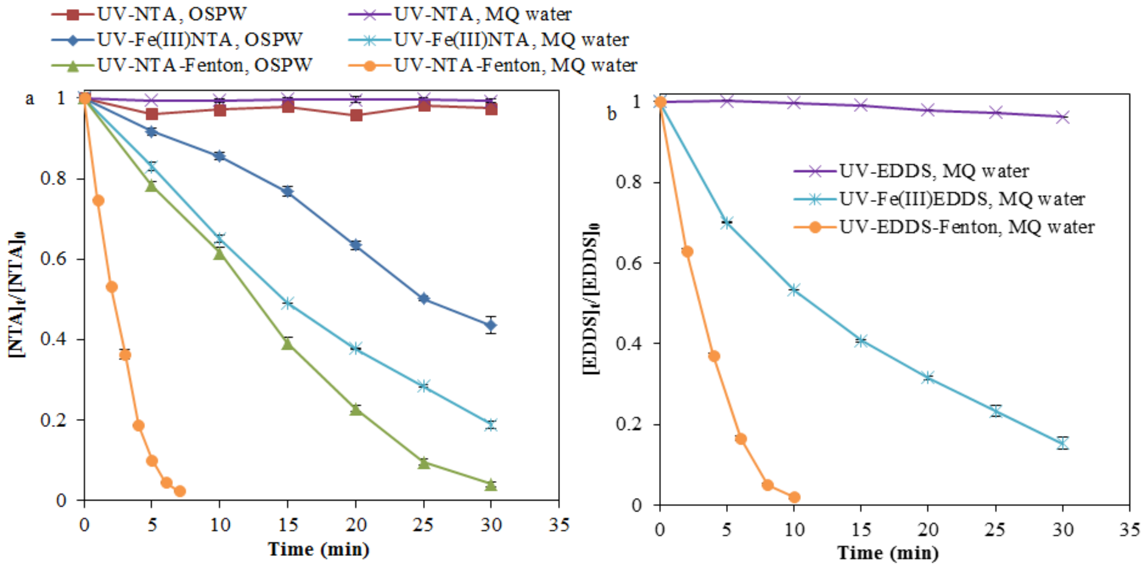


Figure 6-3. a) NTA degradation in MilliQ (MQ) water and in OSPW and b) EDDS degradation in MQ water under different conditions ($[NTA]_0$ = 0.72 mM for UV-NTA, UV-Fe(III)NTA, and UV-NTA-Fenton in MQ water and in the OSPW. $[EDDS]_0$ = 0.72 mM for UV-EDDS, UV-Fe(III)EDDS, and UV-EDDS-Fenton in MQ water. $[Fe]_0$ = 0.089 mM for UV-Fe(III)NTA/EDDS and UV-NTA/EDDS-Fenton. $[H_2O_2]_0$ = 5.88 mM for UV-NTA/EDDS-Fenton).

The acceleration of the degradation of Fe-complexes in the presence of H_2O_2 was primarily attributed to two main reasons: i) the interaction of $^{\bullet}OH$ generated through Eq. 6-2 with NTA and EDDS with rate constants of $4.77\pm0.24\times10^{8}$ $M^{-1}s^{-1}$ (Zhang et al., 2016b) and $2.48\pm0.43\times10^{9}$ $M^{-1}s^{-1}$ (Zhang et al., 2016a), respectively; and ii) the formation of binuclear μ-peroxo adducts, H_2O_2-Fe(III)NTA/EDDS. The second hypothesis was made based on previous reports of H_2O_2-adducts for the reaction of H_2O_2 with Fe(III) (Gallard et al., 1999), Fe(III)EDTA (De Laat et al., 2011; Francis et al., 1985; Walling et al., 1970), and Fe(III)NTA (Nishida et al., 1994). The H_2O_2-adducts exhibit different reactivity in contrast with Fe(III)-chelates, such as that H_2O_2-Fe(III)NTA absorbs light at high wavelength (350-600 nm) where the complex and H_2O_2 do not absorb (De Laat et al., 2011). The highly activated peroxide ion trapped in the binuclear μ-peroxo adduct contains singlet oxygen ($^1\Delta_g$) and exhibits a unique reactivity through its direct interaction with organic substrates. The activity of the peroxide ion depends on the complexes used (Nishida et al., 1992). The μ-peroxo adducts can be converted to high-valence Fe(IV)-oxo species, which is highly reactive towards abundant substrates (Pierre & Fontecave, 1999). Based on these theories, the degradation of Fe(III)L in the presence of H_2O_2 might be to some extent caused by the interaction with the activated peroxide ion or by the oxidation with the Fe(IV)-oxo species. The attribution of the $^•OH$ attack on the NTA degradation was very limited compared with that on EDDS, as suggested by their reaction rate constants with $^•OH$. Therefore, the higher H_2O_2 interference on the NTA degradation should be primarily attributed to the formation of the H_2O_2-adduct.

It is very interesting to notice that the Fe(III)NTA degradation in the OSPW with or without the presence of H_2O_2 was much slower than that in MilliQ water. In OSPW, the Fe(III)NTA degradation in 30 min was 95.9% with the presence of 5.88 mM H_2O_2 and 56.4% without H_2O_2, while the Fe(III)NTA degradation in MilliQ water was 97.5% in 7 min with the presence of 5.88 mM H_2O_2 and 81.0% in 30 min without H_2O_2. Due to the interference of the water matrix, the total EDDS concentration in OSPW could not be determined. However, the H_2O_2 decomposition (**Figure 6-4**b) in the UV-EDDS-Fenton process for the treatment of OSPW slowed down after 15 min (For example, 4.41 mM H_2O_2 decomposed to 1.46 mM in the first 15 min and then decomposed to 1.05 mM in the following 15 min). Moreover, no signal of Fe(III)EDDS can be detected in the HPLC-UV after 15 min, indicating the complete decomposition of EDDS at that time, slightly slower than that in MilliQ water (97.8% degradation in 10 min). The faster photolysis of Fe(III)EDDS in the presence of H_2O_2 in the OSPW than that of Fe(III)NTA was attributed to the higher reaction rate of EDDS with $^•OH$. Some organics in OSPW, such as fulvic and humic acids, could form less reactive co-complexes with Fe(III)L. The heavy metal ions in OSPW (**Table 6-1**) competed with iron for the chelating agents. Furthermore, the high UV absorption of the OSPW decreased the UV energy for the photolysis of Fe(III)L. These three interferences attributed primarily to the hindering effect of OSPW on the photolysis rate of Fe(III)NTA/EDDS.

6.3.3 FT-IR results

The H_2O_2 decomposition in the UV-NTA/EDDS-Fenton processes is given in **Figure 6-4**. In the UV-NTA-Fenton process (0.089 mM Fe and 0.72 mM NTA), 100% decomposition of H_2O_2 occurred in 30 min with H_2O_2 dose lower than 5.88 mM. 98.4%, 92.6%, and 89.1% decomposition of H_2O_2 was achieved for the H_2O_2 dose of 5.88, 7.35, and 8.82 mM, respectively. In the UV-EDDS-Fenton process (0.089 mM Fe and 0.72 mM EDDS), 100% decomposition of H_2O_2 was only achieved for the H_2O_2 dose of 1.47 mM. 98.8%, 75.0%, 59.8%, 52.3%, and 46.0% decomposition of H_2O_2 was achieved for the H_2O_2 dose of 2.94, 4.41, 5.88, 7.35, and 8.82 mM, respectively.

The FT-IR spectra of the raw OSPW and OSPW treated by UV-NTA/EDDS-Fenton processes are shown in **Figure 6-5**, and the removal of acid extractable organic fraction (AEF) in these two processes is given in **Figure 6-6**. The O-H stretch in the phenol-like structures registers at 3600 cm^{-1} (Reinardy et al., 2013; Zhang et al., 2015), while aromatic and alkene C-H stretches both occur over 3000 cm^{-1} with the peaks at 3100-3000 cm^{-1} reflecting the aromatic C-H stretch. C=C aromatic stretches appear often in pairs, with one at 1615-1580 cm^{-1} and the other one at 1510-1450 cm^{-1} (Coates, 2000). The peaks between 670 and 900 cm^{-1} might be attributed to =C-H out-of-plane in aromatic compounds (Coates, 2000). The absorbance at 1743 cm^{-1} and 1706 cm^{-1} are for monomeric and dimeric forms of carboxylic groups, respectively, and they were applied for the AEF calculation because that these values are commonly used by the oil sands industry to evaluate the organic compounds in OSPW (Grewer et al., 2010; Scott et al., 2008; Zhang et al., 2015).

The peak heights of the C=O stretch in carboxylic groups (at 1743 cm^{-1} and 1706 cm^{-1}) in the treated OSPW significantly decreased compared with that in the raw OSPW (**Figure 6-5**). In the UV-Fenton process with NTA, AEF (64.52 mg/L) removal in 30 min (**Figure 6-6**) increased with increasing H_2O_2 dose at $H_2O_2 < 5.88$ mM, and decreased with increasing H_2O_2 dose at $H_2O_2 > 5.88$ mM, with a highest removal of 66.8% at 5.88 mM H_2O_2. In the UV-EDDS-Fenton process, AEF removal increased with increasing H_2O_2 dose at $H_2O_2 < 4.41$ mM, and decreased with increasing H_2O_2 dose at $H_2O_2 > 4.41$ mM, with a highest removal of 50.0% at 4.41 mM H_2O_2. H_2O_2 decreased from 4.41 mM to 1.1 mM (75% decomposition). The lower AEF removal at higher dose of H_2O_2 in these two processes was due to the scavenging effect of H_2O_2 on $^{\bullet}OH$ with a reaction rate constant reported as 2.70×10^{7} $M^{-1}s^{-1}$ (De Laat & Gallard, 1999; Gallard & De Laat, 2000; Huang et al., 2013). The AEF in OSPW includes c-NAs ($C_nH_{2n+z}O_2$), oxy-NAs ($C_nH_{2n+z}O_x$, x = 3-5), and other organics containing carboxylic groups (Grewer et al., 2010; Huang et al., 2015), with the total NAs comprising about 50% of AEF (Garcia-Garcia et al., 2011; Pourrezaei et al., 2011). The results indicate that UV-NTA-Fenton is more efficient in the reduction of AEF level in OSPW compared with UV-EDDS-Fenton, primarily due to the lower scavenging effect of NTA on $^{\bullet}OH$ than that of EDDS, as discussed in Section 6.3.2.

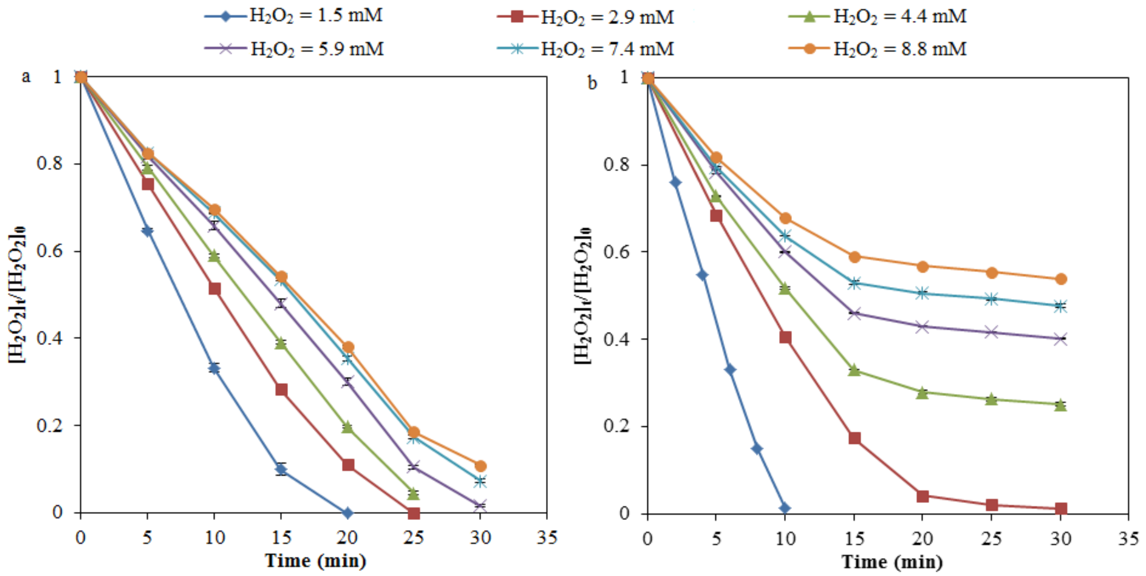


Figure 6-4. H_2O_2 decomposition in the treatment of OSPW by a) UV-NTA-Fenton and b) UV-EDDS-Fenton ($[Fe]_0$ = 0.089 mM, $[NTA]_0 = [EDDS]_0$ = 0.72 mM).

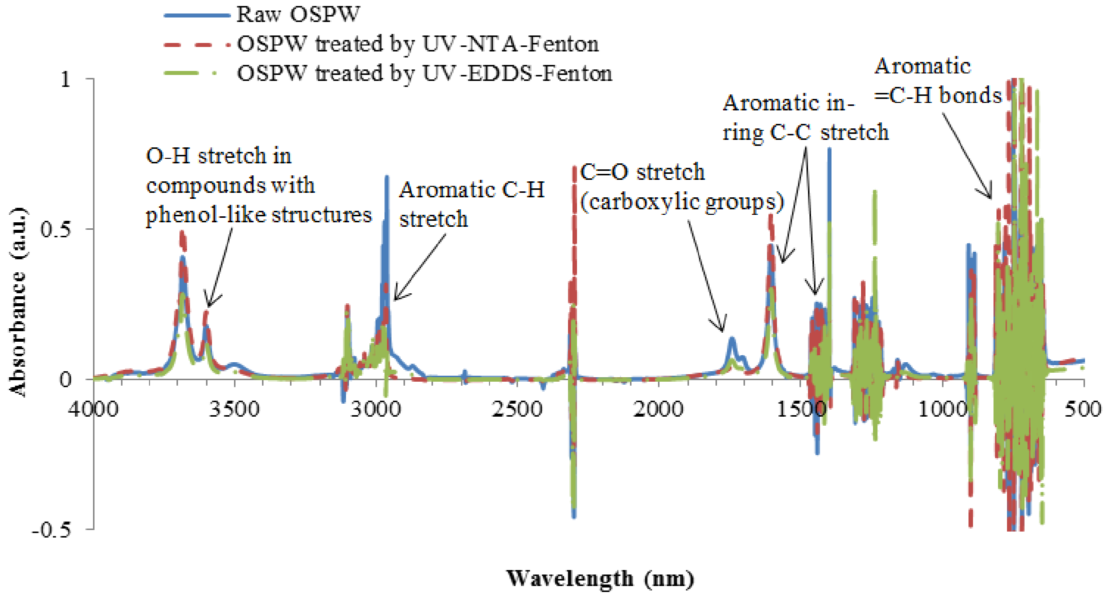


Figure 6-5. FT-IR spectra of the raw OSPW and OSPW treated by the UV-NTA/EDDS-Fenton processes ($[H_2O_2]_0$ = 5.88 mM and 4.4 mM for UV-NTA-Fenton and UV-EDDS-Fenton, respectively. $[Fe]_0$ = 0.089 mM, $[NTA]_0 = [EDDS]_0$ = 0.72 mM, and 30 min UV irradiation).

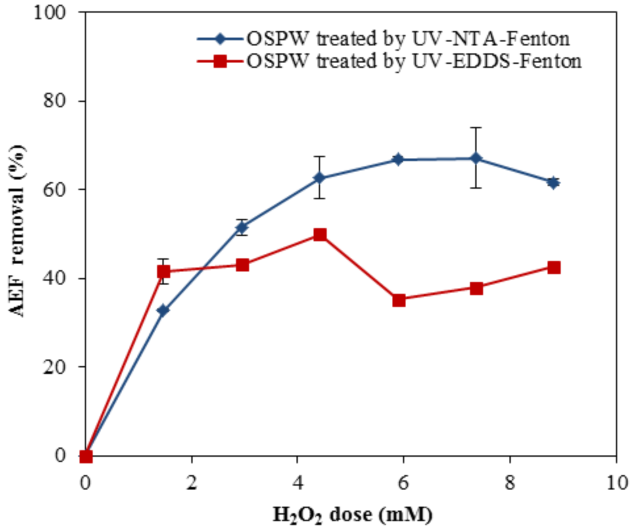


Figure 6-6. The removal of acid extractable organic fraction (AEF) with increasing H_2O_2 dose in the UV-NTA/EDDS-Fenton processes ($[Fe]_0$ = 0.089 mM, $[NTA]_0$ = $[EDDS]_0$ = 0.72 mM, and 30 min UV irradiation).

6.3.4 NMR and SFS results

The ^{1}H NMR spectra of the raw OSPW and treated OSPW were acquired to compare the removal of organics with different processes (**Figure 6-7**a). The peaks at 11.4-12.5 ppm (I), 6.5-8.0 ppm (II), and 0.3-2.2 ppm (III) are assigned to the hydrogen atoms in carboxylic groups, aromatic rings, and aliphatic chains, respectively (Clayden et al., 2012; Wang et al., 2016). In the UV-EDDS-Fenton process, the area for peak I decreased by 61.5%, for peak II by 74.2%, and for peak III by 46.6%, while in the UV-NTA-Fenton process the same peaks were reduced by 90.4%, 93.5% and 80.4%, respectively. In a study of OSPW treated with 200 mg/L potassium ferrate(VI) conducted by Wang et al. (2016), 29.7%, 44.4%, and 23.8% area decrease were achieved for peaks I, II and III, respectively, much lower than these obtained in this study.

SFS analysis was applied to measure fluorophore compounds, which are most likely aromatic compounds present in OSPW. Peak I at 273 nm (**Figure 6-7**b) is the signal of one-ring aromatics, which includes aromatics with one aromatic ring and aromatics containing two or more unfused aromatic rings. Peak II at 310 nm and peak III at 330 nm are the signals of the aromatics with two and three fused rings, respectively (Dinh, 1978; Pourrezaei et al., 2014; Wang et al., 2016). In the UV-NTA-Fenton process, with a H_2O_2 dose over 1.47 mM, the aromatics at Peak II and III were completely removed. The removal of one-ring aromatics at Peak I increased with increasing H_2O_2 dose, with no peak observed at H_2O_2 dose over 4.41 mM. In the UV-EDDS-Fenton process with H_2O_2 from 1.47 mM to 8.82 mM, aromatics at Peak I were significantly removed, and the aromatics at Peak II and III were completely removed. The high emission intensity at wavelengths 400-500 nm (**Figure 6-7**c) was related to the degradation products of Fe(III)EDDS, as indicated by the SFS spectra of the photolyzed complex in **Figure 6-8**. A peak of photolyzed Fe(III)EDDS in MilliQ water showed up at the same wavelength (440 nm) as the peak in **Figure 6-7**c with 1.47 mM H_2O_2. Unfortunately, detailed information of the new peaks is not available in the literature.

