Degradation of Recalcitrant Organics in Oil Sands Process Water (OSPW) Using Combined Electro-Oxidation and Electrochemically Activated Peroxymonosulfate (EO-PMS)

by

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ABSTRACT

In northern Alberta, the bitumen extraction process from oil sands ores consumes large amounts of water that results in the generation of huge volumes of oil sand process water (OSPW). Currently, the treatment of OSPW is considered a major challenge facing the oil sands industry. Moreover, among the different constituents in OSPW, naphthenic acids (NAs) have attracted increasing attention due to their acute toxicity associated with complexity and persistently, which are great hazards towards several organisms. Therefore, great efforts have been made in developing efficient and effective treatment techniques for the remediation of OSPW.

The main objective of this research was to investigate the applicability and effectiveness of using combined electro-oxidation and electrochemically activated peroxymonosulfate (EO-PMS) process for the treatment of OSPW. In the first stage of this study, the coupled EO-PMS process showed high removal efficiency of 5-Phenylvaleric Acid (PVA) as a NA model compound, in which EO was enhanced by the successful electrochemical activation of PMS at different electrodes surface. The removal efficiencies increased with the increase in the PMS concentration and applied current, however, decreased at higher levels. Both sulfate radicals ($SO_4^{\bullet-}$) and hydroxyl radicals ($^{\bullet}OH$) were found to be the primary reaction oxidants for PVA degradation. A complete removal of 50 mg/L PVA was achieved within 1 h under optimal conditions of carbon felt (cathode), platinum Pt (anode), PMS = 4mM, and current I= 250 mA. In the second stage of this study, the combined EO-PMS process using Pt, dimensionally stable anodes (DSA), boron-doped diamond (BDD), and graphite plate anodes and carbon felt used as cathode was able to reduce the classical and oxidized NAs as well as aromatics in OSPW. Applying the EO only showed lower removal of NAs compared when adding PMS to the system using the same Pt anode. DSA, BDD and graphite plate anodes achieved higher reduction of 76%, 88.4% and 89.7% of classical NAs (O_2-NAs) concentration, respectively, while only BDD was able to completely remove all the oxidized NAs. The combined system of EO-PMS presents an efficient technology for the degradation of NAs and has a great potential to be attractive for wastewater treatment in oil sands industry due to its flexibility and high effectiveness at removing constituents of concern from OSPW as part of reclamation approaches.

PREFACE

The research work presented in this thesis is an original work performed by myself (Ali Abdelrahman) under the supervision of Dr. Mohamed Gamal El-Din in the Department of Civil and Environmental Engineering at the University of Alberta. I conducted all of the research experiments, in addition to data analysis and interpretation as well as the manuscript preparation under the supervision of Dr. Mohamed Gamal El-Din. Part of the sample analysis or manuscript edits work included some contribution from some post-doctoral colleagues. Dr. Pamela Chelme-Ayala and Dr. Soliu Ganiyu contributed to the manuscript revision and edits. Dr. Zuo Tong How also helped by measuring the NA concentration using the liquid chromatography- mass spectrometry (LC-MS) and ultra-performance liquid chromatography time-of-flight mass spectrometry (UPLC TOF-MS).

DEDICATION

This thesis work is dedicated to my loving mother & father (Amal & Satti) who have been my source of inspiration and strength, whose endless love and prayers make me able to finish this work.

To my brother (Abdallatif) and sisters (Sarah and Samah) who have always been close to me by their words of encouragement and support.

To all my family, relatives and friends.

To the souls of my grandmother and uncle.

To those honorable 'martyrs' of the December revolution who died fighting for freedom, peace and justice in Sudan.

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ABBREVIATIONS

AO	Anodic oxidation
AOPs	Advanced oxidation processes
BDD	Boron-doped diamond
CHWE	Clark hot water extraction process
CF	Carbon felt
COD	Chemical oxygen demand
DO	Dissolved oxygen
DSA	Dimensionally stable anode
ESI-MS	Electrospray ionization-mass spectrometry
EO	Electro-oxidation
EAOPs	Electrochemical advanced oxidation processes
EO-PMS	Electro-oxidation and electrochemically activated PMS
FTICR	Fourier transform ion cyclotron resonance
FTIR	Fourier transform infrared
GAC	Granular activated carbon
GC	Gas chromatography

GEC	General current efficiency
HPLC	High performance liquid chromatography
H_2O_2	Hydrogen peroxide
IrO_2	Iridium dioxide
PbO_2	Lead dioxide
MeOH	Methanol
MS	Mass spectrometry
NAs	Naphthenic acids
O_3	Ozone
OSPW	Oil sands process water
PAHs	Polycyclic aromatic hydrocarbons
PDS	Peroxydisulfate
PMS	Peroxymonosulfate acid
Pt	Platinum
PVA	5-phenylvaleric acid
ROS	Reactive oxygen species
RuO_2	Ruthenium dioxide