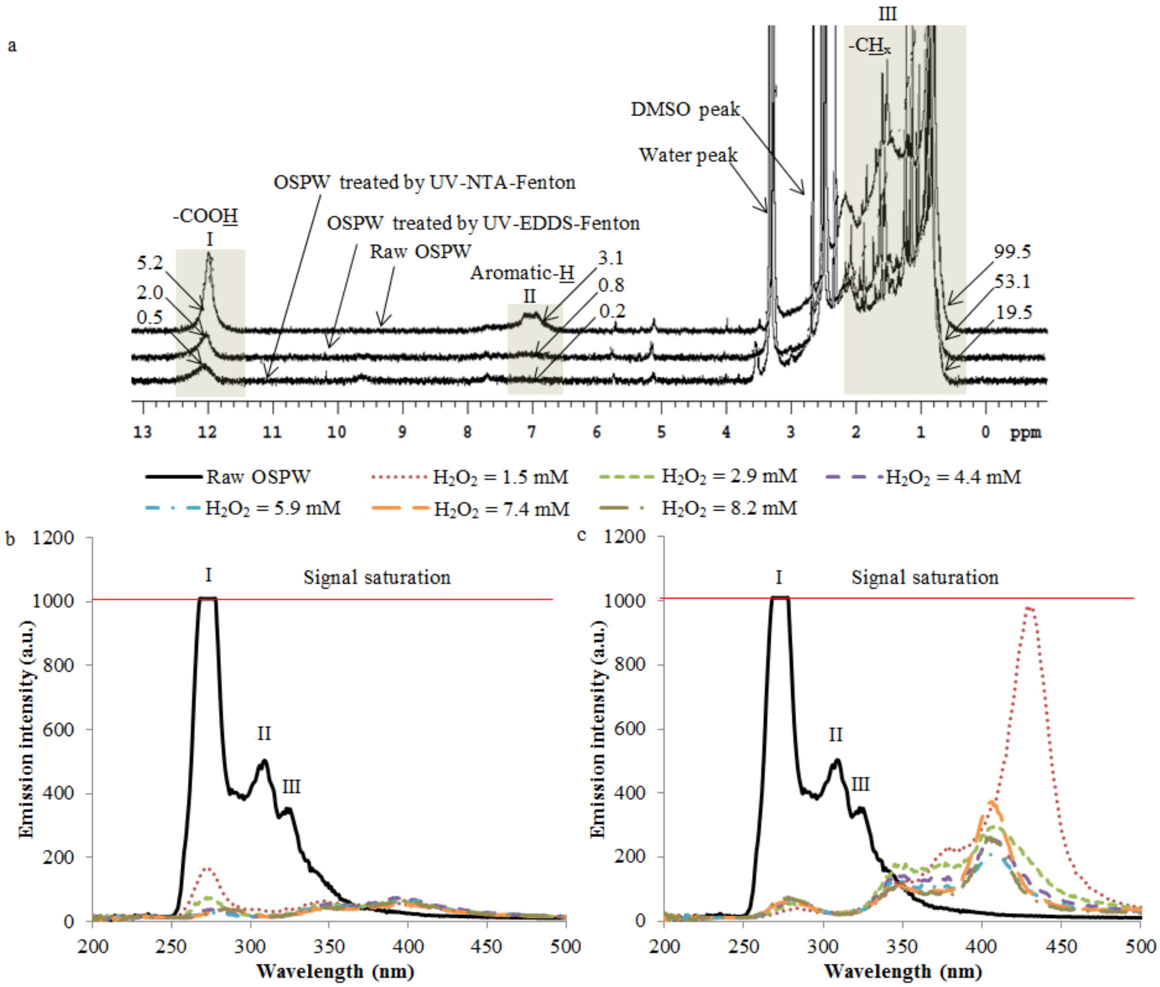


Figure 6-7. a) ^{1}H NMR spectra for the raw OSPW, and OSPW treated by the UV-NTA/EDDS-Fenton processes ($[H_2O_2]_0$ = 5.88 mM and 4.41 mM for UV-NTA-Fenton and UV-EDDS-Fenton, respectively. $[Fe]_0$ = 0.089 mM and $[NTA]_0 = [EDDS]_0$ = 0.72 mM, and 30 min UV irradiation) (the values above the peaks are the relative peak area with the peak of the internal standard DMSO set as 100), b) SFS of the raw OSPW and OSPW treated by UV-NTA/EDDS-Fenton processes with different H_2O_2 dose ($[Fe]_0$ = 0.089 mM, $[NTA]_0 = [EDDS]_0$ = 0.72 mM, and 30 min UV irradiation).

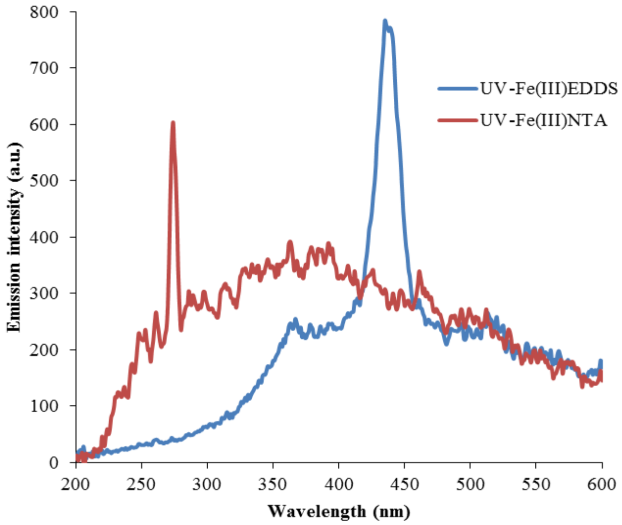


Figure 6-8. SFS of UV irradiated Fe(III)NTA/EDDS in MilliQ water ($[Fe]_0$ = 0.089 mM, $[NTA]_0$ = $[EDDS]_0$ = 0.72 mM, and 30 min UV irradiation).

The results suggest the higher stability of one-ring aromatics than two- and three-fused ring aromatics towards oxidation. Aromatics with two or more fused rings have higher electron density than one-ring aromatics (more unactivated and stable), leading to higher activity towards oxidation (Larson & Weber, 1994; Wang et al., 2016). Moreover, aromatic compounds with greater size and increasing alkyl substitution have higher quantum yields, resulting in higher sensitivity to photochemical oxidation (Garrett et al., 1998; Jacobs et al., 2008; Shu et al., 2014). The production of one-ring aromatics from the decomposition of two- and three-ring aromatics also explains the apparent stability of one-ring aromatics (Wang et al., 2016).

The reactions between $^{\bullet}OH$ and organic matters usually take place by adding the radical to a C=C double bond or by abstracting a H-atom from C-H bonds (von Sonntag et al., 1997). The second-order rate constants of the reaction of $^{\bullet}OH$ with alkenes and aromatics are in a range of 10^9-10^{10} $M^{-1}s^{-1}$ (Buxton et al., 1988; Lindsey & Tarr, 2000). The $^{\bullet}OH$ attack on the aromatic compounds is preferentially by adding to the aromatic rings (Buxton et al., 1988; Semadeni et al., 1995), and the intermediate adducts formed are in an excited state initially and transformed to a stabilized form rapidly, which may decompose back to the reactants or react further with scavenger molecules, such as O_2 (Semadeni et al., 1995). Maki et al. (2001) reported a significant decline in the aromatic fraction and an increase in the resin and asphaltene fractions after sunlight irradiation of crude oil. Photooxidation products of aromatic hydrocarbons were reported as corresponding alcohols, aldehydes, ketones, and acids (Bobinger & Andersson, 2009; Garrett et al., 1998; Payne & Phillips, 1985).

Both ^1H NMR and SFS spectra showed very high removal of aromatics in the UV-NTA-Fenton process, in coincidence with the depleted signals of the aromatic C-H stretch at 3100-3000 cm^{-1} in the FT-IR spectra (**Figure 6-5**), indicating high capability of the process to degrade aromatics.

6.3.5 Toxicity results

Microtox® 81.9% screening test was applied to evaluate the efficiency of the UV-NTA/EDDS-Fenton processes on the removal of the acute toxicity of OSPW towards *Vibrio fischeri.* The inhibition effect of the raw OSPW was 39.5±0.7% (shown in **Figure 6-9**a at 0 mM H_2O_2), pretty close to 40-47% reported previously (Afzal et al., 2012; Shu et al., 2014). The inhibition effect of OSPW treated by the UV-NTA-Fenton process increased to 70.8% at 1.47 mM H_2O_2, then decreased with increasing H_2O_2 dose, and finally reached 61.8% at 8.82 mM H_2O_2. In the UV-EDDS-Fenton process, the inhibition effect of treated OSPW increased gradually with increasing H_2O_2 dose from 39.5% at 0 mM H_2O_2 to 72.0% at 8.82 mM H_2O_2. The increased inhibition effect of the photooxidation treated OSPW agreed well with Shu et al. (2014). Maki et al. (2001) also reported an increase of the toxicity against *Artemia* as the photooxidation of biodegraded oil proceeded. It was reported that the photooxidation process significantly increased the water-soluble fraction (medium-molecular-weight aromatic alcohols and ethers) of oil, which can lead to a higher general toxicity (Frankenfeld, 1973; Payne & Phillips, 1985). The photolysis of the fluorophore organic compounds in the OSPW (**Figure 6-7**b-c), such as petroleum polyaromatic hydrocarbons (PAHs), leading to the production of alcohols, aldehydes, ketones, and acids, which are considered to be responsible for the increased acute toxicity towards *Vibrio fischeri* (Bobinger & Andersson, 2009; Garrett et al., 1998; Payne & Phillips, 1985; Shu et al., 2014).

In order to test the acute toxicity of NTA, EDDS, Fe(III)NTA/EDDS and their products towards *Vibrio fischeri*, UV-NTA/EDDS-Fenton experiments were carried out in MilliQ water with 5.88 mM H_2O_2, 0.089 mM Fe and 0.72 mM NTA/EDDS. The degradation of NTA and EDDS under these conditions is illustrated in **Figure 6-3** with complete depletion of the agents at 12 min. NTA presented 9.4% inhibition effect (**Figure 6-9**b), indicating low acute toxicity of the agent towards *Vibrio fischeri*. The acute and subacute toxicity of NTA has been reported to be negligible (Rubin & Martell, 1980), and the agent shows no adverse effects to aquatic life (Anderson et al., 1985). The slight increase of the toxicity of NTA by the complexation with Fe (17.9% inhibition effect) coincided with a previous report of the toxicity of EDTA and DTPA (Sorvari & Sillanpää, 1996). No significant change of the inhibition effect occurred during the photolysis of Fe(III)NTA, indicating low toxicity of the Fe(III)NTA products (i.e., IDA, glycine, oxalic acid, and CO_2). EDDS and Fe(III)EDDS solution presented 12.7% and 12.1% inhibition effect towards *Vibrio fischeri*, respectively (**Figure 6-9**b). The toxicity of [S,S]-EDDS to fish and *daphnia* has an $EC_{50} > 1000$ mg/L (Fabbricino et al., 2013). The toxicity of the Fe(III)EDDS solution increased gradually as the photolysis of the complex proceeded and reached 61.9% at 12 min (100% decomposition of Fe(III)EDDS). As discussed in Section 6.3.2, the oxidation of

EDDS most probably produced N-(2-aminoethyl) aspartic acid (AEAA), fumarate, and CO_2 (Schowanek et al., 1997). Fumarate is basically non-toxic (Levey et al., 1946). No data of the toxicity of AEAA is available in the literature.

Yu et al. (2014) suggested the acute toxicity of the treated pharmaceutical wastewaters towards *Vibrio fischeri* was significantly correlated with the ammonia concentration based on a Spearman rank correlation analysis. In order to testify the hypothesis, the concentration of ammonia ($pK_b = 4.75$, in the main form of ammonium at the experimental pH 8.3) generated in the UV-NTA/EDDS-Fenton was measured, as well as nitrite and nitrate. No nitrite and low concentration of nitrate (0.5-1.4 mg/L) were achieved in both processes. Ammonium generated increased with time and achieved 3.0 and 5.4 mg/L at the end of the reaction for NTA and EDDS processes, respectively. The acute toxicity of ammonium (0.1-50 mg/L, in the form of ammonium hydroxide), nitrate (0.1-50 mg/L, in the form of sodium nitrate), and nitrite (0.1-50 mg/L, in the form of sodium nitrite) towards *Vibrio fisheri* was also investigated. No inhibition effect of ammonium and nitrate, and very low inhibition effect of nitrite (< 6%) were observed, even at the concentration as high as 50 mg/L, indicating the irrelevance of these species to the acute toxicity towards *Vibrio fisheri*. Therefore, it can be concluded that the high acute toxicity of the photolyzed Fe(III)EDDS was attributed to the production of AEAA.

The comparison of the inhibition effect of treated OSPW (**Figure 6-9**a) with that of NTA, EDDS and their metal-complexes products (**Figure 6-9**b) indicates that the attribution of NTA products to the overall inhibition effect of the treat OSPW in **Figure 6-9**a was much lower than that of the organics (such as PHAs) products. However, the EDDS degradation products, AEAA, attributed significantly to the overall inhibition effect of the treat OSPW in **Figure 6-9**a. NTA is a much better chelating agent than EDDS due to the higher organic removal in the UV-NTA-Fenton process and lower toxicity risk of the agent towards aquatic organisms.

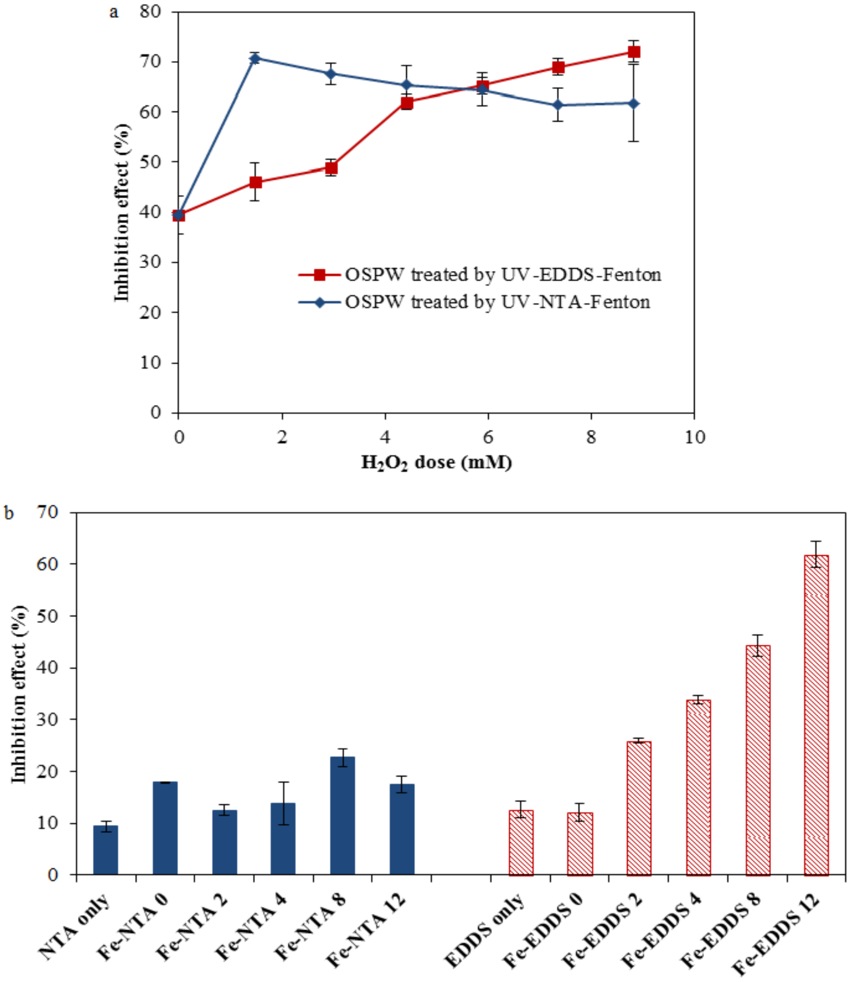


Figure 6-9. a) Effect of H_2O_2 dose on the acute toxicity of OSPW treated by UV-NTA/EDDS-Fenton processes ($[Fe]_0 = 0.089$ mM, $[NTA]_0 = [EDDS]_0 = 0.72$ mM, and 30 min UV irradiation) and b) acute toxicity of NTA, EDDS, Fe(III)NTA/EDDS and their by-products in MilliQ water ($[H_2O_2]_0 = 5.88$ mM, $[Fe]_0 = 0.089$ mM, and $[NTA]_0 = [EDDS]_0 = 0.72$ mM). The numbers (0, 2, 4, 8, 12) denote the sampling time.

NTA is a better option in contrast with EDDS for the application of UV-chelates-Fenton in the treatment of OSPW, and the fast photolysis of the agent precludes researchers' concern about its contamination.

6.3.6 NAs removal

The overall percent distribution of NAs based on carbon number and -z (hydrogen deficiency) in the raw OSPW and in the OSPW treated with the UV-NTA-Fenton, UV-H_2O_2, and NTA-Fenton processes are illustrated in **Figure 6-10**a-d, respectively. The distributions of c-NAs in the raw OSPW with respect of carbon number and –z are provided in **Table 6-2**. The most abundant species in the c-NAs were NAs with two (-z = 4) and three rings (-z = 6) (47.8% of total c-NAs), and c-NAs with carbon number ranging from 13-18 (81% of total c-NAs) as previously reported (Wang et al., 2013). The concentration of the total c-NAs in the raw OSPW was 25.4 mg/L, and it decreased to 0.4 mg/L (98.4% removal), 2.8 mg/L (88.9% removal), and 7.7 mg/L (69.6% removal) for the OSPW treated with the UV-NTA-Fenton, UV-H_2O_2, NTA-Fenton processes, respectively. Only 12.8% NAs removal was achieved by UV irradiation (data not shown here).

NA removal with respect of carbon number and –z is shown in **Figure 6-10**e-f, respectively. Generally, the NA removal increased with increasing carbon with the exception of the smallest NAs in each z-series, in agreement with Pérez-Estrada et al. (2011), which is due to the increment of H number in the molecules available for the $^{\bullet}OH$ abstraction. The high reactivity of the smallest NAs might be attributed to the alkyl substitution patterns (i.e., branching patterns), which decreased the activation energy (Afzal et al., 2012; Pérez-Estrada et al., 2011). NAs with two and three rings as the most abundant species are more recalcitrant than the other NAs (Shu et al., 2014). The carbon centered radicals on the tertiary carbons after H abstraction have higher stability than those on the primary and secondary carbons, leading to higher reactivity of the H atoms on the tertiary carbons. Therefore, the tertiary carbons introduced to NAs by the increment of rings might primarily contribute to the generally increasing reactivity of NAs with –z[97].

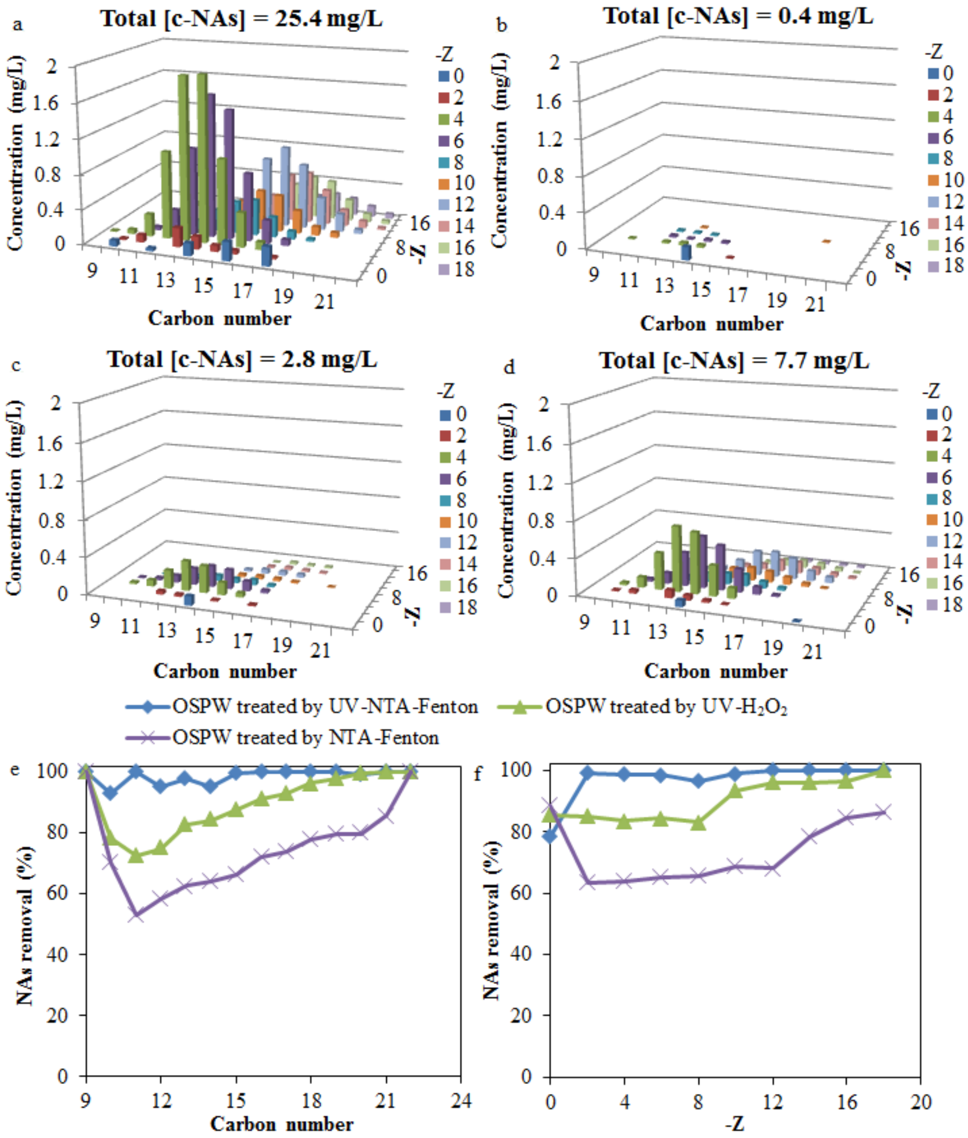


Figure 6-10. NAs distribution in the a) raw OSPW, b) OSPW treated by UV-NTA-Fenton, c) OSPW treated by UV-H_2O_2, d) OSPW treated by NTA-Fenton, and NAs removal with respect of e) carbon number and f) –z number ($[H_2O_2]_0$ = 5.88 mM for all three processes. $[Fe]_0$ = 0.089 mM and $[NTA]_0$ = 0.72 mM for UV-NTA-Fenton and NTA-Fenton. 30 min UV irradiation for UV-NTA-Fenton and UV-H_2O_2).

Table 6-2. c-NAs distributions in the OSPW.

-z	c-NAs (%)	Carbon number	c-NAs (%)
0	2.7	9	0.04
2	2.4	10	0.5
4	25.9	11	1.5
6	21.9	12	5.1
8	5.8	13	12.8
10	7.1	14	17.1
12	14.1	15	14.7
14	8.8	16	14.2
16	7.6	17	11.6
18	3.7	18	10.6
		19	6.3
		20	3.6
		21	1.4
		22	0.5

The initial concentration of NAs + O (oxy-NAs with one additional oxygen atom) in the raw OSPW was 15 mg/L, and it decreased to 2.1 mg/L (86.0% removal), 7.7 mg/L (48.7% removal), and 9.7 mg/L (35.3% removal) after the treatment with the UV-NTA-Fenton, UV-H_2O_2, and NTA-Fenton processes, respectively (**Figure 6-11**a-d).

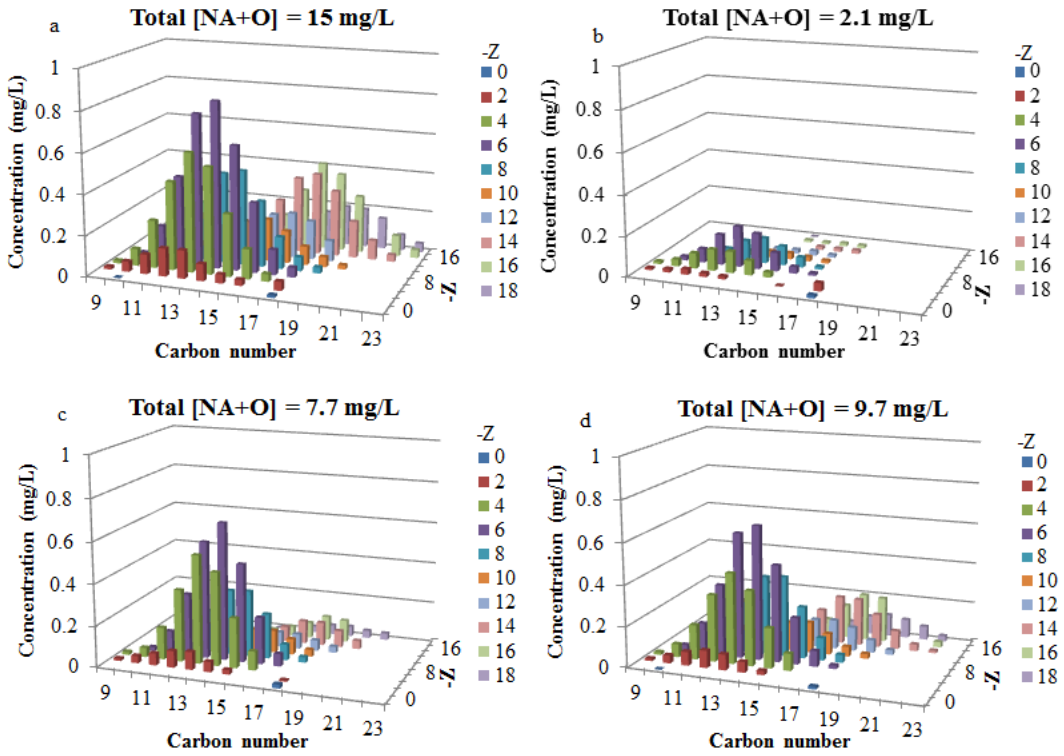


Figure 6-11. NAs + O distribution in the a) raw OSPW, b) OSPW treated by UV-NTA-Fenton, c) OSPW treated by UV-H_2O_2, d) OSPW treated by NTA-Fenton ($[H_2O_2]_0$ = 5.88 mM for all three processes. $[Fe]_0$ = 0.089 mM and $[NTA]_0$ = 0.72 mM for UV-NTA-Fenton and NTA-Fenton. 30 min UV irradiation for UV-NTA-Fenton and UV-H_2O_2).

NAs + 2O (oxy-NAs with two additional oxygen atoms) had an initial concentration of 16.3 mg/L in the raw OSPW, and it decreased to 3.1 mg/L (81.0% removal), 7.4 mg/L (54.6% removal), and 9.1 mg/L (44.2% removal) after the treatment with the UV-NTA-Fenton, UV-H_2O_2, and NTA-Fenton processes, respectively (**Figure 6-12**a-d).

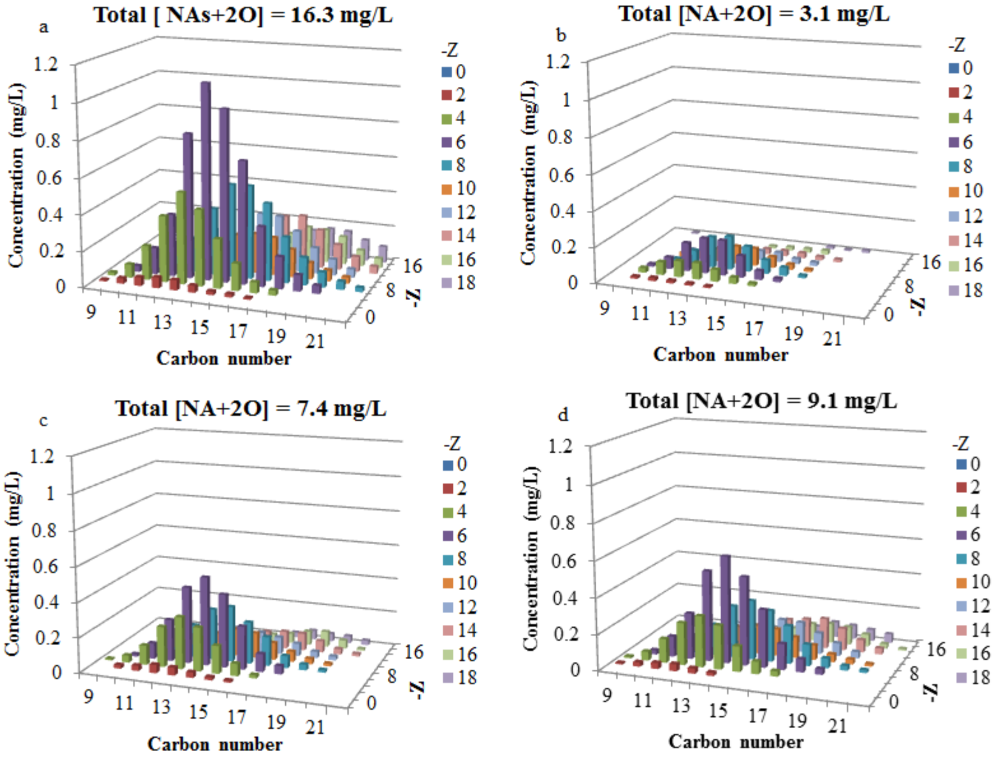


Figure 6-12. NAs+2O distribution in the a) raw OSPW, b) OSPW treated by UV-NTA-Fenton, c) OSPW treated by UV-H_2O_2, and d) OSPW treated by NTA-Fenton ($[H_2O_2]_0$ = 5.88 mM for all three processes. $[Fe]_0$ = 0.089 mM and $[NTA]_0$ = 0.72 mM for UV-NTA-Fenton and NTA-Fenton. 30 min UV irradiation for UV-NTA-Fenton and UV-H_2O_2).

The UV-NTA-Fenton process exhibited the highest removal of c-NAs (98.4%), NAs + O (86%), and NAs + 2O (81%) in contrast with the UV-H_2O_2 and NTA-Fenton processes, which was primarily attributed to the rapid reduction of Fe(III)NTA to Fe(II)NTA by UV light and the fast reaction of Fe(II)NTA and H_2O_2 (Hu et al., 2011), leading to the production of more $^{\bullet}$OH. Wang et al. (2016) reported a removal of c-NAs, NAs + O, and NAs + 2O in OSPW of 64.0%, -18.4%, and -18.0%, respectively, after the treatment with 200 mg/L potassium ferrate(VI). The negative removal was due to the reproduction of NAs + O and NAs + 2O from the oxidation of c-NAs and the transformation of oxy-NAs at high n and z numbers to oxy-NAs at low n and z numbers. This explanation can also be used to illustrate the relative lower degradation of oxy-NAs than c-NAs in this study. The high removal of c-NAs and oxy-NAs in the UV-NTA-Fenton process suggests the high efficiency of this process on the degradation of total NAs in OSPW.

High hydrogen deficiency of NAs might be a function of the number of alicyclic rings or due to the presence of aromatic rings or double bonds (Reinardy et al., 2013). However, the deficiency of aliphatic C-C double bonds in the OSPW was confirmed with the NMR spectra, which showed no signal at 4.5-5.5 ppm assigned to the double bonds (Clayden et al., 2012; Wang et al., 2016). The $^{\bullet}$OH attack on the alicyclic rings in NAs through H abstraction produces organic radicals, which then react with O_2 to form peroxyl radicals, as indicated by the reaction of $^{\bullet}$OH with a model NA compound, cyclohexanoic acid (CHA) (Drzewicz et al., 2010). The reaction between $^{\bullet}$OH and the aromatic rings in NAs, if any, can be referred to the $^{\bullet}$OH attack on aromatic compounds in Section 6.3.4, which are initiated predominantly through the radical addition to the aromatic rings. The oxidation of NAs by $^{\bullet}$OH generated more soluble molecules (i.e., oxy-NAs with less carbon number or fewer cyclic rings), as indicated by the increased solubility of NAs after oxidation.

6.4 Environmental Significance

This is the first application of the UV-chelate-modified Fenton on the OSPW remediation. This work compared, for the first time, the physicochemical characteristics of NTA and EDDS, the photolysis of Fe-NTA/EDDS in MilliQ water and in OSPW, and the efficiency of the UV-NTA/EDDS-Fenton processes for the removal of organics and the OSPW toxicity towards *Vibrio fischeri*. The results indicated that the OSPW matrix imposed some influence on the photolysis of the Fe-NTA/EDDS complexes. Compared to UV-EDDS-Fenton, UV-NTA-Fenton exhibited higher efficiency in the removal of acid extractable organic fraction and aromatics. NA removal in the UV-NTA-Fenton process was much higher in contrast with the UV-H_2O_2 and NTA-Fenton. Overall, NTA is a much better chelating agent than EDDS for the application of the UV-Fenton process on the treatment of OSPW at natural pH. However, the acute toxicity towards *Vibrio fischeri* of the OSPW treated with the UV-NTA-Fenton process increased compared to the raw OSPW, which warrants more research to confirm the causes. The findings obtained in this study have significant impact for the further development of this process and OSPW remediation.

6.5 References

Abida, O., Mailhot, G., Litter, M., & Bolte, M. (2006). Impact of iron-complex (Fe(III)-NTA) on photoinduced degradation of 4-chlorophenol in aqueous solution. *Photochemical & Photobiological Sciences : Official Journal of the European Photochemistry Association and the European Society for Photobiology, 5*(4), 395-402.

Afzal, A., Drzewicz, P., Perez-Estrada, L. A., Chen, Y., Martin, J. W., & Gamal El-Din, M. (2012). Effect of molecular structure on the relative reactivity of naphthenic acids in the UV/H_2O_2 advanced oxidation process. *Environmenal Science & Technology, 46*(19), 10727-10734.

Alberta Energy and Utilities Board. (2005). Alberta's reserves 2004 and supply/demand outlook 2005-2010. Calgary, Alberta, Canada: Alberta Energy and Utilities Board.

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

Anderegg, G. (1982). Critical survey of stability constants of NTA complexes. *Pure and Applied Chemistry, 54*(12), 2693-2758.

Anderegg, G. (1986). The stability of iron (III) complexes formed below pH= 3 with glycinate, iminodiacetate, β-hydroxyethyliminodiacetate, N, N-di-(Hydroxyethyl)-glycinate, nitrilotriacetate and triethanolamine. *Inorganica Chimica Acta, 121*(2), 229-231.

Anderson, R. L., Bishop, W. E., Campbell, R. L., & Becking, G. C. (1985). A review of the environmental and mammalian toxicology of nitrilotriacetic acid. *CRC Critical Reviews in Toxicology, 15*(1), 1-102.

Andrianirinaharivelo, S. L., Pilichowski, J. F., & Bolte, M. (1993). Nitrilotriacetic acid transformation photo-induced by complexation with iron(III) in aqueous solution. *Transition Metal Chemistry, 18*(1), 37-41.

Bielski, B. H. J., Cabelli, D. E., & Arudi, R. L. (1985). Reactivity of H_2O_2/O_2^- radicals in aqueous solution. *Journal of Physical and Chemical Reference Data, 4*, 1041-1100.

Bobinger, S., & Andersson, J. T. (2009). Photooxidation products of polycyclic aromatic compounds containing sulfur. *Environmental Science & Technology, 43*(21), 8119-8125.

Bolton, H., Girvin, D. C., Plymale, A. E., Harvey, S. D., & Workman, D. J. (1996). Degradation of metal-nitrilotriacetate complexes by Chelatobacter heintzii. *Environmental Science & Technology, 30*(3), 931-938.

Bunescu, A., Besse-Hoggan, P., Sancelme, M., Mailhot, G., & Delort, A.-M. (2008). Fate of the nitrilotriacetic Acid-Fe(III) complex during photodegradation and biodegradation by Rhodococcus rhodochrous. *Applied and Environmental Microbiology, 74*(20), 6320-6326.

Buxton, G. V., Greenstock, C. L., Helman, W. P., & Ross, A. B. (1988). Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals. *Journal of Physical and Chemical Reference Data, 17*, 513-886.

Camargo, J. A., Alonso, A., & Salamanca, A. (2005). Nitrate toxicity to aquatic animals: a review with new data for freshwater invertebrates. *Chemosphere, 58*(9), 1255-1267.

Chowdhury, M. J., & Blust, R. (2002). Bioavailability of waterborne strontium to the common carp, Cyprinus carpio, in complexing environments. *Aquatic Toxicology, 58*(3), 215-227.

Clayden, J., Greeves, N., & Warren, S. (2012). Organic Chemistry 2012: Oxford University Press: Oxford, New York.

Coates, J. (2000). Interpretation of infrared spectra, a practical approach. *Encyclopedia of Analytical Chemistry*.

Cuculić, V., Pižeta, I., & Branica, M. (2005). Voltammetry of Dissolved Iron(III)–Nitrilotriacetate–Hydroxide System in Water Solution. *Electroanalysis, 17*(23), 2129-2136.

Dao, Y. H., & De Laat, J. (2011). Hydroxyl radical involvement in the decomposition of hydrogen peroxide by ferrous and ferric-nitrilotriacetate complexes at neutral pH. *Water Research, 45*(11), 3309-3317.

De la Cruz, N., Gimenez, J., Esplugas, S., Grandjean, D., de Alencastro, L. F., & Pulgarin, C. (2012). Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. *Water Research, 46*(6), 1947-1957.

De Laat, J., Dao, Y. H., Hamdi El Najjar, N., & Daou, C. (2011). Effect of some parameters on the rate of the catalysed decomposition of hydrogen peroxide by iron(III)-nitrilotriacetate in water. *Water Research, 45*(17), 5654-5664.

De Laat, J., & Gallard, H. (1999). Catalytic decomposition of hydrogen peroxide by Fe (III) in homogeneous aqueous solution: mechanism and kinetic modeling. *Environmental Science & Technology, 33*(16), 2726-2732.

Dinh, T. V. (1978). Multicomponent analysis by synchronous luminescence spectrometry. *Analytical Chemistry, 50*(3), 396-401.

Drzewicz, P., Afzal, A., Gamal El-Din, M., & Martin, J. W. (2010). 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, 114*(45), 12067-12074.

Fabbricino, M., Ferraro, A., Del Giudice, G., & d'Antonio, L. (2013). Current views on EDDS use for ex situ washing of potentially toxic metal contaminated soils. *Reviews in Environmental Science and Bio/Technology, 12*(4), 391-398.

Francis, K. C., Cummins, D., & Oakes, J. (1985). Kinetic and structural investigations of [Fe^{III} (edta)]–[edta= ethylenediaminetetra-acetate (4–)] catalysed decomposition of hydrogen peroxide. *Journal of the Chemical Society, Dalton Transactions*(3), 493-501.

Frankenfeld, J. W. (1973). In "Proceedings of Joint Conference on Prevention and Control of Oil Spills". Paper presented at the Joint Conference on Prevention and Control of Oil Spills, American Petroleum Institute: Washington, D.C.

Fu, H., Gamal El-Din, M., Smith, D. W., MacKinnon, M., & Zubot, W. (2008). Ozone treatment of naphthenic acids in Athabasca oil sands process-affected water. Paper presented at the First International Oil Sands Tailings Conference,, Edmonton, AB, Canda.

Gallard, H., & De Laat, J. (2000). Kinetic modelling of Fe(III)/H_2O_2 oxidation reactions in dilute aqueous solution using atrazine as a model organic compound. *Water Research, 34*(12), 3107-3116.

Gallard, H., De Laat, J., & Legube, B. (1999). Spectrophotometric study of the formation of iron (III)-hydroperoxy complexes in homogeneous aqueous solutions. *Water Research, 33*(13), 2929-2936.

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

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

Garrett, R. M., Pickering, I. J., Haith, C. E., & Prince, R. C. (1998). Photooxidation of crude oils. *Environmental Science & Technology, 32*(23), 3719-3723.

Gorelova, R., Babich, V., & Gorelov, I. (1971). Potentiometric study of copper complex formation with ethylenediaminedisuccinic and ethylenediaminetetraacetic acids. *Zhurnal Neorganicheskoi Khimii, 16*(7), 1873-&.

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

Gutteridge, J., Maidt, L., & Poyer, L. (1990). Superoxide dismutase and Fenton chemistry. Reaction of ferric-EDTA complex and ferric-bipyridyl complex with hydrogen peroxide without the apparent formation of iron(II). *Biochemical Journal, 269*, 169-174.

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

Hu, X., Wang, X., Ban, Y., & Ren, B. (2011). A comparative study of UV-Fenton, UV-H_2O_2 and Fenton reaction treatment of landfill leachate. *Environmental Technology, 32*(9), 945-951.

Huang, C., Shi, Y., El-Din, M. G., & Liu, Y. (2015). Treatment of oil sands process-affected water (OSPW) using ozonation combined with integrated fixed-film activated sludge (IFAS). *Water Research, 85*, 167-176.

Huang, W., Brigante, M., Wu, F., Hanna, K., & Mailhot, G. (2012). Development of a new homogenous photo-Fenton process using Fe(III)-EDDS complexes. *Journal of Photochemistry and Photobiology A: Chemistry, 239*, 17-23.

Huang, W. Y., Brigante, M., Wu, F., Mousty, C., Hanna, K., & Mailhot, G. (2013). Assessment of the Fe (III)–EDDS complex in Fenton-like processes: from the radical formation to the degradation of bisphenol A. *Environmental Science & Technology, 47*(4), 1952-1959.

Jacobs, L. E., Weavers, L. K., & Chin, Y. P. (2008). Direct and indirect photolysis of polycyclic aromatic hydrocarbons in nitrate ‐ rich surface waters. *Environmental Toxicology and Chemistry, 27*(8), 1643-1648.

Jones, P. W., & Williams, D. R. (2001). Chemical speciation used to assess [S, S ′]-ethylenediaminedisuccinic acid (EDDS) as a readily-biodegradable replacement for EDTA in radiochemical decontamination formulations. *Applied Radiation and Isotopes, 54*(4), 587-593.

Kannel, P. R., & Gan, T. Y. (2012). 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, 47*(1), 1-21.

Klamerth, N., Malato, S., Aguera, A., & Fernandez-Alba, A. (2013). Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: a comparison. *Water Research, 47*(2), 833-840.

Klamerth, N., Malato, S., Aguera, A., Fernandez-Alba, A., & Mailhot, G. (2012). Treatment of municipal wastewater treatment plant effluents with modified photo-Fenton as a tertiary treatment for the degradation of micro pollutants and disinfection. *Environmental Science & Technology, 46*(5), 2885-2892.

Klamerth, N., Malato, S., Maldonado, M. I., Agüera, A., & Fernández-Alba, A. (2011). Modified photo-Fenton for degradation of emerging contaminants in municipal wastewater effluents. *Catalysis Today, 161*(1), 241-246.