SEC	Specific energy consumption
SFS	Synchronous fluorescence spectra
SnO_2	Tin dioxide
TBA	Tert-butyl alcohol
TDS	Total dissolved solids
TOC	Total organic carbon
UPLC-TOF-MS	Ultra-performance liquid chromatography time-of-flight mass spectrometry

1. INTRODUCTION

1.1 Background

The huge amounts of products and different methods of manufacturing in industrial plants result in a wide range of effluent wastewaters with different sources, compositions, quality and toxicity. This has increased the number of both research studies and businesses focusing on industrial waste treatment. Industrial effluents usually contain complex mixtures of organic and inorganic compounds; some of them can be toxic, non-biodegradable and difficult to treat (Sirés et al. 2014). The growing public and social concerns regarding the environmental pollution problems and the presence of hazardous contaminants widely in industrial effluents have brought stringent legislations coupled with economic and social pressures for developing new and more sustainable efficient technologies for industrial wastewater treatment (Panizza and Cerisola 2009, Ramírez et al. 2013). The oil sands industry is one of the major and important industries in Alberta, Canada, that is currently facing critical water demand and wastewater treatment challenges.

1.2 Oil sands in Northern Alberta

Northern Alberta in Canada is a home of one of the world's largest oil sands reserves (after Venezuela and Saudi Arabia), containing over 2.5 trillion barrels of recoverable bitumen (a thick tar-like substance) (Quesnel 2015, Li et al. 2017). The bitumen is usually upgraded to synthetic crude oil, which can be used for the production of petroleum products. Although the bitumen is considered more costly to recover and process compared to the conventional fossil fuel, the increasing global demand for oil and the use of advance technologies in bitumen production have led to the rapid growth of the Alberta oil sands industry (Lu 2013).

There are three major oil sands deposits in northern Alberta; Athabasca in Fort McMurray is the largest oil sands deposit, which covers a surface area of more than 100,000 km^2 (Allen 2008, Jiang et al. 2016). These deposits are significant economic assets, both to Alberta and Canada. Therefore, the proper management of this important asset, especially in terms of environmental impact from mining processes, is critical to ensure the long-term viability of the oil sand resources.

The production rate of bitumen by the Alberta's oil sands industry reached 2.15 million barrels/day (bpd) in 2014, and the number is predicated to reach around 4 million bpd by 2030 (Li et al. 2017). The separation process of bitumen from clay and sand particles in surface mined oil sands commonly occurs by using the modified Clark hot water extraction process (CHWE). In this process, sodium hydroxide is added to increase the mixture pH to around 8, which increases the solubility of oil sands asphaltic acids and this can stimulate the release of surfactants and improve bitumen separation from sand and clay (Allen 2008, Kannel and Gan 2012). The hot water extraction process consumes huge volumes of fresh water at around 2 to 3 barrels of fresh water for every barrel of upgraded bitumen, which results in large volumes of process water of which more than 80 % is recycled (Allen 2008, Quesnel, 2015, Li et al. 2017, Abdalrhman 2019). This process water, commonly known as oil sands process water (OSPW) is a complex mixture that contains sands, silts, clays, water, dissolved ions (primarily Na^+, HCO^{3-}, Cl^- and SO_4^{2-}), heavy metals, unrecoverable bitumen, and inorganic and organic compounds (Kannel and Gan, 2012, Lu 2013). Due to a “zero discharge approach” maintained by the regulatory framework, oil sands companies are not allowed to release their OSPW into the receiving environment. Instead, OSPW is currently sent to be stored in tailings ponds for the long-term (Brown and Ulrich 2015). The volume and number of tailings ponds are growing, which the amount of accumulated OSPW estimated to be more than 1 billion m^3, covering an area of more than 170 km^2 (Abdalrhman 2019). The large volumes of impounded OSPW critically increase the need of developing effective and efficient treatment technologies for OSPW remediation.

1.3 Oil sands process water (OSPW)

1.3.1 Composition and properties of OSPW

The composition of OSPW vary from one site to another, depending on several factors such as the ore quality, extraction process and age. In general, the generated waste slurries from the extraction process are mixtures of water (70 to 80%), solids (20 to 30 %) and residual bitumen (1–3 %) (Allen 2008, Kannel and Gan 2012). In the tailing ponds, the slurries settle and divide into three layers: (i) the upper layer is clarified water that contains total suspended solids (15–70 mg/L) with residual bitumen and it is known as OSPW; (ii) the middle layer is an aqueous suspension of fine particles (silt and clay); and (iii) the bottom layer includes rapidly settled sand particles (Allen 2008). The layer of OSPW is slightly alkaline, with a pH 7.8 to 8.7, and is considered acutely toxic to aquatic organisms because during the extraction processes the organic compounds leach from bitumen (Abdalrhman 2019). OSPW has a moderate hardness (15- 25 mg/L Ca^{2+}, 5-10 mg/L Mg^{2+}) and electrical conductivity of 3.0-3.7 mS/cm. In addition, OSPW is considered to be slightly salty water, with total dissolved solids (TDS) concentrations of 2000 to 2500 mg/L (Allen, 2008, Gamal El-Din et al. 2011). Moreover, the dominated dissolved solids are sodium (500-700 mg/L), bicarbonate (800-1000 mg/L), chloride (75-550 mg/L) and sulphate (200-300 mg/L) (Allen 2008).