Krishnan, K. A., Sheela, A., & Anirudhan, T. (2003). Kinetic and equilibrium modeling of liquid ‐ phase adsorption of lead and lead chelates on activated carbons. *Journal of Chemical Technology and Biotechnology, 78*(6), 642-653.

Kušić, H., Koprivanac, N., Božić, A. L., & Selanec, I. (2006). Photo-assisted Fenton type processes for the degradation of phenol: a kinetic study. *Journal of Hazardous Materials, 136*(3), 632-644.

Larson, R. A., & Weber, E. J. (1994). Reaction mechanisms in environmental organic chemistry: CRC press, Boca Raton, Florida.

Levey, S., Lasichak, A., Brimi, R., Orten, J., Smyth, C. J., & Smith, A. H. (1946). A study to determine the toxicity of fumaric acid. *Journal of the American Pharmaceutical Association, 35*(10), 298-304.

Li, J., Mailhot, G., Wu, F., & Deng, N. S. (2010). Photochemical efficiency of Fe(III)-EDDS complex: OH radical production and 17β-estradiol degradation. *Journal of Photochemistry and Photobiology A: Chemistry, 212*(1), 1-7.

Lindsey, M. E., & Tarr, M. A. (2000). Inhibition of hydroxyl radical reaction with aromatics by dissolved natural organic matter. *Environmental Science & Technology, 34*(3), 444-449.

Lipczynska-Kochany, E., & Kochany, J. (2008). Effect of humic substances on the Fenton treatment of wastewater at acidic and neutral pH. *Chemosphere, 73*(5), 745-750.

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

Majer, J., Jokl, V., Dvorakova, E., & Juracova, M. (1968). New complexones. XIII. Potentiometric and electrophoretic study of ethylenediamine-N, N′ -disuccinic acid and its metal chelates. *Chem Zvesti, 22*, 415-423.

Majer, J., Springer, V., & Kopecka, B. (1966). New complexones. VIII. Ethylenediamino-N, N′ -disuccinic acid and investigation of its heavy metal complexes by spectrophotometry. *Chemické Zvesti, 20*, 414-422.

Maki, H., Sasaki, T., & Harayama, S. (2001). Photo-oxidation of biodegraded crude oil and toxicity of the photo-oxidized products. *Chemosphere, 44*(5), 1145-1151.

Martell, A. E., & Smith, R. M. (1974-1989). *Critical stability constants* (Vol. 1-6). New York: Plenum Press.

Melnyk, D. L., Horwitz, S. B., & Peisach, J. (1981). Redox potential of iron-bleomycin. *Biochemistry, 20*(18), 5327-5331.

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

Moschopedis, S. E., Fryer, J. F., & Speight, J. G. (1977). Water-soluble constituents of Athabasca bitumen. *Fuel, 56*(1), 109-110.

Munoz, M., Alonso, J., Bartroli, J., & Valiente, M. (1990). Automated spectrophotometric determination of titanium(IV) in water and brines by flow injection based on its reaction with hydrogen peroxide. *Analyst, 115*(3), 315-318.

Natarajan, P., & Endicott, J. F. (1973). Photoredox behavior of transition metal-ethylenediaminetetraacetate complexes. Comparison of some Group VIII metals. *The Journal of Physical Chemistry, 77*(17), 2049-2054.

Nishida, Y., Goto, A., Akamatsu, T., Ohba, S., Fujita, T., Tokii, T., & Okada, S. (1994). Iron Chelates in Biological Systems. Its Relevance to Induction of Pathogenesis of Tissue Damage and Carcinogenesis. *Chemistry Letters*(3), 641-644.

Nishida, Y., Nasu, M., & Akamatsu, T. (1992). Reaction between binuclear iron(III) compounds and DMPO (5, 5-dimethyl-3, 4-dihydropyrrole N-oxide). *Journal of the Chemical Society, Chemical Communications* (2), 93-94.

Orama, M., Hyvönen, H., Saarinen, H., & Aksela, R. (2002). Complexation of [S, S] and mixed stereoisomers of N, N′ -ethylenediaminedisuccinic acid (EDDS) with Fe (III), Cu (II), Zn (II) and Mn (II) ions in aqueous solution. *Journal of the Chemical Society, Dalton Transactions*(24), 4644-4648.

Pavelčík, F., & Majer, J. (1978). The crystal and molecular structure of lithium [(S, S)-N, N'-ethylenediaminedisuccinato] cobaltate (III) trihydrate. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry, 34*(12), 3582-3585.

Payne, J. R., & Phillips, C. R. (1985). Photochemistry of petroleum in water. *Environmental Science & Technology, 19*(7), 569-579.

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

Pierre, J., & Fontecave, M. (1999). Iron and activated oxygen species in biology: the basic chemistry. *Biometals*, 12(3), 195-199.

Pignatello, J. J., Oliveros, E., & MacKay, A. (2006). Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology, 36*(1), 1-84.

Pourrezaei, P. (2013). Physico-Chemical Processes for Oil Sands Process-Affected Water Treatment. (Doctor of Philosophy), University of Alberta, Edmonton, A.B.

Pourrezaei, P., Alpatova, A., Khosravi, K., Drzewicz, P., Chen, Y., Chelme-Ayala, P., & Gamal El-Din, M. (2014). Removal of organic compounds and trace metals from oil sands process-affected water using zero valent iron enhanced by petroleum coke. *Journal of Environmental Management, 139*, 50-58.

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

Rao, P., & Hayon, E. (1975). Redox potentials of free radicals. IV. Superoxide and hydroperoxy radicals, O_2^- and HO_2. *The Journal of Physical Chemistry, 79*(4), 397-402.

Rastogi, A., Al-Abed, S. R., & Dionysiou, D. D. (2009). Effect of inorganic, synthetic and naturally occurring chelating agents on Fe(II) mediated advanced oxidation of chlorophenols. *Water Research, 43*(3), 684-694.

Reinardy, H. C., Scarlett, A. G., Henry, T. B., West, C. E., Hewitt, L. M., Frank, R. A., & Rowland, S. J. (2013). Aromatic naphthenic acids in oil sands process-affected water, resolved by GCxGC-MS, only weakly induce the gene for vitellogenin production in zebrafish (Danio rerio) larvae. *Environmental Science & Technology, 47*(12), 6614-6620.

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

Rubin, M., & Martell, A. E. (1980). The implications of trace metal-nitrilotriacetetic acid speciation on its environmental impact and toxicology. *Biological Trace Element Research, 2*(1), 1-19.

Schowanek, D., Feijtel, T. C., Perkins, C. M., Hartman, F. A., Federle, T. W., & Larson, R. J. (1997). Biodegradation of [S, S],[R, R] and mixed stereoisomers of ethylene diamine disuccinic acid (EDDS), a transition metal chelator. *Chemosphere, 34*(11), 2375-2391.

Scott, A. C., Young, R. F., & Fedorak, P. M. (2008a). Comparison of GC-MS and FTIR methods for quantifying naphthenic acids in water samples. *Chemosphere, 73*(8), 1258-1264.

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

Semadeni, M., Stocker, D. W., & Kerr, J. A. (1995). The temperature dependence of the OH radical reactions with some aromatic compounds under simulated tropospheric conditions. *International Journal of Chemical Kinetics, 27*(3), 287-304.

Shu, Z., Li, C., Belosevic, M., Bolton, J. R., & El-Din, M. G. (2014). Application of a solar UV/chlorine advanced oxidation process to oil sands process-affected water remediation. *Environmental Science & Technology, 48*(16), 9692-9701.

Smith, R. M., & Martell, A. E. (1987). Critical stability constants, enthalpies and entropies for the formation of metal complexes of aminopolycarboxylic acids and carboxylic acids. *Science of the Total Environment, 64*(1-2), 125-147.

Sorvari, J., & Sillanpää, M. (1996). Influence of metal complex formation on heavy metal and free EDTA and DTPA acute toxicity determined by Daphnia magna. *Chemosphere, 33*(6), 1119-1127.

Spuhler, D., Rengifo-Herrera, J. A., & Pulgarin, C. (2010). The effect of Fe^{2+}, Fe^{3+}, H_2O_2 and the photo-Fenton reagent at near neutral pH on the solar disinfection (SODIS) at low temperatures of water containing Escherichia coli K12. *Applied Catalysis B: Environmental, 96*(1), 126-141.

Subramanian, B., Christou, S., Efstathiou, A., Namboodiri, V., & Dionysiou, D. (2011). Regeneration of three-way automobile catalysts using biodegradable metal chelating agent—S, S-ethylenediamine disuccinic acid (S, S-EDDS). *Journal of Hazardous Materials, 186*(2), 999-1006.

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

Sunda, W. G., Engel, D. W., & Thuotte, R. M. (1978). Effect of chemical speciation on toxicity of cadmium to grass shrimp, Palaemonetes pugio: importance of free cadmium ion. *Environmental Science & Technology, 12*(4), 409-413.

Tachiev, G., Roth, J., & Bowers, A. (2000). Kinetics of hydrogen peroxide decomposition with complexed and “free” iron catalysts. *International Journal of Chemical Kinetics, 32*(1), 24-35.

Tolkacheva, L., Saprunova, T., Nikolskii, V., & Yakovlev, A (2012). Environmentally friendly complexones. The thermodynamic characteristics of the formation of Al^{3+} ion complexes with ethylenediaminedisuccinic acid in aqueous solutions. *Chemistry Journal of Moldova. Gneral, Industrial and Ecological Chemistry*, 7(1), 70-73.

Tomita, Y., Ando, T., & Ueno, K. (1965). Infrared Spectra of Nitrilotriacetate Chelates in Aqueous Solution. *The Journal of Physical Chemistry, 69*(2), 404-407.

Trott, T., Henwood, R. W., & Langford, C. H. (1972). Sunliight photochemistry of ferric nitrilotriacetate complexes. *Environmental science & technology, 6*(4), 367-368.

Vermilyea, A. W., & Voelker, B. M. (2009). Photo-Fenton reaction at near neutral pH. *Environmental Science & Technology, 43*(18), 6927-6933.

von Sonntag, C., Dowideit, P., Fang, X., Mertens, R., Pan, X., Schuchmann, M. N., & Schuchmann, H.-P. (1997). The fate of peroxyl radicals in aqueous solution. *Water Science and Technology, 35*(4), 9-15.

Walling, C., Kurz, M., & Schugar, H. J. (1970). Iron (III)-ethylenediaminetetraacetic acid-peroxide system. *Inorganic Chemistry, 9*(4), 931-937.

Wang, C., Klamerth, N., Huang, R., Elnakar, H., & Gamal El-Din, M. (2016). Oxidation of Oil Sand Process-affected Water by Potassium Ferrate (VI). *Environmental Science & Technology, 50(8), 4238-4247*.

Wang, N., Chelme-Ayala, P., Perez-Estrada, L., Garcia-Garcia, E., Pun, J., Martin, J. W., . . . Gamal El-Din, M. (2013a). Impact of ozonation on naphthenic acids speciation and toxicity of oil sands process-affected water to Vibrio fischeri and mammalian immune system. *Environmental Science & Technology, 47*(12), 6518-6526.

Wang, Y. N. (2011). Application of Coagulation-Flocculation Process for Treating Oil Sands Process-Affected Water. (Master of Science), University of Alberta, Edmonton, AB, Canada.

Wang, Z., Bush, R. T., & Liu, J. (2013b). Arsenic(III) and iron(II) co-oxidation by oxygen and hydrogen peroxide: Divergent reactions in the presence of organic ligands. *Chemosphere, 93*(9), 1936-1941.

Wei, C. S., Huang, W. Y., Zhang, R. J., Wang, Y. H., Luo, L. M., Mo, H., & Xiao, L. H. (2014). Assessment of the Fe^{3+}-EDTA Complex in UV-Fenton-Like Processes: The Degradation of Methylene Blue. Paper presented at the Applied Mechanics and Materials.

Whitburn, J. S., Wilkinson, S. D., & Williams, D. R. (1999). Chemical speciation of ethylenediamine-N, N′ -disuccinic acid (EDDS) and its metal complexes in solution. *Chemical Speciation & Bioavailability, 11*(3), 85-93.

Willkinson, S. D. (1998). Chemical Speciation of a Biodegradable Replacement Ligand for EDTA. (Doctor of Philosophy), University of Wales, Cardiff.

Wood, P. M. (1988). The potential diagram for oxygen at pH 7. *Biochemical Journal, 253*(1), 287-289.

Wu, Y., Passananti, M., Brigante, M., Dong, W., & Mailhot, G. (2014). Fe(III)–EDDS complex in Fenton and photo-Fenton processes: from the radical formation to the degradation of a target compound. *Environmental Science And Pollution Research, 21*(21), 12154-12162.

Xue, X., Hanna, K., Despas, C., Wu, F., & Deng, N. (2009). Effect of chelating agent on the oxidation rate of PCP in the magnetite/H_2O_2 system at neutral pH. *Journal of Molecular Catalysis A: Chemical, 311*(1), 29-35.

Yu, X., Zuo, J., Tang, X., Li, R., Li, Z., & Zhang, F. (2014). Toxicity evaluation of pharmaceutical wastewaters using the alga Scenedesmus obliquus and the bacterium Vibrio fischeri. *Journal of Hazardous Materials*, 266, 68-74.

Zhang, L. H., Zhu, Z. L., Zhang, R. H., Zheng, C. S., Zhang, H., Qiu, Y. L., & Zhao, J. F. (2008). Extraction of copper from sewage sludge using biodegradable chelant EDDS. *Journal of Environmental Sciences, 20*(8), 970-974.

Zhang, Y., Klamerth, N., Ashagre Messele, S., Chelme-Ayala, P., & Gamal El-Din, M. (2016a). Kinetics Study on the Degradation of a Model Naphthenic Acid by Ethylenediamine-N,N'-Disuccinic Acid-Modified Fenton Process. *Journal of Hazardous Materials*, under review.

Zhang, Y., Klamerth, N., & Gamal El-Din, M. (2016b). Degradation of a Model Naphthenic Acid by Nitrilotriacetic Acid-Modified Fenton Process. *Chemical Engineering Journal, 292*, 340-347.

Zhang, Y., McPhedran, K. N., & Gamal El-Din, M. (2015). Pseudomonads biodegradation of aromatic compounds in oil sands process-affected water. *Science of the Total Environment, 521*, 59-67.

7 GENERAL CONCLUSIONS AND RECOMMENDATIONS

7.1 Thesis Overview

OSPW generated from an alkaline hot water process for bitumen extraction in the oil sands industry has brought several environmental concerns, such as the possible contamination of groundwaters by long-time filtration, the leaching of NAs from tailing ponds to surface waters, and the toxicity of OSPW to aquatic organisms due to the presence of large amount of recalcitrant NAs. Various treatment processes, such as biodegradation, adsorption, and membrane filtration, have been employed to treat OSPW at the bench scale. However, none of them can be successfully applied on the OSPW remediation at the industrial scale due to the flaws of these processes, such as long half-life of NAs in the biodegradation and the failure of the process in the removal of NAs with large molecular weights, poor performance of the adsorption approach in the removal of target pollutants in OSPW, and membrane durability and cost limitation for membrane filtration. Significant research gaps still exist for the treatment of OSPW in practice. As such, researchers have been focusing on the development of new and feasible approaches for the OSPW remediation.

To address these needs, in this research NTA/EDDS-modified Fenton process with or without the presence of UV irradiation has been employed to degrade the contaminants in OSPW at natural pH and reduce the overall toxicity of OSPW. In the first stage of the research, CHA as a simple model compound for NAs was used to optimize the reaction conditions and investigate the reaction mechanisms of the NTA/EDDS-Fenton processes. The doses of the reagents (H_2O_2 and Fe-NTA/EDDS), oxidizing species, CHA oxidation products, and reaction kinetics of $^{\bullet}OH$ with CHA, NTA, and EDDS were investigated. The UV irradiation was introduced to the treatment process in the second stage of the research. The efficiency of seven processes (UV irradiation, UV-H_2O_2, Fenton, UV-Fenton, NTA-Fenton, UV-Fe-NTA, and UV-NTA-Fenton) was studied and compared in the CHA, H_2O_2, and NTA decomposition. In the third stage of the research, the removal of phenol and H_2S as toxic contaminants in OSPW was investigated in the Fe(III)TPP-catalytic desulfurization process. At the end of the research, UV-NTA/EDDS-Fenton processes were applied and compared on the removal of AEF and aromatics in OSPW and on the decrease of the overall toxicity of OSPW towards *Vibrio fischeri*. UV-NTA-Fenton was also compared with UV-H_2O_2 and NTA-Fenton processes on the total NA removal.

7.2 Conclusions

The main conclusions of the research are listed as follows:

- NTA/EDDS-Fenton processes were very efficient in degrading CHA at pH 8. 87% and 64% CHA removal was achieved for NTA-Fenton (4.41 mM H_2O_2, 0.27 mM Fe, and NTA:Fe = 2:1) and EDDS-Fenton (2.94 mM H_2O_2, 0.45 mM Fe, and EDDS:Fe = 2:1), respectively. The CHA degradation was closely related to the dose of H_2O_2 in both processes. Fe-NTA dose affected primarily the overall reaction time and Fe-EDDS dose affected the CHA removal and reaction time.
- The consecutive addition of H_2O_2 and Fe-EDDS resulted in a higher removal of CHA in the EDDS-Fenton process. However, the influence of H_2O_2 dosing mode on the CHA removal was negligible in the NTA-Fenton process. The difference was primarily due to the different reactivity of EDDS and NTA towards $^{\bullet}OH$ with a second-order rate constant at pH 8 of $2.48 \pm 0.43 \times 10^9\ M^{-1}s^{-1}$ for the former and $4.77 \pm 0.24 \times 10^8\ M^{-1}s^{-1}$ for the latter, respectively.

- ${}^{\bullet}OH$ was the main radical responsible for the CHA degradation. A second-order rate constant of ${}^{\bullet}OH$ with CHA at pH 8 was obtained in this research as $4.09 \pm 0.39 \times 10^9$ $M^{-1}s^{-1}$. The role of ${}^{\bullet}O_2^-$ was probably through its influence on ${}^{\bullet}OH$ generation. Oxy-CHA, hydroxyl-CHA, and dihydroxyl-CHA were detected as the CHA oxidation products because of the ${}^{\bullet}OH$ attack.

- Based on the redox potentials of Fe(III/II)NTA, Fe(III/II)EDDS, $O_2/O_2^{\bullet-}$, and $H_2O_2/O_2^{\bullet-}$, it was concluded that H_2O_2 could not reduce the Fe(III)NTA/EDDS complex, and the reduction of the complex was $O_2^{\bullet-}$-dependent not H_2O_2-dependent.

- Compared to UV-H_2O_2, Fenton, UV-Fenton, NTA-Fenton, and UV-Fe-NTA processes, UV-NTA-Fenton at pH 3 exhibited the highest H_2O_2 decomposition (100% in 25 min), CHA removal (100% in 12 min) with a rate constant of 0.27 ± 0.025 min^{-1}, and NTA degradation (100% in 6 min).

- ${}^{\bullet}OH$ generation in the H_2O_2 photolysis under MP UV lamp irradiation was much higher than that under LP UV lamp irradiation.

- The total amount of Fe at the end of reaction in the UV-NTA-Fenton system at pH 8 was much higher than that in the UV-Fe-NTA system, which was primarily attributed to the formation of H_2O_2-Fe(III)NTA adduct in the former system.

- The use of borate buffer benefited the Fe amount due to the co-complexing effect of tetraborate ion; however, the CHA degradation in the UV-NTA-Fenton process in the buffer solution was much lower than that in MilliQ water (67.8% in 60 min in the former solution compared to 92.3% in the latter).

- The formation of Fe(III)TPP-HS^- intermediate in the reaction of Fe(III)TPP and HS^- was proposed and considered primarily responsible for the high absorbance above 300 nm where Fe(III)TPP and HS^- solution showed no absorption.

- 91.8%, 90.2%, 88.5% and 85.7% of HS^- were removed with Fe(III)TPP in 50 min for HS^- initial doses of 2, 4, 6, and 8 mM, respectively. A second-order rate constant of the direct reaction between Fe(III)TPP and HS^- at pH 9 was obtained as $4.36\pm0.17\ M^{-1}s^{-1}$.
- The oxidation of Fe(II)TPP by O_2 was found to follow a four-step reaction mechanism, and the reaction kinetic parameters were calculated based on the $E_{1/2}$ values of Fe(III/II)TPP (0.061, -0.014, -0.039, -0.064, -0.089, and -0.139 V (vs. SHE) at pH 4, 5, 6, 7, 8, and 9, respectively).
- Low level of phenol degradation was achieved in the Fe(III)TPP-catalytic desulfurization process probably due to the scavenging effect of other species on $^{\bullet}OH$.
- No significant difference was observed for the photolysis rate of Fe-NTA and Fe-EDDS under the same conditions in MilliQ water. OSPW matrix hindered the degradation of Fe-NTA/EDDS primarily due to the presence of some chelating agents (such as fulvic and humic acids) and heavy metal ions.
- UV-NTA-Fenton was much more efficient than UV-EDDS-Fenton in the removal of AEF and aromatics. Both processes promoted the acute toxicity of OSPW towards *Vibrio fischeri*. NTA toxicity did not change much during the photolysis of Fe(III)NTA; however, the acute toxicity of EDDS increased significantly as the photolysis of Fe(III)EDDS proceeded.
- Considering the contaminants removal and toxicity effect, NTA is much better than EDDS for the application of UV-chelate-Fenton processes in the treatment of OSPW.

- UV-NTA-Fenton exhibited higher efficiency than UV-H_2O_2 and NTA-Fenton processes in the removal of total classical NAs, NA+O, and NA+2O.
- UV-NTA-Fenton is a very promising approach for the treatment of OSPW. The findings obtained in this study have significant impact for the further development of this process and OSPW remediation.

7.3 Recommendations

The following recommendations were drawn based on the results obtained in this study.

- Degradation kinetics of other model compounds for NAs with structures dissimilar to CHA should be investigated to confirm the influence of the NA structures on the reactivity towards $^{\bullet}OH$.
- The scavenging effect of the high amount of inorganic ions in OSPW, such as chloride, sulfate, and bicarbonate, on $^{\bullet}OH$ needs to be investigated.
- More studies should be conducted on the influence of OSPW matrix on the stability of Fe-NTA/EDDS and reactivity of the complex towards H_2O_2.
- The toxicity of treated OSPW, NTA, EDDS, and their products warrants other toxicity studies (such as goldfish primary kidney macrophage (PKMs)).
- The total cost should be considered for the application of UV-NTA-Fenton in the treatment of OSPW *in situ*, especially the electricity cost for UV irradiation.
- The combination of UV-NTA-Fenton with biodegradation process might be an economical and efficient approach for the organic and toxicity removal in the OSPW

remediation, which deserves more studies to confirm its effectiveness.

8 APPENDICES

8.1 Appendix A: Chemicals and Analytical Instruments

Table 8-1. Structures and molecule weights of CHA, NTA, and EDDS

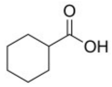
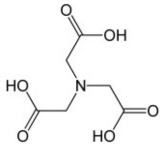
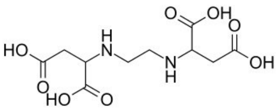
Name	**Formula**	**Molecule weight**	**Structure**
Cyclohexanecarboxylic acid (CHA)	$C_7H_{12}O_2$	128.17	
Nitrilotriacetic acid (NTA)	$C_6H_9NO_6$	191.14	
Ethylenediamine-N,N'-disuccinic acid (EDDS)	$C_{10}H_{16}N_2O_2$	292.24	

Table 8-2. Analytical instruments

Parameter	Analytical instrument
CHA	HPLC-ion trap MS (Varian 500-MS)
NTA, EDDS, and pCBA	HPLC-UV (Agilent Technologies, 1260Infinity)
H_2O_2	Titanium (IV) oxysulfate method (DIN 38402H15 at 410 nm), GENESYS™ 10S UV-Vis spectrophotometer
Fe(II) and Fe(III)	Spectrophotometric method (ISO 6332), GENESYS™ 10S UV-Vis spectrophotometer
Chemical oxygen demand (COD)	COD analyzer (Thermo Scientific, Genesys 20)
Dissolved organic carbon (DOC)	TOC (total organic carbon) analyzer (Thermo Scientific, Genesys 20)
Total acid-extractable organics	FT-IR spectrometer (Thermo Scientific, Nicolet 8700)
Toxicity	Microtox analysis (Microtox, M500)
pH	pH meter (Fisher Scientific, AR 50)
HS^-	Methylene Blue Method 8131 (HACH)
Phenol	HPLC-UV (WatersTM 717 plus Autosampler, Waters 600-MS System Controller, and WatersTM 996 photodiode Array Detector).
$E_{1/2}$	Metrohm Autolab electrochemical workstation
NAs	Ultra-performance liquid chromatography time-of-flight mass spectrometry (UPLC TOF-MS)
Fluorophore compounds	PerkinElmer Spectrum 100 FT-IR Spectrometer (PerkinElmer Life and Analytical Sciences, Woodbridge, ON, CA)
Synchronous fluorescence spectra	Varian Cary Eclipse fluorescence spectrometer (Mississauga, ON, Canada)
^{1}H nuclear magnetic resonance analysis	Agilent/Varian Unity Inova Spectrometer (Agilent Technologies, Santa Clara, CA, USA)

Figure 8-1. Medium-pressure UV lamp apparatus.

8.2 Appendix B: Results of Preliminary Experiments

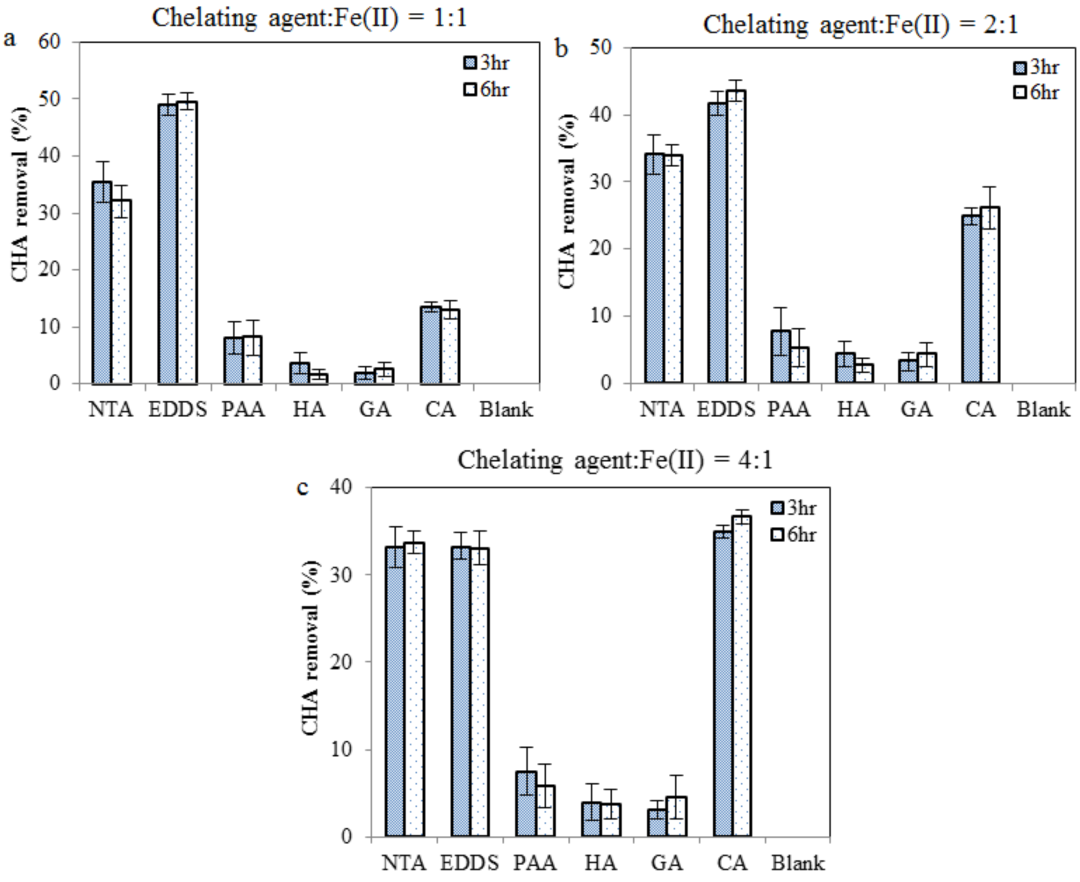


Figure 8-2. Removal of CHA in modified Fenton processes with different chelating agents a) HA=50mg/L; b) HA=100mg/L, and c) HA=200mg/L ($[CHA]_0$ = 0.39 mM, $[H_2O_2]_0$ = 1.47 mM, and $[Fe]_0$ = 0.89 mM). PAA: polyacrylic acids, HA: humic acid, GA: glutamic acid, and CA: citric acid.

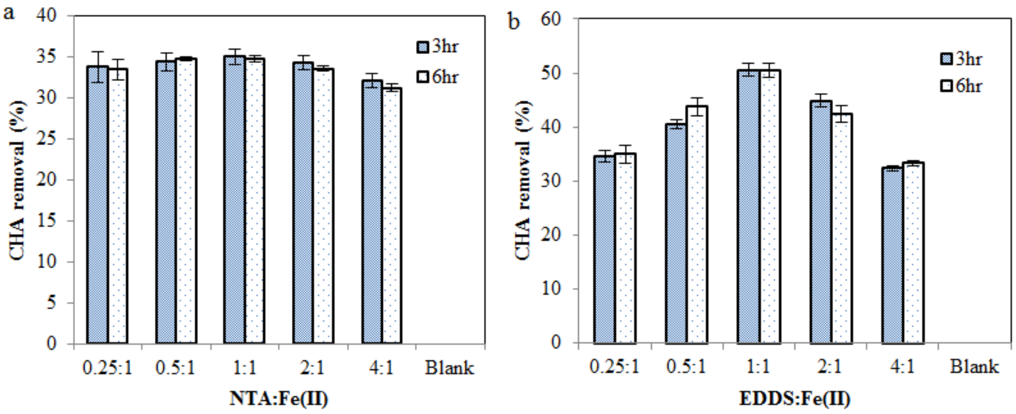


Figure 8-3. Removal of CHA with increasing ratios of chelating agents:Fe a) NTA and b) EDDS in the modified Fenton processes ($[CHA]_0 = 0.39$ mM, $[H_2O_2]_0 = 1.47$ mM, and $[Fe]_0 = 0.89$ mM).

9 BIBLIOGRAPHY

Abida, O., Mailhot, G., Litter, M., & Bolte, M. (2006). Impact of iron-complex (Fe(III)-NTA) on photoinduced degradation of 4-chlorophenol in aqueous solution. *Photochemical & photobiological sciences : Official journal of the European Photochemistry Association and the European Society for Photobiology, 5*(4), 395-402.

Adhoum, N., & Monser, L. (2004). Removal of phthalate on modified activated carbon: application to the treatment of industrial wastewater. *Separation and Purification Technology, 38*(3), 233-239.

Afzal, A. (2013). Application of Advanced Oxidation Processes for Treatment of Napthenic Acids in Oil Sands Process Water. (Doctor of Philosophy), University of Alberta, Edmonton, Alberta, Canada.

Afzal, A., Drzewicz, P., Martin, J. W., & Gamal El-Din, M. (2012a). Decomposition of cyclohexanoic acid by the UV/H_2O_2 process under various conditions. *Science of the Total Environment, 426*, 387-392.

Afzal, A., Drzewicz, P., Perez-Estrada, L. A., Chen, Y., Martin, J. W., & Gamal El-Din, M. (2012b). Effect of molecular structure on the relative reactivity of naphthenic acids in the UV/H_2O_2 advanced oxidation process. *Environmental Science & Technology, 46*(19), 10727-10734.

Al-Tawabini, B. S. (2002). Treatment of Water Contaminated with Dimethyl Phthalate by Fenton, Photo-Fenton and UV/H_2O_2 Processes. (Docter of Philosophy), King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia.

Alberta Energy and Utilities Board. (2005). Alberta's reserves 2004 and supply/demand outlook 2005-2010. Calgary, Alberta, Canada: Alberta Energy and Utilities Board.

Alcántara, S., Velasco, A., Muñoz, A., Cid, J., Revah, S., & Razo-Flores, E. (2004). Hydrogen sulfide oxidation by a microbial consortium in a recirculation reactor system: sulfur formation under oxygen limitation and removal of phenols. *Environmental Science & Technology, 38*(3), 918-923.

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

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

Alpatova, A., Kim, E.-S., Dong, S., Sun, N., Chelme-Ayala, P., & Gamal El-Din, M. (2014). Treatment of oil sands process-affected water with ceramic ultrafiltration membrane: Effects of operating conditions on membrane performance. *Separation and Purification Technology*, 122, 170-182.

Anbar, M., Meyerstein, D., & Neta, P. (1966). Reactivity of aliphatic compounds towards hydroxyl radicals. *Journal of the Chemical Society B: Physical Organic*, 742-747.

Anderegg, G. (1982). Critical survey of stability constants of NTA complexes. *Pure and Applied Chemistry, 54*(12), 2693-2758.

Anderegg, G. (1986). The stability of iron (III) complexes formed below pH= 3 with glycinate, iminodiacetate, β-hydroxyethyliminodiacetate, N, N-di-(Hydroxyethyl)-glycinate, nitrilotriacetate and triethanolamine. *Inorganica Chimica Acta, 121*(2), 229-231.

Anderson, J. C., Wiseman, S. B., Wang, N., Moustafa, A., Perez-Estrada, L., Gamal El-Din, M., . . . Giesy, J. P. (2012). Effectiveness of ozonation treatment in eliminating toxicity of oil sands process-affected water to Chironomus dilutus. *Environmental Science & Technology, 46*(1), 486-493.

Anderson, R. L., Bishop, W. E., Campbell, R. L., & Becking, G. C. (1985). A review of the environmental and mammalian toxicology of nitrilotriacetic acid. *CRC Critical Reviews in Toxicology, 15*(1), 1-102.

Andrianirinaharivelo, S. L., Pilichowski, J. F., & Bolte, M. (1993). Nitrilotriacetic acid transformation photo-induced by complexation with iron(III) in aqueous solution. *Transition Metal Chemistry, 18*(1), 37-41.

Arana, J., Rendón, E. T., Rodrıguez, J. D., Melián, J. H., Dıaz, O. G., & Pena, J. P. (2001). Highly concentrated phenolic wastewater treatment by the Photo-Fenton reaction, mechanism study by FTIR-ATR. *Chemosphere, 44*(5), 1017-1023.

Armstrong, S. A. (2008). Dissipation and phytotoxicity of oil sands naphthenic acids in wetland plants. (Docter of Philosophy), University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

Bard, A. J., & Faulkner, L. R. (1980). Electrochemical methods: fundamentals and applications (Vol. 2): Wiley, New York.

Basu, S., & Wei, I. W. (1998a). Advanced chemical oxidation of 2, 4, 6 trichlorophenol in aqueous phase by fenton's reagent-part i: effects of the amounts of oxidant and catalyst on the treatment reaction. *Chemical Engineering Communications, 164*(1), 111-137.

Basu, S., & Wei, I. W. (1998b). Advanced chemical oxidation of 2, 4, 6 trichlorophenol in aqueous phase by Fenton's Reagent-Part II: Effects of various reaction parameters on the treatment reaction. *Chemical Engineering Communications, 164*(1), 139-151.

Bautista, P., Mohedano, A. F., Casas, J. A., Zazo, J. A., & Rodriguez, J. J. (2008). An overview of the application of Fenton oxidation to industrial wastewaters treatment. *Journal of Chemical Technology and Biotechnology, 83*(10), 1323-1338.

Beeta, S. (2011). Removal of Benzene from Wastewater by Enzyme-Catalyzed Oxidative Polymerization Combined with a Modified Fenton Reaction. (Doctor of Philosophy), University of Windsor, Windsor, Ontario, Canada.

Behar, D., Czapski, G., Rabani, J., Dorfman, L. M., & Schwarz, H. A. (1970). Acid dissociation constant and decay kinetics of the perhydroxyl radical. *Journal of Physical Chemistry, 74*(17), 3209-3213.

Biaglow, J. E., & Kachur, A. V. (1997). The generation of hydroxyl radicals in the reaction of molecular oxygen with polyphosphate complexes of ferrous ion. *Radiation Research, 148*(2), 181-187.

Bielski, B. H. J., Cabelli, D. E., & Arudi, R. L. (1985). Reactivity of H_2O_2/O_2^- radicals in aqueous solution. *Journal of Physical and Chemical Reference Data, 4*, 1041-1100.

Bissey, L. L., Smith, J. L., & Watts, R. J. (2006). Soil organic matter-hydrogen peroxide dynamics in the treatment of contaminated soils and groundwater using catalyzed H_2O_2 propagations (modified Fenton's reagent). *Water Research, 40*(13), 2477-2484.

Bobinger, S., & Andersson, J. T. (2009). Photooxidation products of polycyclic aromatic compounds containing sulfur. *Environmental Science & Technology, 43*(21), 8119-8125.

Bojanowska-Czajka, A., Drzewicz, P., Kozyra, C., Nałęcz-Jawecki, G., Sawicki, J., Szostek, B., & Trojanowicz, M. (2006). Radiolytic degradation of herbicide 4-chloro-2-methyl phenoxyacetic acid (MCPA) by γ-radiation for environmental protection. *Ecotoxicology and Environmental Safety, 65*(2), 265-277.

Bolton, H., Girvin, D. C., Plymale, A. E., Harvey, S. D., & Workman, D. J. (1996). Degradation of metal-nitrilotriacetate complexes by Chelatobacter heintzii. *Environmental Science & Technology, 30*(3), 931-938.

Borkowski, M., Richmann, M., Reed, D. T., & Xiong, Y. (2010). Complexation of Nd (III) with tetraborate ion and its effect on actinide (III) solubility in WIPP brine. *Radiochimica Acta, 98*(9-11), 577-582.

Bose, P., Aparna, B. M., & Kumar, S. (2002). Critical evaluation of treatment strategies involving adsorption and chelation for wastewater containing copper, zinc and cyanide. *Advances in Environmental Research, 7*(1), 179-195.

Brown, E., & Mazzarella, J. (1987). Mechanism of oxidation of ferrous polydentate complexes by dioxygen. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 222*(1), 173-192.

Bucheli ‐ Witschel, M., & Egli, T. (2001). Environmental fate and microbial degradation of aminopolycarboxylic acids. *FEMS Microbiology Reviews, 25*(1), 69-106.

Bunescu, A., Besse-Hoggan, P., Sancelme, M., Mailhot, G., & Delort, A.-M. (2008). Fate of the nitrilotriacetic Acid-Fe (III) complex during photodegradation and biodegradation by Rhodococcus rhodochrous. *Applied and Environmental Microbiology, 74*(20), 6320-6326.

Burns, J. M., Craig, P. S., Shaw, T. J., & Ferry, J. L. (2010). Multivariate Examination of Fe(II)/Fe(III) Cycling and Consequent Hydroxyl Radical Generation†. *Environmental Science & Technology, 44*(19), 7226-7231.

Burrowes, A., Marsh, R., Ramdin, N., Evans, C., Kirsch, M., Philp, L., . . . Sankey, G. (2005). Alberta's reserves 2004 and supply/demand outlook 2005-2014. Calgary, Alberta, Canada: Alberta Energy and Utilities Board.

Buxton, G. V., Greenstock, C. L., Helman, W. P., & Ross, A. B. (1988). Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals. *Journal of Physical and Chemical Reference Data, 17*, 513-886.

Cadena, F., Garcia, R., & Peters, R. W. (1990). Adsorption of benzene from aqueous solutions by bentonite treated with quaternary amines. *Environmental Progress, 9*(4), 245-253.

Camargo, J. A., Alonso, A., & Salamanca, A. (2005). Nitrate toxicity to aquatic animals: a review with new data for freshwater invertebrates. *Chemosphere, 58*(9), 1255-1267.

Chen, D., Martell, A. E., & McManus, D. (1995). Studies on the mechanism of chelate degradation in iron-based, liquid redox H_2S removal processes. *Canadian Journal of Chemistry, 73*(2), 264-274.

Chen, K. Y., & Morris, J. C. (1972). Kinetics of oxidation of aqueous sulfide by oxygen. *Environmental Science & Technology, 6*(6), 529-537.

Chen, P. H. (1997). Adsorption of organic compounds in water using a synthetic adsorbent. *Environment International, 23*(1), 63-73.

Chowdhury, M. J., & Blust, R. (2002). Bioavailability of waterborne strontium to the common carp, Cyprinus carpio, in complexing environments. *Aquatic Toxicology, 58*(3), 215-227.

Clayden, J., Greeves, N., & Warren, S. (2012). Organic Chemistry 2012: Oxford University Press: Oxford, New York.

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

Clemente, J. S., Prasad, N., MacKinnon, M. D., & Fedorak, P. M. (2003). A statistical comparison of naphthenic acids characterized by gas chromatography-mass spectrometry. *Chemosphere, 50*(10), 1265-1274.