OSPW contains a number of organic compounds that have been detected, including bitumen, naphthenic acids (NAs), humic and fulvic acids, phenols, phthalates, asphaltenes, xylenes, creosols, polycyclic aromatic hydrocarbons (PAHs), benzene, ethylbenzene and toluene (Allen 2008, Kannel and Gan 2012).

1.3.2 Naphthenic acids (NAs)

Among the other organic compounds of OSPW, NAs have attracted more attention due to their high toxicity toward different organisms and their corrosive behavior toward the process equipment (Kannel and Gan 2012, Abdalrhman 2019). Based on the composition and age, even at low relatively concentrations, NAs can have toxic effects. The concentrations of NAs in OSPW range between 20 to 70 mg/L, with up to high of 130 mg/L in fresh process water (Holowenko et al. 2002, Allen 2008). NAs occur naturally as a part of the bitumen mixture; they are the products of the incomplete degradation of petroleum hydrocarbons by the indigenous microbial communities in the reservoirs (Brown and Ulrich 2015).

NAs are defined as a complex mixture of predominantly alkyl-substituted cyclo-aliphatic saturated carboxylic acids with acyclic aliphatic acids (paraffinic or fatty) in addition to aromatic olefinic, hydroxy, and dibasic acids as minor components of NAs. The structure of NAs are most frequently represented using the general formula $C_nH_{2n+z}O_x$, where n is the carbon number and varies in the range of 7 to 30, z is either zero or a negative even integer ranging from 0 to -18 and represents the number of hydrogen deficiency, and x is the number of oxygen atoms, which for classical NAs ($x = 2$) and for oxidized NAs ($x \geq 3$) (Clemente et al. 2003, Wang et al. 2013, Abdalrhman 2019). Some examples of typical NAs structures are shown in Figure 1.1. NAs with one ring belong to the Z = -2 family and those with two rings belong to the Z = - 4 family and so on.

As NAs are a complex mixture, their physical and chemical properties may vary depending on the chemical composition and molecular structures (Kannel and Gan, 2012). Table 1.1 shows some physical and chemical properties of NAs reported by Lu (Lu 2013).

Due to the high complexity of the OSPW mixture, the quantification and identification of NAs in OSPW is considered a challenging analytical task. Numerous analytical methods have been utilized for NA quantification and identification in the environmental samples. The most developed analytical techniques including Fourier transform infrared spectroscopy (FTIR), gas chromatography (GC), negative ion electrospray ionization–mass spectrometry (ESI–MS), high performance liquid chromatography (HPLC) have been applied for the characterization of NA mixtures (Holowenko et al. 2002, Clemente and Fedorak 2005, Lu et al. 2013). In addition, various high-resolution techniques have also been used to characterize NAs, including HPLC coupled with time of flight (TOF-MS), LC/MS/MS, Orbitrap-MS, and Fourier Transform Ion Cyclotron Resonance (FTICR) MS (Headley et al. 2013, Brown and Ulrich 2015). For research purpose, currently the most common technique used to analyze the composition of NA mixture is mass spectrometry (MS), in which an individual NA profile is characterized in a sample by plotting the relative response of each mass corresponding to a particular n and Z combination (Martin et al. 2008).