Coates, J. (2000). Interpretation of infrared spectra, a practical approach. *Encyclopedia of Analytical Chemistry*.

Colodette, J., Rothenberg, S., & Dence, C. (1988). Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemimechanical pulps. I: hydrogen peroxide stability in the absence of stabilizing systems. *Journal of Pulp and Paper Science, 14*(6), J126-J132.

Cuculić, V., Pižeta, I., & Branica, M. (2005). Voltammetry of Dissolved Iron (III)–Nitrilotriacetate–Hydroxide System in Water Solution. *Electroanalysis, 17*(23), 2129-2136.

Dao, Y. H., & De Laat, J. (2011). Hydroxyl radical involvement in the decomposition of hydrogen peroxide by ferrous and ferric-nitrilotriacetate complexes at neutral pH. *Water Research, 45*(11), 3309-3317.

De, A. K., Chaudhuri, B., Bhattacharjee, S., & Dutta, B. K. (1999). Estimation of $^{\bullet}OH$ radical reaction rate constants for phenol and chlorinated phenols using UV/H_2O_2 photo-oxidation. *Journal of Hazardous Materials, 64*(1), 91-104.

De la Cruz, N., Gimenez, J., Esplugas, S., Grandjean, D., de Alencastro, L. F., & Pulgarin, C. (2012). Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. *Water Research, 46*(6), 1947-1957.

De Laat, J., Dao, Y. H., Hamdi El Najjar, N., & Daou, C. (2011). Effect of some parameters on the rate of the catalysed decomposition of hydrogen peroxide by iron(III)-nitrilotriacetate in water. *Water Research, 45*(17), 5654-5664.

De Laat, J., & Gallard, H. (1999). Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modeling. *Environmental Science & Technology, 33*(16), 2726-2732.

De Laat, J., & Legube, B. (1998). Influence du pH sur la vitesse d'oxydation de compose′ s organiques par Fe II/H_2O_2. Me′ canismes re′ actionnels et mode′ lisation. *New Journal of Chemistry, 22*(3), 263-268.

De Latt, J., & Gallard, H. (1999). Catalytic decomposition of hydrogen peroxide by Fe(III) in homogenerous aqueous solution: Mechanism and kinetic modeling. *Environmental Science & Tecbnology, 33*, 2726-2732.

DeBerry, D. (1997). Chemical evolution of liquid redox processes. *Environmental Progress, 16*(3), 193-199.

DeBerry, D. W. (1993). Rates and mechanisms of reaction of hydrogen sulfide with Iron chelates. Topical Report. Gas Research Institute.

DeBerry, D. W., Petrinec, B., & Trofe, T. (1991). New insights from investigation of fundamental mechanism of liquid redox chemistry. Paper presented at the Liquid Redox Sulfur Recovery Conference, Texas.

DeLeon, E. R., Stoy, G. F., & Olson, K. R. (2012). Passive loss of hydrogen sulfide in biological experiments. *Analytical Biochemistry, 421*(1), 203-207.

Demmink, J., & Beenackers, A. (1997). Oxidation of ferrous nitrilotriacetic acid with oxygen: A model for oxygen mass transfer parallel to reaction kinetics. *Industrial & Engineering Chemistry Research, 36*(6), 1989-2005.

Demmink, J., & Beenackers, A. (1998). Gas desulfurization with ferric chelates of EDTA and HEDTA: new model for the oxidative absorption of hydrogen sulfide. *Industrial & Engineering Chemistry Research, 37*(4), 1444-1453.

Deng, N., Wu, F., Luo, F., & Liu, Z. (1997). Photodegradation of dyes in aqueous solutions containing Fe(III)-oxalato complexes. *Chemosphere, 35*(11), 2697-2706.

Deng, N., Wu, F., Luo, F., & Xiao, M. (1998). Ferric citrate-induced photodegradation of dyes in aqueous solutions. *Chemosphere, 36*(15), 3101-3112.

Deshmukh, G. M., Shete, A., & Pawar, D. M. (2013). Oxidative absorption of hydrogen sulfide using an iron - chelate based process: chelate degradation. *Journal of Chemical Technology and Biotechnology, 88*(3), 432-436.

Dinh, T. V. (1978). Multicomponent analysis by synchronous luminescence spectrometry. *Analytical Chemistry, 50*(3), 396-401.

Dokholyan, B. K., & Magomedov, A. K. (1984). The effect of sodium naphthenate on the viability and physiological and biochemical indices of fish. *Voprosy Ikhtiologii, 23*(6), 11-26.

Dominski, M. (2007). Surface mined oil sands: tailings practices, performance, and projections. Paper presented at the The 3rd international Heavy Oil Conference, Calgary, AB, Canada.

Dorn, P. B., Van Compernolle, R., Mueller, G. R., Sun, P. J., Glaze, D. E., Hwang, J. C., & Hansen, S. R. (1992). Toxicity identification and derivation of a water quality based effluent limit for a west coast refinery. Lancasyer, PA, USA: Technomic Pub Inc.

Dos Santos Afonso, M., & Stumm, W. (1992). Reductive dissolution of iron (III)(hydr) oxides by hydrogen sulfide. *Langmuir, 8*(6), 1671-1675.

Doujaiji, B., & Al-Tawfiq, J. A. (2010). Hydrogen sulfide exposure in an adult male. *Annals of Saudi Medicine, 30*(1), 76-80.

Doyle, D. H., & Brown, A. B. (1997). Field test of produced water treatment with polymer modified bentonite. Paper presented at the SPE Rocky Mountain Regional Meeting.

Drzewicz, P., Afzal, A., Gamal El-Din, M., & Martin, J. W. (2010). 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, 114*(45), 12067-12074.

Dubinina, E., Gavrovskaya, S., Kuzmich, E., Leonova, N., Morozova, M., Kovrugina, S., & Smirnova, T. (2002). Oxidative modification of proteins: oxidation of tryptophan and production of dityrosine in purified proteins using Fenton's system. *Biochemistry (Moscow), 67*(3), 343-350.

ElShafei Gamal, M. S., Yehia, F. Z., Dimitry, O. I. H., Badawi, A. M., & Eshaq, G. (2010). Degradation of nitrobenzene at near neutral pH using Fe^{2+}-glutamate complex as a homogeneous Fenton catalyst. *Applied Catalysis B: Environmental, 99*(1-2), 242-247.

Environment Canada. (1998). Canadian water quality guidelines for phenols. Ottawa, Canada: Unpub.

ERCB, E. R. C. B. (2012). Alberta's Energy Reserves 2011 and Supply/Demand Outlook 2012-2021. In Government of Alberta, C., AB, Canada, 2012 (Ed.).

Esplugas, S., Bila, D. M., Krause, L. G. T., & Dezotti, M. (2007). Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. *Journal of Hazardous Materials, 149*(3), 631-642.

Fabbricino, M., Ferraro, A., Del Giudice, G., & d'Antonio, L. (2013). Current views on EDDS use for ex situ washing of potentially toxic metal contaminated soils. *Reviews in Environmental Science and Bio/Technology, 12*(4), 391-398.

Fattah, Q., & Wort, D. (1970). Metabolic responses of bush bean plants to naphthenate application. *Canadian Journal of Botany, 48*(5), 861-866.

Faust, B. C., & Hoigné, J. (1990). Photolysis of Fe(III)-hydroxy complexes as sources of OH radicals in clouds, fog and rain. *Atmospheric Environment. Part A. General Topics, 24*(1), 79-89.

Faust, B. C., & Zepp, R. G. (1993). Photochemistry of aqueous iron(III)-polycarboxylate complexes: Roles in the chemistry of atmospheric and surface waters. *Environmental Science & Technology, 27*(12), 2517-2522.

Feng, W., & Nansheng, D. (2000). Photochemistry of hydrolytic iron(III) species and photoinduced degradation of organic compounds. A minireview. *Chemosphere, 41*(8), 1137-1147.

Fenton, H. J. H. (1894). Oxidation of Tartaric acid in the presence of iron. *Journal of the Chemical Society, Transactions, 65*, 899-910.

Flury, M., & Gimmi, T. (2002). Solute diffusion, in Methods of Soil Analysis: Part 4 Physical Methods. Madison, WI: Soil Science Society of America.

Francis, K. C., Cummins, D., & Oakes, J. (1985). Kinetic and structural investigations of [Fe^{III} (edta)]-[edta= ethylenediaminetetra-acetate (4–)] catalysed decomposition of hydrogen peroxide. *Journal of the Chemical Society, Dalton Transactions*(3), 493-501.

Frank, R. A., Fischer, K., Kavanagh, R., Burnison, B. K., Arsenault, G., Headley, J. V., . . . Solomon, K. R. (2008). Effect of carboxylic acid content on the acute toxicity of oil sands naphthenic acids. *Environmental Science & Technology, 43*(2), 266-271.

Frankenfeld, J. W. (1973). *In* "Proceedings of Joint Conference on Prevention and Control of Oil Spills". Paper presented at the Joint Conference on Prevention and Control of Oil Spills, American Petroleum Institute: Washington, D.C.

Fu, H., Gamal El-Din, M., Smith, D. W., MacKinnon, M., & Zubot, W. (2008). Ozone treatment of naphthenic acids in Athabasca oil sands process-affected water. Paper presented at the First International Oil Sands Tailings Conference,, Edmonton, AB, Canda.

Fukushima, M., & Tatsumi, K. (1999). Photocatalytic reaction by iron(III)-humate complex and its effect on the removal of organic pollutant. *Toxicological & Environmental Chemistry, 73*(1-2), 103-116.

Gallard, H., & De Laat, J. (2000). Kinetic modelling of Fe(III)/H_2O_2 oxidation reactions in dilute aqueous solution using atrazine as a model organic compound. *Water Research, 34*(12), 3107-3116.

Gallard, H., De Laat, J., & Legube, B. (1999). Spectrophotometric study of the formation of iron(III)-hydroperoxy complexes in homogeneous aqueous solutions. *Water Research, 33*(13), 2929-2936.

Gallup, D. L., Isacoff, E. G., & Smith, D. N. (1996). Use of Ambersorb® carbonaceous adsorbent for removal of BTEX compounds from oil-field produced water. *Environmental Progress, 15*(3), 197-203.

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

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

García Einschlag, F. S., Lopez, J., Carlos, L., Capparelli, A. L., Braun, A. M., & Oliveros, E. (2002). Evaluation of the efficiency of photodegradation of nitroaromatics applying the UV/H_2O_2 technique. *Environmental Science & Technology, 36*(18), 3936-3944.

Garrett, R. M., Pickering, I. J., Haith, C. E., & Prince, R. C. (1998). Photooxidation of crude oils. *Environmental Science & Technology, 32*(23), 3719-3723.

Georgi, A., Schierz, A., & Kopinke, F. D. (2006). Activation of hydrogen peroxide by complexes of iron(III) with humic acid for chemical degradation of organic compounds in water. Paper presented at the Proceeding of the EAAOP Conference (Environmental Applications of Advanced Oxidation Processes), Chania, Greece, September.

Georgi, A., Schierz, A., Trommler, U., Horwitz, C. P., Collins, T. J., & Kopinke, F. D. (2007). Humic acid modified Fenton reagent for enhancement of the working pH range. *Applied Catalysis B: Environmental, 72*(1-2), 26-36.

Ghabbour, E. A., Jansen, S. A., Paciolla, M. D., Sein, L. T., Fataftah, A., Cherkasskiy, A., . . . Kolla, S. (1997). Tight metal binding by humic acids and its role in biomineralization†. *Journal of the Chemical Society, Dalton Transactions*(21), 4047-4060.

Goldstein, S., Aschengrau, D., Diamant, Y., & Rabani, J. (2007). Photolysis of aqueous H_2O_2: quantum yield and applications for polychromatic UV actinometry in photoreactors. *Environmental Science & Technology, 41*(21), 7486-7490.

Gorelova, R., Babich, V., & Gorelov, I. (1971). Potentiometric study of copper complex formation with ethylenediaminedisuccinic and ethylenediaminetetraacetic acids. *Zhurnal Neorganicheskoi Khimii, 16*(7), 1873-&.

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

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

Gulley, J. R. (1992). Study of Oilsands Sludge Reclamation Under the Tailings Sludge Abandonment Research Program: Suncor Incorporated.

Gustafson, R. L., & Martell, A. E. (1963). Hydrolytic Tendencies of Ferric Chelates[1]. *The Journal of Physical Chemistry, 67*(3), 576-582.

Gutteridge, J., Maidt, L., & Poyer, L. (1990). Superoxide dismutase and Fenton chemistry. Reaction of ferric-EDTA complex and ferric-bipyridyl complex with hydrogen peroxide without the apparent formation of iron(II). *Biochemical Journal, 269*, 169-174.

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

Hansen, B. R., & Davies, S. R. (1994). Review of potential technologies for the removal of dissolved components from produced water. *Chemical Engineering Research & Design, 72*(2), 176-188.

Harris, D. C., & Aisen, P. (1973). Facilitation of Fe(II) antoxidation by Fe(III) complexing agents. *Biochimica et Biophysica Acta (BBA)-General Subjects, 329*(1), 156-158.

Hayes, T. M. E. (2007). Examining the ecological effects of naphthenic acids and major ions on phytoplankton in the Athabasca oil sands region. (Docter of Philosophy), University of Waterloo, Waterloo, ON, Canada.

He, Y. H., Wiseman, S. B., Hecker, M., Zhang, X. W., Wang, N., Perez, L. A., . . . Giesy, J. P. (2011). Effect of ozonation on the estrogenicity and androgenicity of oil sands process-affected water. *Environmental Science & Technology, 45*(15), 6268-6274.

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

Headley, J. V., Peru, K. M., McMartin, D. W., & Winkler, M. (2002). Determination of dissolved naphthenic acids in natural waters by using negative-ion electrospray mass spectrometry. *Journal of AOAC International, 85*(1), 182-187.

Herney-Ramirez, J., Vicente, M. A., & Madeira, L. M. (2010). Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review. *Applied Catalysis B: Environmental, 98*(1), 10-26.

Hewgill, F., & Proudfoot, G. (1976). Regioselective oxidation of aliphatic acids by complexed hydroxyl radicals. *Australian Journal of Chemistry, 29*(3), 637-647.

Hitchcock, W. W., & Puckett, J. M. (2013). United States Patent No.

Ho, J., Coote, M. L., Cramer, C. J., & Truhlar, D. G. (2012). Theoretical calculation of reduction potentials. *Organic Electrochemistry, 5*.

Hofman-Caris, C., Harmsen, D., & Beerendonk, E. (2003). Degradation of priority compounds by UV and UV oxidation. *Advanced Oxidation Processes, TECHNEAU*.

Holowenko, F. M., MacKinnon, M. D., & Fedorak, P. M. (2000). Methanogens and sulfate-reducing bacteria in oil sands fine tailings waste. *Canadian Journal of Microbiology, 46*(10), 927-937.

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

Homlok, R., Takács, E., & Wojnárovits, L. (2010). Radiolytic degradation of 2, 4-dichlorophenoxyacetic acid in dilute aqueous solution: pH dependence. *Journal of Radioanalytical and Nuclear Chemistry, 284*(2), 415-419.

Hu, X., Wang, X., Ban, Y., & Ren, B. (2011). A comparative study of UV-Fenton, UV-H_2O_2 and Fenton reaction treatment of landfill leachate. *Environmental Technology, 32*(9), 945-951.

Huang, C., Shi, Y., El-Din, M. G., & Liu, Y. (2015). Treatment of oil sands process-affected water (OSPW) using ozonation combined with integrated fixed-film activated sludge (IFAS). *Water Research, 85*, 167-176.

Huang, C. P., Dong, C. D., & Tang, Z. H. (1993). Advanced chemical oxidation: its present role and potential future in hazardous waste treatment. *Waste management, 13*(5), 361-377.

Huang, W., Brigante, M., Wu, F., Hanna, K., & Mailhot, G. (2012). Development of a new homogenous photo-Fenton process using Fe(III)-EDDS complexes. *Journal of Photochemistry and Photobiology A: Chemistry, 239*, 17-23.

Huang, W. Y., Brigante, M., Wu, F., Mousty, C., Hanna, K., & Mailhot, G. (2013). Assessment of the Fe (III)-EDDS complex in Fenton-like processes: from the radical formation to the degradation of bisphenol A. *Environmental Science & Technology, 47*(4), 1952-1959.

Hug, S. J., & Leupin, O. (2003). Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. *Environmental Science & Technology, 37*(12), 2734-2742.

Islam, M. S., Dong, T., Sheng, Z., Zhang, Y., Liu, Y., & Gamal El-Din, M. (2014). Microbial community structure and operational performance of a fluidized bed biofilm reactor treating oil sands process-affected water. *International biodeterioration & biodegradation*, 91, 111-118.

Jacobs, L. E., Weavers, L. K., & Chin, Y. P. (2008). Direct and indirect photolysis of polycyclic aromatic hydrocarbons in nitrate-rich surface waters. *Environmental Toxicology and Chemistry, 27*(8), 1643-1648.

Jaworska, J. S., Schowanek, D., & Feijtel, T. C. (1999). Environmental risk assessment for trisodium [S, S]-ethylene diamine disuccinate, a biodegradable chelator used in detergent applications. *Chemosphere, 38*(15), 3597-3625.

Jones, D., Scarlett, A. G., West, C. E., & Rowland, S. J. (2011). Toxicity of individual naphthenic acids to Vibrio fischeri. *Environmental Science & Technology, 45*(22), 9776-9782.

Jones, P. W., & Williams, D. R. (2001). Chemical speciation used to assess [S, S′]-ethylenediaminedisuccinic acid (EDDS) as a readily-biodegradable replacement for EDTA in radiochemical decontamination formulations. *Applied Radiation and Isotopes, 54*(4), 587-593.

Kachur, A. V., Tuttle, S. W., & Biaglow, J. E. (1998). Autoxidation of ferrous ion complexes: a method for the generation of hydroxyl radicals. *Radiation research, 150*(4), 475-482.

Kadlec, R. H., & Knight, R. L. (1996). Treatment wetlands. Boca Raton: CRC Lewis Publishers.

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

Kanicky, J., Poniatowski, A., Mehta, N., & Shah, D. (2000). Cooperativity among molecules at interfaces in relation to various technological processes: effect of chain length on the p K a of fatty acid salt solutions. *Langmuir, 16*(1), 172-177.

Kannel, P. R., & Gan, T. Y. (2012). 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, 47*(1), 1-21.

Kasperski, K. (2001). Extraction and water chemistry. Canadian Oil Sands Network for Research and Development (CONRAD) Oil sands extraction fundamentals and process water workshop. May 7-8, 2004.

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

Kavitha, V., & Palanivelu, K. (2003). Degradation of 2-chlorophenol by Fenton and photo-Fenton processes-A comparative study. *Journal of Environmental Science and Health, Part A, 38*(7), 1215-1231.

Kavitha, V., & Palanivelu, K. (2004). The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere, 55*(9), 1235-1243.

Keenan, C. R., & Sedlak, D. L. (2008). Ligand-enhanced reactive oxidant generation by nanoparticulate zero-valent iron and oxygen. *Environmental Science & Technology, 42*(18), 6936-6941.

Kim, E.-S., Liu, Y., & Gamal El-Din, M. (2013). An in-situ integrated system of carbon nanotubes nanocomposite membrane for oil sands process-affected water treatment. *Journal of Membrane Science*, 429, 418-427.

Klamerth, N., Malato, S., Aguera, A., & Fernandez-Alba, A. (2013). Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: a comparison. *Water Research, 47*(2), 833-840.

Klamerth, N., Malato, S., Aguera, A., Fernandez-Alba, A., & Mailhot, G. (2012). Treatment of municipal wastewater treatment plant effluents with modified photo-Fenton as a tertiary treatment for the degradation of micro pollutants and disinfection. *Environmental Science & Technology, 46*(5), 2885-2892.

Klamerth, N., Malato, S., Maldonado, M. I., Agüera, A., & Fernández-Alba, A. (2011). Modified photo-Fenton for degradation of emerging contaminants in municipal wastewater effluents. *Catalysis Today, 161*(1), 241-246.

Kleinberg, J., William, J., Argersinger, J. R., & Ernest, G. (1960). *Inorganic Chemistry*. Lexington, Massachusetts, United States: D.C. Heath and Company.

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

Koch, S., Ackermann, G., & Schülller, K. (1986). Über ternäre komplexe mit aminopolycarbonsäuren and sulfid. *Zeitschrift Für Chemie, 26*, 339.

Kochany, J., & Lipczynska-Kochany, E. (2007). Fenton reaction in the presence of humates. Treatment of highly contaminated wastewater at neutral pH. *Environmental Technology, 28*(9), 1007-1013.

Kołodyńska, D. (2011). Chelating agents of a new generation as an alternative to conventional chelators for heavy metal ions removal from different waste waters: INTECH Open Access Publisher.

Koppenol, W. H., & Liebman, J. F. (1984). The oxidizing nature of the hydroxyl radical. A comparison with the ferryl ion (FeO^{2+}). *The Journal of Physical Chemistry, 88*(1), 99-101.

Kozhevnikov, I. V. (1998). Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. *Chemical Reviews, 98*(1), 171-198.

Krishnan, K. A., Sheela, A., & Anirudhan, T. (2003). Kinetic and equilibrium modeling of liquid ‐ phase adsorption of lead and lead chelates on activated carbons. *Journal of Chemical Technology and Biotechnology, 78*(6), 642-653.

Kušić, H., Koprivanac, N., Božić, A. L., & Selanec, I. (2006). Photo-assisted Fenton type processes for the degradation of phenol: a kinetic study. *Journal of Hazardous Materials, 136*(3), 632-644.

Kwan, W. P., & Voelker, B. M. (2003). Rates of hydroxyl radical generation and organic compound oxidation in mineral-catalyzed Fenton-like systems. *Environmental Science & Technology, 37*(6), 1150-1158.

Land, E., & Ebert, M. (1967). Pulse radiolysis studies of aqueous phenol. Water elimination from dihydroxycyclohexadienyl radicals to form phenoxyl. *Transactions of the Faraday Society, 63*, 1181-1190.

Langford, C. H., Wingham, M., & Sastri, V. S. (1973). Ligand photooxidation in copper (II) complexes of nitrilotriacetic acid. Implications for natural waters. *Environmental Science & Technology, 7*(9), 820-822.

Larson, R. A., & Weber, E. J. (1994). Reaction mechanisms in environmental organic chemistry. Boca Raton, Florida: CRC press.

Lati, J., & Meyerstein, D. (1978). Oxidation of first-row bivalent transition-metal complexes containing ethylenediaminetetra-acetate and nitrilotriacetate ligands by free radicals: a pulse-radiolysis study. *Journal of the Chemical Society, Dalton Transactions*(9), 1105-1118.

Lee, C., & Sedlak, D. L. (2009). A novel homogeneous Fenton-like system with Fe(III)-phosphotungstate for oxidation of organic compounds at neutral pH values. *Journal of Molecular Catalysis A: Chemical, 311*(1), 1-6.

Lee, C. H., Keenan, C. R., & Sedlak, D. L. (2008). Polyoxometalate-enhanced oxidation of organic compounds by nanoparticulate zero-valent iron and ferrous ion in the presence of oxygen. *Environmental Science & Technology, 42*(13), 4921-4926.

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

Leung, S. S. C., MacKinnon, M. D., & Smith, R. E. (2001). Aquatic reclamation in the Athabasca, Canada, oil sands: naphthenate and salt effects on phytoplankton communities. *Environmental Toxicology and Chemistry, 20*(7), 1532-1543.

Levey, S., Lasichak, A., Brimi, R., Orten, J., Smyth, C. J., & Smith, A. H. (1946). A study to determine the toxicity of fumaric acid. *Journal of the American Pharmaceutical Association, 35*(10), 298-304.

Lewis, R. L. (2000). Dangerous Properties of Industrial Materials. New York: Wiley Intersicence.

Li, J. (2010). 17beta-estradiol degradation photoinduced by iron complex, clay and iron oxide minerals: effect of the iron complexing agent ethylenediamine-N, N'-disuccinic acid. (Master of Science), Université Blaise Pascal-Clermont-Ferrand II; Université de Wuhan.

Li, J., Mailhot, G., Wu, F., & Deng, N. S. (2010). Photochemical efficiency of Fe(III)-EDDS complex: OH radical production and 17β-estradiol degradation. *Journal of Photochemistry and Photobiology A: Chemistry, 212*(1), 1-7.

Li, Y. C., Bachas, L. G., & Bhattacharyya, D. (2005). Kinetics studies of trichlorophenol destruction by chelate-based Fenton reaction. *Environmental Engineering Science, 22*(6), 756-771.

Li, Y. C., Bachas, L. G., & Bhattacharyya, D. (2007). Selected chloro-organic detoxifications by polychelate (poly (acrylic acid)) and citrate-based Fenton reaction at neutral pH environment. *Industrial & Engineering Chemistry Research, 46*(24), 7984-7992.

Li, Z. M., Shea, P. J., & Comfort, S. D. (1998). Nitrotoluene destruction by UV-catalyzed Fenton oxidation. *Chemosphere, 36*(8), 1849-1865.

Limited, G. A. (2002). Oil sands regional aquatics monitoring program (RAMP) 2001. Vol. 1-Chemical and biological monitoring *Reported prepared for the RAMP Steering Committee*. Fort McMurray, Alberta.

Lindsey, M. E., & Tarr, M. A. (2000). Inhibition of hydroxyl radical reaction with aromatics by dissolved natural organic matter. *Environmental Science & Technology, 34*(3), 444-449.

Lipczynska-Kochany, E., & Kochany, J. (2008). Effect of humic substances on the Fenton treatment of wastewater at acidic and neutral pH. *Chemosphere, 73*(5), 745-750.

Liu, H. (2015). Community Structure and Microbial Activity of Sulfate Reducing Bacteria in Wastewater Biofilms and Mature Fine Tailings Analyzed by Microsensors and Molecular Biology Techniques. (Doctor of Philosophy), University of Alberta, Edmonton, Alberta, Canada.

Lloyd, R. V., Hanna, P. M., & Mason, R. P. (1997). The origin of the hydroxyl radical oxygen in the Fenton reaction. *Free Radical Biology and Medicine, 22*(5), 885-888.

Lokesh, B. R., & Cunningham, M. L. (1986). Further studies on the formation of oxygen radicals by potassium superoxide in aqueous medium for biochemical investigations. *Toxicology Letters, 34*(1), 75-84.

Lonergan, M., Lieberman, M., & Lewis, N. (1995). Mechanistic studies of redox sensors for the liquid redox process. Paper presented at the GRI Sulfur Recovery Conference, Austin, Texas.

MacKinnon, M. (2004a). Oil sands water quality issues: properties, treatment, and discharge options [online]. Canadian Oil Sands Network for Research and Development (CONRAD) Oil Sands Water Usage Workshop, February 24-25, 2005.

Mackinnon, M., & Boerger, H. (1986). Description of two treatments for detoxifying oil sands tailings pond water. *Water Pollution Research Journal of Canada, 21*, 496-512.

MacKinnon, M., & Sethi, A. (1993). A comparison of the physical and chemical properties of the tailings ponds at the Syncrude and Suncor oil sands plants. Paper presented at the Proceedings of the Fine Tailings Symposium: Oil Sands-Our Petroleum Future Conference.

Mackinnon, M. D. (2001). Process-affected waters: impact of operating factors on recycle water quality. *Canadian Oil Sands Network for Research and Development (CONRAD) Oil*

Sands Extraction Fundamentals and Process Water Workshop, May 7-8, 2004. Athabasca, Alberta: Athabasca University.

MacKinnon, M. D. (2004b). Oild sands water quality issues: properties, treatment, and discharge options, from http://www.conrad.ab.ca/seminars/water_usage/2004/Agenda.htm

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

Majer, J., Jokl, V., Dvorakova, E., & Juracova, M. (1968). New complexones. XIII. Potentiometric and electrophoretic study of ethylenediamine-N, N′ -disuccinic acid and its metal chelates. *Chem Zvesti, 22*, 415-423.

Majer, J., Springer, V., & Kopecka, B. (1966). New complexones. VIII. Ethylenediamino-N, N′ -disuccinic acid and investigation of its heavy metal complexes by spectrophotometry. *Chemické Zvesti, 20*, 414-422.

Maki, H., Sasaki, T., & Harayama, S. (2001). Photo-oxidation of biodegraded crude oil and toxicity of the photo-oxidized products. *Chemosphere, 44*(5), 1145-1151.

Malato, S., Fernández-Ibáñez, P., Maldonado, M. I., Blanco, J., & Gernjak, W. (2009). Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today, 147*(1), 1-59.

Marine, N. (1999). Canadian Water Quality Guidelines for the Protection of Aquatic Life. *Canadian Council of Ministers of the Environment, Winnipeg*, 1-5.

Marklund, S. (1976). Spectrophotometric study of spontaneous disproportionation of superoxide anion radical and sensitive direct assay for superoxide dismutase. *Journal of Biological Chemistry, 251*(23), 7504-7507.

Marr, J. B., Mohammed, M., MacKinnon, M., & Rogers, M. (1996). Removal of naphthenic acid from water via pH adjustment, coagulation and sand filtration. Paper presented at the International Water Conference, Pittsburgh.

Martell, A. E., Motekaitis, R. J., Chen, D., Hancock, R. D., & McManus, D. (1996). Selection of new Fe(III)/Fe(II) chelating agents as catalysts for the oxidation of hydrogen sulfide to sulfur by air. *Canadian Journal of Chemistry, 74*(10), 1872-1879.

Martell, A. E., & Smith, R. M. (1974). Critical stability constants (Vol. 1). New York, Plenum Press: Springer.

Martell, A. E., & Smith, R. M. (1974-1989). Critical stability constants (Vol. 1-6). New York: Plenum Press.

McManus, D., & Martell, A. E. (1997). The evolution, chemistry and applications of chelated iron hydrogen sulfide removal and oxidation processes. *Journal of Molecular Catalysis A: Chemical, 117*(1), 289-297.

Melnyk, D. L., Horwitz, S. B., & Peisach, J. (1981). Redox potential of iron-bleomycin. *Biochemistry, 20*(18), 5327-5331.

Metsärinne, S., Tuhkanen, T., & Aksela, R. (2001). Photodegradation of ethylenediaminetetraacetic acid (EDTA) and ethylenediamine disuccinic acid (EDDS) within natural UV radiation range. *Chemosphere, 45*(6), 949-955.

Mikula, R. J., Kasperski, K. L., Burns, R. D., & MacKinnon, M. D. (1996). Nature and fate of oil sands fine tailings. *Advances in Chemistry Series*(251).

Mills, G., Schmidt, K., Matheson, M., & Meisel, D. (1987). Thermal and photochemical reactions of sulfhydryl radicals. Implications for colloid photocorrosion. *Journal of Physical Chemistry, 91*(6), 1590-1596.

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

Moschopedis, S. E., Fryer, J. F., & Speight, J. G. (1977). Water-soluble constituents of Athabasca bitumen. *Fuel, 56*(1), 109-110.

Motekaitis, R. J., & Martell, A. E. (1994). The iron(III) and iron(II) complexes of nitrilotriacetic acid. *Journal of Coordination Chemistry, 31*(1), 67-78.

Munoz, M., Alonso, J., Bartroli, J., & Valiente, M. (1990). Automated spectrophotometric determination of titanium (IV) in water and brines by flow injection based on its reaction with hydrogen peroxide. *Analyst, 115*(3), 315-318.

Nadtochenko, V. A., & Kiwi, J. (1998). Photolysis of $FeOH^{2+}$ and $FeCl^{2+}$ in aqueous solution. Photodissociation kinetics and quantum yields. *Inorganic Chemistry, 37*(20), 5233-5238.

Nagaraju, V., Goje, T., & Crouch, A. M. (2007). Determination of Copper and Iron Using [S, S']-Ethylenediaminedisuccinic Acid as a Chelating Agent in Wood Pulp by Capillary Electrophoresis. *Analytical Sciences, 23*(4), 493-496.

Nam, S., Renganathan, V., & Tratnyek, P. G. (2001). Substituent effects on azo dye oxidation by the Fe(III)–EDTA–H_2O_2 system. *Chemosphere, 45*(1), 59-65.

Nassar, N. N., Husein, M. M., & Pereira-Almao, P. (2010). Ultradispersed particles in heavy oil: Part II, sorption of H 2 S (g). *Fuel Processing Technology, 91*(2), 169-174.

Natarajan, P., & Endicott, J. F. (1973). Photoredox behavior of transition metal-ethylenediaminetetraacetate complexes. Comparison of some Group VIII metals. *The Journal of Physical Chemistry, 77*(17), 2049-2054.

Nelson, L. R., MacKinnon, M., & Gulley, J. R. (1993). Application of toxicity testing in the evaluation of reclamation options for oil sands fine tails. Paper presented at the Oil Sands-Our Petroleum Future Conference,, Edmonton, Alberta, Canada.

Neyaglov, A., Digurov, N., Bukharkina, T., Mazgarov, A., & Fakhriev, A. (1991). Kinetics and reaction mechanism of the liquid-phase oxidation of hydrogen sulfide by a chelate complex of trivalent iron (Fe^{3+} $EDTA^-$). *Kinetics and Catalysis, 32*(3), 485-489.

Neyens, E., & Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials, 98*(1-3), 33-50.

Nishida, Y., Goto, A., Akamatsu, T., Ohba, S., Fujita, T., Tokii, T., & Okada, S. (1994). Iron Chelates in Biological Systems. Its Relevance to Induction of Pathogenesis of Tissue Damage and Carcinogenesis. *Chemistry Letters*(3), 641-644.

Nishida, Y., Nasu, M., & Akamatsu, T. (1992). Reaction between binuclear iron(III) compounds and DMPO (5, 5-dimethyl-3, 4-dihydropyrrole N-oxide). *Journal of the Chemical Society, Chemical Communications* (2), 93-94.

Nix, P. G. (1983). Detoxification of tailings pond top water. Report prepared for Suncor Energy Inc. Fort McMurray, Alberta.

OECD. (1996). OECD Guidelines for Testing of Chemicals. *Degradation and Accumulation*. Paris.

Oil Sands Ministerial Strategy Committee. (2006). Responding to the rapid growth of oil sands development, from http://alberta.ca/home/395.cfm

Olson, K. R. (2005). Vascular actions of hydrogen sulfide in nonmammalian vertebrates. *Antioxidants & Redox Signaling, 7*(5-6), 804-812.

Onstein, P., Stefan, M. I., & Bolton, J. R. (1999). Competition kinetics method for the determination of rate constants for the reaction of hydroxyl radicals with organic pollutants using the UV/H_2O_2 advanced oxidation technology: the rate constants for the tert-butyl formate ester and 2, 4-dinitrophenol. *Journal of Advanced Oxidation Technologies, 4*(2), 231-236.

Orama, M., Hyvönen, H., Saarinen, H., & Aksela, R. (2002). Complexation of [S, S] and mixed stereoisomers of N, N′ -ethylenediaminedisuccinic acid (EDDS) with Fe(III), Cu(II), Zn(II) and Mn(II) ions in aqueous solution. *Journal of the Chemical Society, Dalton Transactions*(24), 4644-4648.

Ou, X. X., Quan, X., Chen, S. Y., Zhang, F. J., & Zhao, Y. Z. (2008). Photocatalytic reaction by Fe(III)-citrate complex and its effect on the photodegradation of atrazine in aqueous solution. *Journal of Photochemistry and Photobiology A: Chemistry, 197*(2), 382-388.

Owens, G., Ferguson, V. K., McLaughlin, M. J., Singleton, I., Reid, R. J., & Smith, F. (2000). Determination of NTA and EDTA and speciation of their metal complexes in aqueous solution by capillary electrophoresis. *Environmental Science & Technology, 34*(5), 885-891.

Panadés, R., Ibarz, A., & Esplugas, S. (2000). Photodecomposition of carbendazim in aqueous solutions. *Water Research, 34*(11), 2951-2954.

Panias, D., Taxiarchou, M., Paspaliaris, I., & Kontopoulos, A. (1996). Mechanisms of dissolution of iron oxides in aqueous oxalic acid solutions. *Hydrometallurgy, 42*(2), 257-265.

Park, M. G., & Choi, M. H. (2006). United States Patent No. US/0128799 A1.

Pavelčik, F., & Majer, J. (1978). New complexanes. XXXIV. Preparation and properties of the meso and rac forms of ethy! enediamine-iV, iV'-disuccinic acid. *Chemické Zvesti, 32*(1), 37-41.

Pavelčík, F., & Majer, J. (1978). The crystal and molecular structure of lithium [(S, S)-N, N'-ethylenediaminedisuccinato] cobaltate(III) trihydrate. *Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry, 34*(12), 3582-3585.

Payne, J. R., & Phillips, C. R. (1985). Photochemistry of petroleum in water. *Environmental Science & Technology, 19*(7), 569-579.

Peller, J., Wiest, O., & Kamat, P. V. (2003). Mechanism of Hydroxyl Radical-Induced Breakdown of the Herbicide 2, 4-Dichlorophenoxyacetic Acid (2, 4-D). *Chemistry-A European Journal, 9*(21), 5379-5387.

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

Pereira, M. C., Oliveira, L. C. A., & Murad, E. (2012). Iron oxide catalysts: Fenton and Fentonlike reactions-a review. *Clay Minerals, 47*(3), 285-302.

Pereira, V. J., Weinberg, H. S., Linden, K. G., & Singer, P. C. (2007). UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm. *Environmental Science & Technology, 41*(5), 1682-1688.

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

Perez, M., Torrades, F., Domenech, X., & Peral, J. (2002). Fenton and photo-Fenton oxidation of textile effluents. *Water Research, 36*(11), 2703-2710.

Perrin, D. D., Dempsey, B., & Serjeant, E. P. (1981). p*K*a prediction for organic acids and bases (Vol. 1). London: Chapman and Hall: Springer.

Peters, L. E., MacKinnon, M., Van Meer, T., van den Heuvel, M. R., & Dixon, D. G. (2007). Effects of oil sands process-affected waters and naphthenic acids on yellow perch (Perca flavescens) and Japanese medaka (Orizias latipes) embryonic development. *Chemosphere, 67*(11), 2177-2183.

Petersen, R. L., Symons, M. C., & Taiwo, F. (1989). Application of radiation and electron spin resonance spectroscopy to the study of ferryl myoglobin. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, 85*(8), 2435-2443.

Petre, C. F., & Larachi, F. (2006). Reaction between hydrosulfide and iron/cerium (hydr) oxide: Hydrosulfide oxidation and iron dissolution kinetics. *Topics in Catalysis, 37*(2-4), 97-106.

Petre, C. F., & Larachi, F. (2007). Anoxic alkaline oxidation of bisulfide by Fe/Ce oxides: Reaction pathway. *AI Ch. E. Journal, 53*(8), 2170-2187.

Philip, C., & Brooks, D. W. (1974). Iron(III) chelate complexes of hydrogen sulfide and mercaptans in aqueous solution. *Inorganic Chemistry, 13*(2), 384-386.

Pierre, J., & Fontecave, M. (1999). Iron and activated oxygen species in biology: the basic chemistry. *Biometals, 12*(3), 195-199.

Pignatello, J. J., Oliveros, E., & MacKay, A. (2006). Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology, 36*(1), 1-84.

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

Pouran, S. R., Aziz, A. A., & Daud, W. M. A. W. (2015). Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters. *Journal of Industrial and Engineering Chemistry, 21*, 53-69.

Pourrezaei, P. (2013). Physico-Chemical Processes for Oil Sands Process-Affected Water Treatment. (Doctor of Philosophy), University of Alberta, Edmonton, A.B.

Pourrezaei, P., Alpatova, A., Khosravi, K., Drzewicz, P., Chen, Y., Chelme-Ayala, P., & Gamal El-Din, M. (2014). Removal of organic compounds and trace metals from oil sands process-affected water using zero valent iron enhanced by petroleum coke. *Journal of Environmental Management, 139*, 50-58.

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

Quagraine, E. K., Peterson, H. G., & Headley, J. V. (2005). 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, 40*(3), 685-722.

Rabani, J., & Nielsen, S. O. (1969). Absorption spectrum and decay kinetics of O_2^- and HO_2 in aqueous solutions by pulse radiolysis. *Journal of Physical Chemistry, 73*(11), 3736-3744.

Rao, P., & Hayon, E. (1975). Redox potentials of free radicals. IV. Superoxide and hydroperoxy radicals, O_2^- and HO_2. *The Journal of Physical Chemistry, 79*(4), 397-402.

Rastogi, A., Al-Abed, S. R., & Dionysiou, D. D. (2009). Effect of inorganic, synthetic and naturally occurring chelating agents on Fe(II) mediated advanced oxidation of chlorophenols. *Water Research, 43*(3), 684-694.

Reinardy, H. C., Scarlett, A. G., Henry, T. B., West, C. E., Hewitt, L. M., Frank, R. A., & Rowland, S. J. (2013). Aromatic naphthenic acids in oil sands process-affected water, resolved by GCxGC-MS, only weakly induce the gene for vitellogenin production in zebrafish (Danio rerio) larvae. *Environmental Science & Technology, 47*(12), 6614-6620.