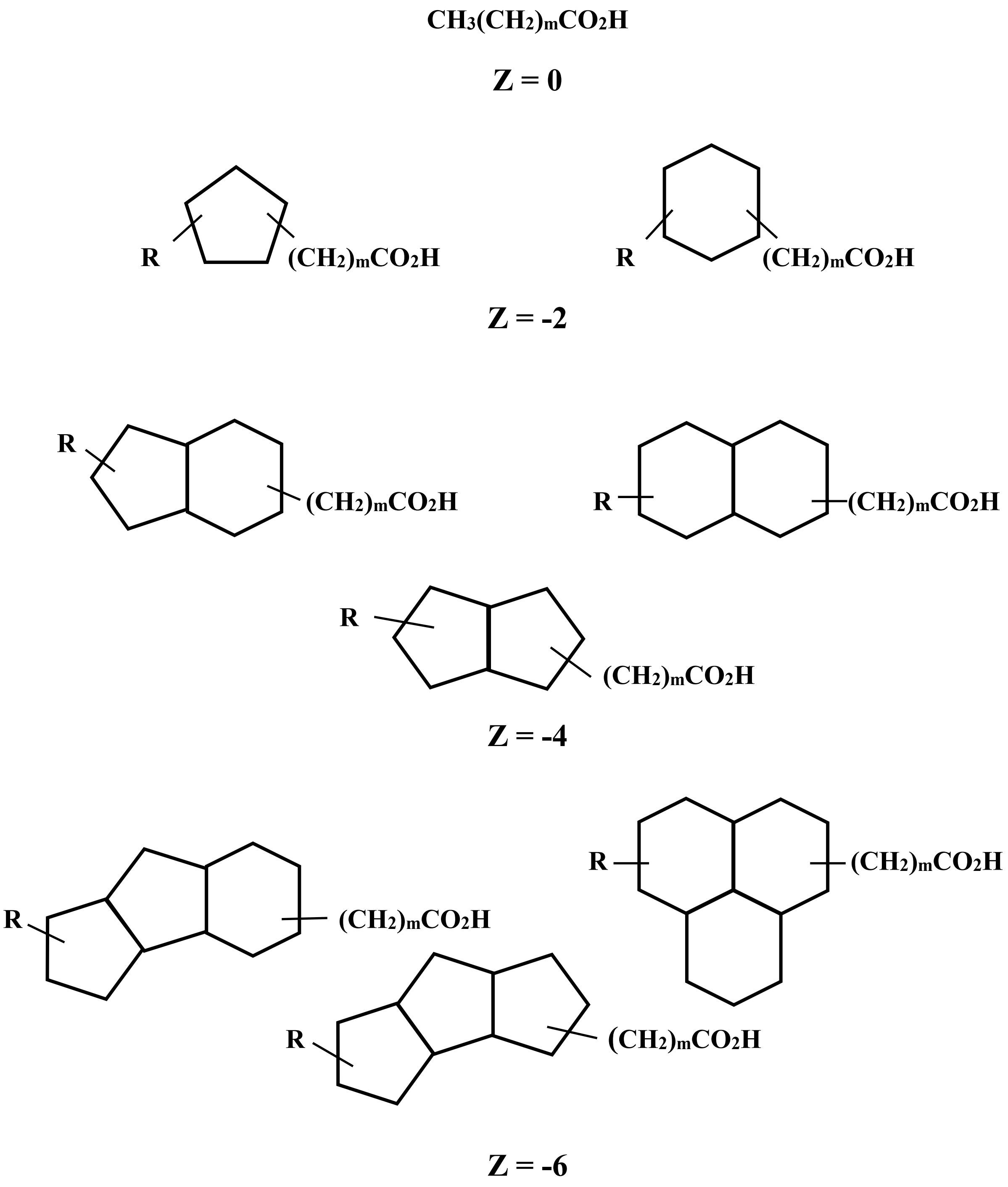

Figure 1.1 Structures of some NAs with the general formula $C_nH_{2n+Z}O_2$, where R is an alkyl chain and m is number of CH_2 units (adapted from Holowenko et al. 2002).

Table 1.1 Physical and chemical properties of NAs.

Parameters	**Properties**
Color	Pale yellow, dark amber, yellowish brown
State	Viscous liquid
Odor	Musty hydrocarbon odor
Solubility	Soluble in water at pH 7 or alkaline pH (at NAs < 50 mg/L)
Density	Between 0.97 and 0.99 g/cm^3
Molecular weight	Generally between 150 and 450 atomic mass units
Boiling point	250 - 350 °C
Dissociation constant (pK_a)	5 to 6
Log (K_{ow}) (octanol water partition coefficient)	4 at pH 1 2.4 at pH 7 2.1 at pH 10
Henry's law constant	8.6×10^{-6} atm m^3/mole
Vapor pressure	2.4×10^{-6} atm
Partition coefficient (mL/g)	0.2 for coarse sands and 2.5 for oil sands fines; 1.3 for water and 17.8 for synthetic groundwater

1.3.3 Toxicity of OSPW and NAs

Most of the research studies conducted on OSPW NAs have reported a connection between the toxicity of OSPW and NAs. Brown and Ulrich reported that many studies found that NAs are the main cause of OSPW toxicity (Brown and Ulrich 2015). NAs have been shown to be acutely and chronically toxic to a variety of organisms including zooplanktons, phytoplanktons, plants, fish, mammals, and bacteria (Clemente and Fedorak 2005, Allen 2008, Wang et al. 2013). Because of the presence of NAs, fresh tailings water from oil sands processing is considered acutely toxic to aquatic organisms ($LC_{50} < 10$ % v/v for rainbow trout) and mammals (oral $LC_{50} = 3.0$ g/kg body weight) (Headley and McMartin 2004). Although there is a relationship between the toxicity and the concentration of NAs, to describe the toxic effects of NAs by determining only the total NA concentration is still not enough because other factors such as molecular structure and composition of NA mixture can have an important role (Clemente and Fedorak 2005, Abdalrhman 2019). Moreover, it is still not feasible to determine which individual compounds with NA structure in OSPW are more toxic due to the inherent complexity of NA mixtures (Lu 2013). Some studies have demonstrated that the NA mixtures with lower molecular weight compounds are directly connected to higher toxicity towards various organisms (Holowenko et al. 2002, Lu 2013). In addition, other parameters including salinity, pH, molecular size and hydrophobicity can also affect the toxicity of NAs. Recent studies have reported that NAs, despite of their major contribution, are not the only cause of OSPW toxicity and some other organic and inorganic compounds may contribute to the toxicity directly or through synergistic effects (Garcia-Garcia et al. 2011, Brown and Ulrich 2015).

1.3.4 Degradation of NAs

Due to the regulation and zero discharge approach, OSPW must be stored in tailings ponds until it can be remediated (Allen 2008). Different processes including biodegradation, coagulation/flocculation, adsorption/sorption, and advanced oxidation processes have been used for OSPW treatment and removal of NAs and their toxicity in aquatic and wastewater environments.

1.3.4.1 Biodegradation

Biological treatment refers to the use of microbes to remove the organic contaminants from wastewater. They are considered the most popular and cost effective process for wastewater treatment that make it widespread (Abdalrhman 2019).

As mentioned earlier in this chapter, OSPW is considered very toxic to many organisms, although biodegradation by using indigenous microbial communities from oil sands tailings water has been widely investigated for OSPW remediation (Herman et al. 1994, Brown and Ulrich 2015). The biodegradation of both commercial and OSPW extracted NAs effectively resulted in toxicity reduction, as determined by Microtox test (Herman et al. 1994). Clemente et al. reported the use of different microorganisms native to tailing ponds to degrade Kodak and Merichem commercial NA mixtures (Clemente et al. 2004). It was found that for the same microbial community, the biodegradation efficiency was higher for commercial NAs which 48% of the NAs carbon was released as CO_2, while only 2 % of carbon released from OSPW-extracted NAs as CO_2 (Herman et al. 1994).

The relationship between NA structure and biodegradability of both commercial and OSPW NAs was also investigated (Han et al. 2008). It has also been reported that the commercial NA mixtures are more biodegradable compared to the native NAs present in OSPW mixture and that NAs with lower molecular weights and fewer rings have more tendency to biodegradation (Han et al. 2008, Lu 2013). A number of studies have reported several of microorganisms with the ability to degrade and metabolize recalcitrant NAs, including *Nitrosomonas, Truepera, Candidatus Nitrotoga, Arenimonas, Mesorhizobium, Bradyrhizobiaceae, Nitrosospira, Mycobacterium* and *Limnobacter* (Quinlan and Tam 2015). However, the biodegradation of NAs and other organic contaminants will need to be coupled with other treatment processes to become more effective and efficient in removing all the toxic and refractory organic pollutants from OSPW (Brown and Ulrich 2015).

1.3.4.2 Coagulation/flocculation

Coagulation/Flocculation (CF) is the most common and widely used process to remove suspended solids and colloidal particles from water and wastewater. CF is considered a potential pretreatment step in OSPW treatment that would improve the performance of main remediation process by decreasing the particle and organic loading on the subsequent treatment processes (Pourrezaei et al. 2011). The removal of NAs from OSPW using CF process was successfully applied by using aluminum sulfate (alum) and cationic polymer polydiallyldimethylammonium chloride (polyDADMAC), which resulted in 37% removal of the classical NAs and 86% removal of oxidized NAs (Pourrezaei et al. 2011). Quinlan and Tam reported the use of electrocoagulation method for NA removal from wastewater, achieving a considerable removal up to 93% (Quinlan and Tam 2015). Nevertheless, coagulation/flocculation processes are associated with number of limitations including the large volumes of produced sludge and the high operating cost accompanied with the excess chemicals needed (Quinlan and Tam 2015).

1.3.4.3 Adsorption

Among the possible techniques for water and wastewater treatments, the adsorption process using solid adsorbents has been widely studied as one of the most efficient methods for the removal of organic contaminants in wastewater treatment (Rashed 2013). Many studies have investigated the effectiveness of using different types of adsorbents for the removal of NAs from OSPW such as: granular activated carbon (GAC) (Mohamed et al. 2008), petroleum coke-derived activated carbons (Gamal El-Din et al. 2011, Sarkar 2013), activated carbons from sawdust (Iranmanesh et al. 2014), spent fluid catalytic cracking catalyst (Gong and Yao 2012) and clays and synthetic resins (Zou et al. 1997, Quinlan and Tam 2015). Although activated carbon is the most common adsorbent studied for NA removal from OSPW because of its high porosity and large specific surface area that achieved high adsorption efficiency, the preparation and regeneration of commercial activated carbons are economically expensive (Quinlan and Tam 2015; Abdalrhman 2019).