Resch, P., Field, R. J., Schneider, F., & Burger, M. (1989). Reduction of methylene blue by sulfide ion in the presence and absence of oxygen: simulation of the methylene blue-O_2-HS^- CSTR oscillations. *The Journal of Physical Chemistry, 93*(25), 8181-8186.

Rhule, J. T., Hill, C. L., Judd, D. A., & Schinazi, R. F. (1998). Polyoxometalates in medicine. *Chemical Reviews, 98*(1), 327-358.

Rigg, T., Taylor, W., & Weiss, J. (1954). The rate constant of the reaction between hydrogen peroxide and ferrous ions. *The Journal of Chemical Physics, 22*(4), 575-577.

Rivas, F. J., Beltran, F. J., Frades, J., & Buxeda, P. (2001). Oxidation of p-hydroxybenzoic acid by Fenton's reagent. *Water Research, 35*(2), 387-396.

Rockhold, W. (1955). Toxicity of naphthenic acids and their metal salts. *A.M.A. Archives of Industrial Health, 12*, 477-482.

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

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

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

Rubin, M., & Martell, A. E. (1980). The implications of trace metal-nitrilotriacetetic acid speciation on its environmental impact and toxicology. *Biological Trace Element Research, 2*(1), 1-19.

Rush, J., & Koppenol, W. (1988). Reactions of iron(II) nitrilotriacetate and iron(II) ethylenediamine-N, N'-diacetate complexes with hydrogen peroxide. *Journal of the American Chemical Society, 110*(15), 4957-4963.

Rush, J., Maskos, Z., & Koppenol, W. (1990). Distinction between hydroxyl radical and ferryl species. *Methods in Enzymology, 186*, 148-156.

Sada, E., Kumazawa, H., & Machida, H. (1987). Oxidation kinetics of Fe^{II}-EDTA and Fe^{II}-NTA chelates by dissolved oxygen. *Industrial & Engineering Chemistry Research, 26*(7), 1468-1472.

Safarzadeh-Amiria, A., Waltonb, J., Mahmouda, I., & Sharifia, N. (2016). Iron(III)-Polyphosphate Chelates, True Catalysts for the Liquid Redox Sulfur Recover Process. Trojan Technologies.

Sahul, K., & Sharma, B. (1987). Gamma radiolysis of nitrilotriacetic acid (NTA) in aqueous solutions. *Journal of Radioanalytical and Nuclear Chemistry, 109*(2), 321-327.

Samoilova, R. I., Crofts, A. R., & Dikanov, S. A. (2011). Reaction of superoxide radical with quinone molecules. *Journal of Physical Chemistry A, 115*(42), 11589-11593.

Schalley, C. A. (2007). Analytical methods in supramolecular chemistry. Winheim, Gemany: Wiley-VCH.

Schmidt, C. K., Fleig, M., Sacher, F., & Brauch, H. J. (2004). Occurrence of aminopolycarboxylates in the aquatic environment of Germany. *Environmental Pollution, 131*(1), 107-124.

Schneppensieper, T., Seibig, S., Zahl, A., Tregloan, P., & van Eldik, R. (2001). Influence of chelate effects on the water-exchange mechanism of polyaminecarboxylate complexes of iron(III). *Inorganic Chemistry, 40*(15), 3670-3676.

Schouwenaars, R., & Buitrn, G. (2000). Production of activated carbon from petroleum coke and itsapplication in water treatment for the removal of metals and phenol. *Water Science & Technology, 42*(5-6), 119-126.

Schowanek, D., Feijtel, T. C., Perkins, C. M., Hartman, F. A., Federle, T. W., & Larson, R. J. (1997). Biodegradation of [S, S], [R, R] and mixed stereoisomers of ethylene diamine disuccinic acid (EDDS), a transition metal chelator. *Chemosphere, 34*(11), 2375-2391.

Scott, A. C., Young, R. F., & Fedorak, P. M. (2008a). Comparison of GC-MS and FTIR methods for quantifying naphthenic acids in water samples. *Chemosphere, 73*(8), 1258-1264.

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

Scott, J. A., Karanjkar, A. M., & Rowe, D. L. (1995). Biofilm covered granular activated carbon for decontamination of streams containing heavy metals and organic chemicals. *Minerals Engineering, 8*(1), 221-230.

Semadeni, M., Stocker, D. W., & Kerr, J. A. (1995). The temperature dependence of the OH radical reactions with some aromatic compounds under simulated tropospheric conditions. *International Journal of Chemical Kinetics, 27*(3), 287-304.

Sharma, B. K., & Sahul, K. (1982). Co-60 gamma radiolysis of iron(III)-nitrilotriacetate in aqueous solutions. *Radiation Physics and Chemistry, 20*, 341-346.

Shimizu, K., Hutcheson, R., Engelmann, M. D., & Cheng, I. F. (2007). Cyclic voltammetric and aqueous equilibria model study of the pH dependant iron(II/III) ethylenediamminetetraacetate complex reduction potential. *Journal of Electroanalytical Chemistry, 603*(1), 44-50.

Shu, Z., Bolton, J. R., Belosevic, M., & Gamal El-Din, M. (2013). Photodegradation of emerging micropollutants using the medium-pressure UV/H_2O_2 Advanced Oxidation Process. *Water Research, 47*(8), 2881-2889.

Shu, Z., Li, C., Belosevic, M., Bolton, J. R., & El-Din, M. G. (2014). Application of a solar UV/chlorine advanced oxidation process to oil sands process-affected water remediation. *Environmental Science & Technology, 48*(16), 9692-9701.

Sillanpää, M. E., Kurniawan, T. A., & Lo, W.-h. (2011). Degradation of chelating agents in aqueous solution using advanced oxidation process (AOP). *Chemosphere, 83*(11), 1443-1460.

Smith, B. A., Teel, A. L., & Watts, R. J. (2004). Identification of the reactive oxygen species responsible for carbon tetrachloride degradation in modified Fenton's systems. *Environmental Science & Technology, 38*(20), 5465-5469.

Smith, R. M., & Martell, A. E. (1987). Critical stability constants, enthalpies and entropies for the formation of metal complexes of aminopolycarboxylic acids and carboxylic acids. *Science of the Total Environment, 64*(1-2), 125-147.

Song, N., Wang, D., Shan, Z., & Shi, L. (2013). Influence of pH and dissolved organic matter on photolysis of metsulfuron-methyl. *Procedia Environmental Sciences, 18*, 585-591.

Sorvari, J., & Sillanpää, M. (1996). Influence of metal complex formation on heavy metal and free EDTA and DTPA acute toxicity determined by Daphnia magna. *Chemosphere, 33*(6), 1119-1127.

Spuhler, D., Rengifo-Herrera, J. A., & Pulgarin, C. (2010). The effect of Fe^{2+}, Fe^{3+}, H_2O_2 and the photo-Fenton reagent at near neutral pH on the solar disinfection (SODIS) at low temperatures of water containing Escherichia coli K12. *Applied Catalysis B: Environmental, 96*(1), 126-141.

Stefan, M. I., & Bolton, J. R. (2002). UV direct photolysis of N-nitrosodimethylamine (NDMA): Kinetic and product study. *Helvetica Chimica Acta, 85*(5), 1416-1426.

Steudel, R. (1996). Mechanism for the formation of elemental sulfur from aqueous sulfide in chemical and microbiological desulfurization processes. *Industrial & Engineering Chemistry Research, 35*(4), 1417-1423.

Stolzberg, R. J., & Hume, D. N. (1975). Rapid formation of iminodiacetate from photochemical degradation of iron(III) nitrilotriacetate solutions. *Environmental Science & Technology, 9*(7), 654-656.

Stumm, W., & Lee, G. F. (1961). Oxygenation of ferrous iron. *Industrial & Engineering Chemistry, 53*(2), 143-146.

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

Su, C., & Suarez, D. L. (1995). Coordination of adsorbed boron: A FTIR spectroscopic study. *Environmental Science & Technology, 29*(2), 302-311.

Subramanian, B., Christou, S., Efstathiou, A., Namboodiri, V., & Dionysiou, D. (2011). Regeneration of three-way automobile catalysts using biodegradable metal chelating agent-[S, S]-ethylenediamine disuccinic acid ([S, S]-EDDS). *Journal of Hazardous Materials, 186*(2), 999-1006.

Sum, O. S. N., Feng, J. Y., Hub, X. J., & Yue, P. L. (2005). Photo-assisted fenton mineralization of an azo-dye acid black 1 using a modified laponite clay-based Fe nanocomposite as a heterogeneous catalyst. *Topics in catalysis, 33*(1-4), 233-242.

Sun, S.-P., Zeng, X., & Lemley, A. T. (2013). Kinetics and mechanism of carbamazepine degradation by a modified Fenton-like reaction with ferric-nitrilotriacetate complexes. *Journal of Hazardous Materials, 252*, 155-165.

Sun, Y., & Pignatello, J. J. (1993). Activation of hydrogen peroxide by iron(III) chelates for abiotic degradation of herbicides and insecticides in water. *Journal of Agricultural and Food Chemistry, 41*(2), 308-312.

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

Sunda, W. G., Engel, D. W., & Thuotte, R. M. (1978). Effect of chemical speciation on toxicity of cadmium to grass shrimp, Palaemonetes pugio: importance of free cadmium ion. *Environmental Science & Technology, 12*(4), 409-413.

Swart, N. C., & Weaver, A. J. (2012). The Alberta oil sands and climate. *Nature Climate Change, 2*(3), 134-136.

Tachiev, G., Roth, J., & Bowers, A. (2000). Kinetics of hydrogen peroxide decomposition with complexed and “free” iron catalysts. *International Journal of Chemical Kinetics, 32*(1), 24-35.

Tang, W. Z., & Tassos, S. (1997). Oxidation kinetics and mechanisms of trihalomethanes by Fenton's reagent. *Water Research, 31*(5), 1117-1125.

Teel, A. L., Warberg, C. R., Atkinson, D. A., & Watts, R. J. (2001). Comparison of mineral and soluble iron Fenton's catalysts for the treatment of trichloroethylene. *Water Research, 35*(4), 977-984.

Tolkacheva, L., Saprunova, T., Nikolskii, V., & Yakovlev, A. (2012). Environmentally friendly complexones. The thermodynamic characteristics of the formation of Al^{3+} ion complexes with ethylenediaminedisuccinic acid in aqueous solutions. *Chemistry Journal of Moldova. Gneral, Industrial and Ecological Chemistry, 7*(1), 70-73.

Tollefsen, K. E., Petersen, K., & Rowland, S. J. (2012). Toxicity of synthetic naphthenic acids and mixtures of these to fish liver cells. *Environmental Science & Technology, 46*(9), 5143-5150.

Tomita, Y., Ando, T., & Ueno, K. (1965). Infrared Spectra of Nitrilotriacetate Chelates in Aqueous Solution. *The Journal of Physical Chemistry, 69*(2), 404-407.

Trott, T., Henwood, R. W., & Langford, C. H. (1972a). Sunlight photochemistry of ferric nitrilotriacetate complexes. *Environmental Science & Technology, 6*(4), 367-368.

Trott, T., Henwood, R. W., & Langford, C. H. (1972b). Sunliight photochemistry of ferric nitrilotriacetate complexes. *Environmental Science & Technology, 6*(4), 367-368.

Umar, M., Aziz, H. A., & Yusoff, M. S. (2010). Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate. *Waste management, 30*(11), 2113-2121.

Veil, J. A., Quinn, J. J., & Garcia, J. P. (2009, March 23-25, 2009). Water issues relating to heavy oil production. Paper presented at the 2009 SPE Americas E & P Environmental and Safety Conference, San Antonio.

Vermilyea, A. W., & Voelker, B. M. (2009). Photo-Fenton reaction at near neutral pH. *Environmental Science & Technology, 43*(18), 6927-6933.

Vione, D., Merlo, F., Maurino, V., & Minero, C. (2004). Effect of humic acids on the Fenton degradation of phenol. *Environmental Chemistry Letters, 2*(3), 129-133

Von Sonntag, C., Dowideit, P., Fang, X., Mertens, R., Pan, X., Schuchmann, M. N., & Schuchmann, H.-P. (1997). The fate of peroxyl radicals in aqueous solution. *Water Science and Technology, 35*(4), 9-15.

Walling, C., Kurz, M., & Schugar, H. J. (1970). Iron(III)-ethylenediaminetetraacetic acid-peroxide system. *Inorganic Chemistry, 9*(4), 931-937.

Walling, C., Partch, R. E., & Weil, T. (1975). Kinetics of the decomposition of hydrogen peroxide catalyzed by ferric ethylenediaminetetraacetate complex. *Proceedings of the National Academy of Sciences, 72*(1), 140-142.

Wang, C., Alpatova, A., McPhedran, K. N., & Gamal El-Din, M. (2015). Coagulation/flocculation process with polyaluminum chloride for the remediation of oil sands process-affected water: Performance and mechanism study. *Journal of Environmental Management*, 160, 254-262.

Wang, C., Klamerth, N., Huang, R., Elnakar, H., & Gamal El-Din, M. (2016). Oxidation of Oil Sand Process-affected Water by Potassium Ferrate (VI). *Environmental Science & Technology, 50(8), 4238-4247*.

Wang, L., Wang, F., Li, P., & Zhang, L. (2013a). Ferrous-tetrapolyphosphate complex induced dioxygen activation for toxic organic pollutants degradation. *Separation and Purification Technology, 120*, 148-155.

Wang, N. (2011a). Ozonation and biodegradation of oil sands process water. (Master of Science), University of Alberta, Edmonton, AB, Canada.

Wang, N., Chelme-Ayala, P., Perez-Estrada, L., Garcia-Garcia, E., Pun, J., Martin, J. W., . . . Gamal El-Din, M. (2013b). Impact of ozonation on naphthenic acids speciation and toxicity of oil sands process-affected water to Vibrio fischeri and mammalian immune system. *Environmental Science & Technology, 47*(12), 6518-6526.

Wang, T. H., Kang, S. F., & Lin, Y. H. (1999). Comparison among Fenton-related processes to remove 2, 4-dinitrophenol. *Journal of Environmental Science & Health Part A, 34*(6), 1267-1281.

Wang, Y. N. (2011b). Application of Coagulation-Flocculation Process for Treating Oil Sands Process-Affected Water. (Master of Science), University of Alberta, Edmonton, AB, Canada.

Wang, Z., Bush, R. T., & Liu, J. (2013c). Arsenic(III) and iron(II) co-oxidation by oxygen and hydrogen peroxide: Divergent reactions in the presence of organic ligands. *Chemosphere, 93*(9), 1936-1941.

Wardle, B. (2009). Principles and applications of photochemistry. Chichester, West Sussex, United Kingdom: John Wiley & Sons.

Wei, C. S., Huang, W. Y., Zhang, R. J., Wang, Y. H., Luo, L. M., Mo, H., & Xiao, L. H. (2014). Assessment of the Fe^{3+}-EDTA Complex in UV-Fenton-Like Processes: The Degradation of Methylene Blue. Paper presented at the Applied Mechanics and Materials.

Weschler, C., Mandich, M., & Graedel, T. (1986). Speciation, photosensitivity, and reactions of transition metal ions in atmospheric droplets. *Journal of Geophysical Research, D: Atmospheres, 91*(D4), 5189-5204.

Whitburn, J. S., Wilkinson, S. D., & Williams, D. R. (1999). Chemical speciation of ethylenediamine-N, N′ -disuccinic acid (EDDS) and its metal complexes in solution. *Chemical Speciation & Bioavailability, 11*(3), 85-93.

White, E. M., Vaughan, P. P., & Zepp, R. G. (2003). Role of the photo-Fenton reaction in the production of hydroxyl radicals and photobleaching of colored dissolved organic matter in a coastal river of the southeastern United States. *Aquatic Sciences, 65*(4), 402-414.

Willkinson, S. D. (1998). Chemical Speciation of a Biodegradable Replacement Ligand for EDTA. (Doctor of Philosophy), University of Wales, Cardiff.

Wood, P. M. (1988). The potential diagram for oxygen at pH 7. *Biochemical Journal, 253*(1), 287-289.

Wort, D. J., & Patel, K. M. (1970). Response of Plants to Naphthenic and Cycloalkanecarboxylic Acids. *Agronomy Journal, 62*(5), 644-&.

Wort, D. J., Severson, J. G., & Peirson, D. R. (1973). Mechanism of Plant Growth Stimulation by Naphthenic Acid Effects on Nitrogen Metabolism of Phaseolus Vulgaris L. *Plant Physiology, 52*(2), 162-165.

Wu, Y., Passananti, M., Brigante, M., Dong, W., & Mailhot, G. (2014). Fe(III)-EDDS complex in Fenton and photo-Fenton processes: from the radical formation to the degradation of a target compound. *Environmental Science and Pollution Research, 21*(21), 12154-12162.

Wubs, H. J., & Beenackers, A. (1994). Kinetics of absorption of hydrogen sulfide into aqueous ferric solutions of EDTA and HEDTA. *AI Ch. E. J., 40*(3), 433-444.

Xue, X., Hanna, K., Despas, C., Wu, F., & Deng, N. (2009). Effect of chelating agent on the oxidation rate of PCP in the magnetite/H_2O_2 system at neutral pH. *Journal of Molecular Catalysis A: Chemical, 311*(1), 29-35.

Yamasaki, M., & Shibahara, T. (1992). Structure of Incomplete Cubane-Type Sulfur-Bridged Molybdenum Cluster Compound, $Na_2[Mo_3S_4(Hnta)_3]$• $5H_2O$ (H_3NTA = nitrilotriacetic acid). *Analytical Sciences, 8*(5), 727-729.

Yan, Q., Yu, D., Wang, Z., Zou, H., & Ruan, W. (2008). Phenol inhibition and restoration of the bioactivity of anaerobic granular sludge. *Applied Biochemistry and Biotechnology, 150*(3), 259-265.

Yang, Y., Zhang, X., & Wang, Z. (2002). Oilfield produced water treatment with surface-modified fiber ball media filtration. *Water Science & Technology, 46*(11-12), 165-170.

Yao, W., & Millero, F. J. (1996). Oxidation of hydrogen sulfide by hydrous Fe(III) oxides in seawater. *Marine Chemistry, 52*(1), 1-16.

Ying, L., Youzhi, L., Guisheng, Q., Huidong, G., & Zhengfeng, Z. (2014). Selection of Chelated Fe(III)/Fe(II) Catalytic Oxidation Agents for Desulfurization Based on Iron Complexation Method. *China Petroleum Processing and Petrochemical Technology, 16*(2), 50-58.

Yu, X., Zuo, J., Tang, X., Li, R., Li, Z., & Zhang, F. (2014). Toxicity evaluation of pharmaceutical wastewaters using the alga Scenedesmus obliquus and the bacterium Vibrio fischeri. *Journal of Hazardous Materials*, 266, 68-74.

Yue, B., Zhou, Y., Xu, J. Y., Wu, Z. Z., Zhang, X., Zou, Y. F., & Jin, S. L. (2002). Photocatalytic degradation of aqueous 4-chlorophenol by silica-immobilized polyoxometalates. *Environmental Science & Technology, 36*(6), 1325-1329.

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

Zhang, L. H., Zhu, Z. L., Zhang, R. H., Zheng, C. S., Zhang, H., Qiu, Y. L., & Zhao, J. F. (2008). Extraction of copper from sewage sludge using biodegradable chelant EDDS. *Journal of Environmental Sciences, 20*(8), 970-974.

Zhang, Y., Klamerth, N., Ashagre Messele, S., Chelme-Ayala, P., & Gamal El-Din, M. (2016a). Kinetics Study on the Degradation of a Model Naphthenic Acid by Ethylenediamine-N,N’-Disuccinic Acid-Modified Fenton Process. *Journal of Hazardous Materials*, under review.

Zhang, Y., Klamerth, N., & Gamal El-Din, M. (2016b). Degradation of a Model Naphthenic Acid by Nitrilotriacetic Acid-Modified Fenton Process. *Chemical Engineering Journal, 292*, 340-347.

Zhang, Y., McPhedran, K. N., & Gamal El-Din, M. (2015). Pseudomonads biodegradation of aromatic compounds in oil sands process-affected water. *Science of the Total Environment, 521*, 59-67.

Zhou, S. Q., Huang, H. P., & Liu, Y. M. (2008). Biodegradation and origin of oil sands in the Western Canada sedimentary basin. *Petroleum Science, 5*(2), 87-94.

Zubot, W. A. (2010). Removal of Naphthenic Acids from Oil Sands Process Water using Petroleum Coke. (Master of Science), University of Alberta, Edmonton, AB, Canada.

Zuo, Y., & Hoigne, J. (1992). Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III)-oxalato complexes. *Environmental Science & Technology, 26*(5), 1014-1022.