1.3.4.4 Advanced oxidation processes (AOPs)

Advanced oxidation processes (AOPs) have been widely studied in the literature and found to be effective treatments for the removal of recalcitrant hazardous species in water and wastewater. There are various recognized AOPs that have been studied for the degradation of NAs in OSPW, depending on the reagents or activation approaches used. Among the former, ozone is the most common (Brown and Ulrich 2015, Quinlan and Tam 2015, Xu et al. 2017). It was found that the ozonation of NA-containing OSPW showed a significant increase in their biodegradability and a reduction in the toxicity towards *Vibrio fischeri* (Gamal El-Din et al. 2011, Wang et al. 2013).

The earlier work on NA abatement by ozonation was conducted more than a decade ago and ozonation of OSPW resulted in decreasing the proportion of higher molecular weight NAs by more than 95% and removed the toxicity of OSPW (Scott et al. 2008). Many studies after that have used ozonation for OSPW treatment with focus on improving the biodegradability, NAs removal rate and toxicity reduction (Martin et al. 2010, Wang et al. 2013). However, the use of ozonation alone cannot achieve a complete degradation due to the complexity of NAs OSPW, which can also result in the formation of different by-products, such as ketones, peroxides, aldehydes carboxylic constituents and brominated organics (Kannel and Gan 2012). A recent study examined the effect of combining ozone with hydrogen peroxide (O_3/ H_2O_2), which showed to be more efficient by removing up to 99.7% and 90% of the NAs in both batch and semi-batch mode, respectively (Afzal et al. 2015). There are also other types of AOPs that been used for the remediation of OSPW and NAs including: UV/H_2O_2 process (Drzewicz et al. 2010); UV/chlorine process (Shu et al. 2014); microwave treatment (Mishra et al. 2010) and Fenton-based oxidation processes (Zhang et al. 2017). Despite of their high effective performance in removing NAs from OSPW, the restrictions that limited those techniques were the high needed doses, the significant energy and operating cost and other technical restrictions (the alkaline pH of OSPW in the case of Fenton or the turbidity of OSPW in the case of UV-based AOPs).

1.3.5 Electrochemical advanced oxidation processes

The advanced oxidation processes (AOPs) are based on the in situ generation of highly reactive and oxidizing agents such as hydroxyl radicals ($^{\bullet}OH$) in large quantities enough to effectively degrade highly recalcitrant organic compounds (Glaze et al. 1987, Oturan and Aaron 2014). During recent years, new class of AOPs based on the electrochemical technology have been developed to produce directly or indirectly $^{\bullet}OH$ on the anode surface, within the so-called electrochemical advanced oxidation processes (EAOPs) (Brillas et al. 2009, Sirés et al. 2014).

EAOPs have gained increasing interest as most promising techniques for the degradation of different recalcitrant compounds, including but not limited to phenolic compounds, perfluorinated organics, chlorinated organics and disinfection byproducts. The role of these technologies in environmental protection has been the main topic of numerous books and reviews (Anglada et al. 2009, Panizza and Cerisola 2009, Chaplin 2014, Sirés et al. 2014, Martínez-Huitle et al. 2015, Särkkä et al. 2015, Moreira et al. 2017). However, recently few studies have investigated the use of EAOPs for OSPW treatment (Abdalrhman et al. 2019, Abdalrhman and Gamal El-Din 2020, Ganiyu and Gamal El-Din 2020). The EAOPs are found to be more efficient, highly safe and environmentally friendly, due to its several advantages such as versatility, amenability, excellent oxidants production, little or no addition of chemical reagents is needed in treatment process and possibility of energy recovery by capturing the H_2 that is produced from cathodic reactions. In addition, electrochemical oxidation is generally known by using simple equipment, as well as the ease of operation (Anglada et al. 2009, Chaplin 2014, Brito et al. 2018, Durán et al. 2018). Electrochemical oxidation process consists of electrochemical cell with electrode materials and the cell configuration can be divided or undivided. Based on where the oxidants production take place, EAOP can be classified into anodic and cathodic processes (Brillas et al. 2009, Panizza and Cerisola 2009, Sirés et al. 2014, Martínez-Huitle et al. 2015). The cathodic reduction mainly involves the electrogeneration of hydrogen peroxide (H_2O_2) through the reduction of O_2 at cathode (Brillas et al. 2009, Panizza and Cerisola 2009).

The electro-oxidation (EO) or anodic oxidation of wastewater pollutants can take place through either two different mechanisms. (1) Direct anodic oxidation, in which pollutants diffuse from bulk solution to anode surface where it can be destroyed on the surface (direct electron transfer to the anode) by transferring electrons from the substrate (R) to the anode (Eq. (1.1)); (2) Indirect oxidation, where strong oxidizing agents are electro-generated at the anode surface (i.e., hydroxyl radicals $^{\bullet}OH$) (Eq. (1.2)) and then destroy the pollutants in the bulk solution (Eq. (1.3)) (Brillas et al. 2009, Sirés et al. 2014, Martínez-Huitle et al. 2015). During anodic oxidation, organic compounds have two pathways to follow: electrochemical conversion (partial oxidation), or electrochemical combustion (complete oxidation to CO_2 and other inorganic compounds) (Anglada et al. 2009). However, the feasibility of this process could be affected by the nature of anodic material, the electro-generation of physiosorbed and chemisorbed hydroxyl radicals, beside the oxygen evolution reaction (OER) (Brito et al. 2018).

$$R \rightarrow (R^{\bullet})^{+} + e^{-} \qquad (1.1)$$

$$M + H_2O/OH^{-} \rightarrow M\,[^{\bullet}OH] + H^{+} + e^{-} \qquad (1.2)$$

$$M(^{\bullet}OH) + R \rightarrow M\,[\,] + RO + H^{+} + e^{-} \qquad (1.3)$$

Anode materials are divided into active and non-active electrodes depending on their oxygen evolution overpotential and the interaction between electrogenerated $^{\bullet}OH$ and the anode surface (Panizza and Cerisola 2009, Sirés et al. 2014, Martínez-Huitle et al. 2015).

Ruthenium dioxide (RuO_2), iridium dioxide (IrO_2), platinum (Pt), graphite and other Sp^2 carbon-based electrodes are typical examples of active anode materials with low O_2-overpotentials, which produce $^{\bullet}OH$ that are chemosorbed at the anode surface and less effective for mineralization. On the other hand, non-active anodes such as lead dioxide (PbO_2), tin dioxide (SnO_2), boron-doped diamond (BDD) and sub-stoichiometric TiO_2 electrodes present high O_2-overpotentials, in which the generated $^{\bullet}OH$ are weakly physisorbed on the anode surface (Sirés et al. 2014, Martínez-Huitle et al. 2015, Moreira et al. 2017, Ganiyu and Martinez-Huitle 2019).

Recent studies have investigated the role of sulfate radicals ($SO_4^{\bullet -}$) in EAOP for the degradation of refractory organic pollutants (Farhat et al. 2015, Oh et al. 2016, Matzek et al. 2018). Sulfate radicals ($SO_4^{\bullet -}$) are considered strong oxidants with similar redox potentials (2.5-3.1 V vs 2.7 V) but longer half-lives (30-40 μs vs 20 ns) compared to $^{\bullet}OH$ (Farhat et al. 2015, Moreira et al. 2017). Generally, the common way of $SO_4^{\bullet -}$generation is by activating persulfate such as peroxymonosulfate (PMS) and peroxydisulfate (PDS) using the thermal energy (Fan et al. 2015), ultrasound (Yin et al. 2018), UV radiation (Zhang et al. 2019), transition metal (Hu et al. 2019) and electrochemical oxidation (Bu et al. 2019, Ganiyu et al. 2020). Among these methods, electrochemical activation has attracted increasing attention in recent years due to its environmental friendliness and the ease of operation and control, which make it to be a promising activation technology (Sires et al. 2014, Farhat et al. 2015, Song et al. 2018).

1.4 Research significance

OSPW is a complex mixture of suspended solids, salts, inorganic compounds, dissolved organic compounds and trace metals that is generated during the surface extraction of minable bitumen. Currently, the treatment of OSPW is considered a major challenge facing the oil sands industry. Moreover, NAs in OSPW have attracted increasing attention; due to their acute toxicity associated with complexity and persistently, which are great hazards towards several organisms. Therefore, the development of efficient and effective technique is extremely needed for possible remediation of organic constituents (especially NAs) in OSPW. However, as previously discussed in Section (1.3.4), most of the current proposed treatment methods have some major drawbacks such as high cost and large amount of sludge (physical and chemical processes), very slow rate (biodegradation), or have technical restrictions (Fenton and UV-based AOPs) and, therefore, they are not feasible to be applied at large scale.

In this context, electro-oxidation (EO) has been considered a promising and efficient approach for degrading persistence organic compounds in industrial wastewater such as OSPW. However, few studies have reported the use of electrochemical-oxidation for OSPW remediation.

In recent years, sulfate radicals ($SO4^{\bullet -}$)-based AOPs technology have been widely studied for the degradation of various types of recalcitrant organic compounds. The electrochemical activation of sulfate free radicals has attracted research interest due to the simplicity, adaptability and outstanding performance. Therefore, the goal of this research was to investigate the applicability and effectiveness of combining electro-oxidation and electrochemically activated peroxymonosulfate (EO-PMS) for OSPW treatment.

The hypotheses on which this research was based include:

- In comparison to $^{\bullet}OH$, $SO_4^{\bullet -}$ exhibits higher selectivity and reactivity towards certain functional groups of target pollutants (e.g., carboxylic, anilinic, and phenolic). Thus, it can be expected to have better mass transfer performance and contact chance in degrading the most persistent contaminants.

- The combination of electro-oxidation and electrochemical activation of PMS (EO-PMS) can lead to the continuous generation of strong oxidants of $SO_4^{\bullet -}$ beside $^{\bullet}OH$, therefore, improving the system performance by enhancing the degradation rate and increasing the removal efficiency significantly.

1.5 Research objectives

The main objectives of this research that were evaluated can be summarized as follow:

(1) Investigate the electrochemical activation of PMS at the surface of different electrode materials by using 5-Phenylvaleric Acid (PVA) as NA model compound.

(2) Examine the significant effect of various operating parameters on the oxidation process, such as electrode material, PMS anion concentration and applied current.

(3) Identify the primary oxidizing species produced in EO-PMS system by using radical scavengers and estimate the relative participation in the degradation.

(4) Optimize the experimental conditions and apply it for the treatment of real OSPW.

(5) Assess the effectiveness of combined EO-PMS process using different anode materials for OSPW organics degradation.

(6) Evaluate the process performance by assessing the NA degradation and mineralization of dissolved organics in real OSPW.

1.6 Thesis structure

The thesis consists of four chapters that were logically organized according to the research stages and objectives presented above.

Chapter 1 includes a general introduction to the research background and objectives. Briefly, it presents an overall review of the oil sands production, OSPW, previous conducted treatment processes for OSPW, electro-oxidation fundamentals, research significance and objectives.

Chapter 2 presents the degradation of a synthetic NA model solution (5-Phenylvaleric Acid /PVA) by combined electro-oxidation and electrochemically activated PMS (EO-PMS). The effects of different operating parameters on the oxidation process were examined such electrode material, PMS anion concentration and applied current. The removal of the PVA and mineralization of dissolved organics were evaluated. In addition, the role of $SO_4^{\bullet-}$ and $^{\bullet}OH$ in the EO-PMS process was evaluated using radical scavengers.

Chapter 3 focuses on the treatment of real OSPW by combined EO-PMS process using different types of anode materials including Pt, dimensionally stable anodes (DSA), graphite plate and BDD mesh electrodes. The degradation of NAs and recalcitrant organics in OSPW by EO-PMS was investigated and compared.

Chapter 4 provides a general conclusion of the research findings presented in Chapters 2 and 3, in addition to recommendations for some future works.

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2. DEGRADATION OF SYNTHETIC NAPHTHENIC ACID SOLUTION (PVA)

2.1 Introduction

It well known that the oil sands in Northern Alberta represent one of the major sources of Canadian economy sector (Alberta Energy Regulator 2014, Abdalrhman 2019). The current commercial process of bitumen extraction consumes huge amount of caustic hot water and this results in the generation of large volumes of process water known as oil sands process water (OSPW) which are stored in large tailings ponds (Allen 2008). OSPW has a significant environmental threat due to its potential toxicity toward various organisms including plants, aquatic and terrestrial organisms (Kannel and Gan 2012, Quesnel 2015, Li et al. 2017). It has been reported that the major contributor to toxicity in OSPW is a group of carboxylic acids known as naphthenic acids (NAs) which are generated from the extraction of bitumen from Alberta's oil sands (Kannel and Gan 2012, Abdalrhman 2019). NAs are known to be very recalcitrant and the chemical composition of NAs is very complex. They are a mixture of alkyl-substituted acyclic, cycloaliphatic groups with a general formula of $C_nH_{2n+Z}O_2$, where n represents the number of carbon atoms and Z is zero or a negative even integer that reflects the hydrogen atoms lost due to ring formation (Fang et al. 2018). Therefore, one of the high priorities for oil sands industry is the development of effective and efficient treatment processes to remove NAs in OSPW before been released into the environment (Abdalrhman and Gamal El-Din 2017).

Different advanced oxidation processes (AOPs) have been studied for the removal of refractory NA compounds from OSPW, including ozonation, UV radiation (UV/H_2O_2, UV/Fenton), and potassium ferrate (VI) (Kannel and Gan 2012, Xu et al. 2016, Abdalrhman et al. 2019). However, the use of AOPs is associated with high cost. In addition, the organic compounds cannot be completely degraded by ozone (O_3), and photolysis is limited to the physical properties of surface waters (turbidity, color, etc.). Electrochemical advanced oxidation processes (EAOPs) have been considered an efficient and promising approach for degrading persistence organic compounds in industrial wastewater. EAOPs are known for the generation of enormous reactive and oxidizing species like $^{\bullet}OH$, and mainly based on the oxidants production at the surface of anode or cathode can be classified into anodic and cathodic processes (Panizza and Cerisola 2009, Sirés et al. 2014, Martinez-Huitle and Panizza 2018). Although few studies have examined the use of this method for the treatment of OSPW, Abdelrahman et al. investigated the degradation of model NA compounds by anodic oxidation on graphite anode (Abdelrahman et al. 2019).

In recent years, the huge progress in the removal of various types of recalcitrant organic compounds from wastewaters has led to the development of another type AOPs, which is based on the generation of oxidant species like sulfate radicals ($SO_4^{\bullet-}$) with longer half-life than $^{\bullet}OH$ (Liu et al. 2018, Ganiyu and Martinez-Huitle 2019, Ganiyu et al. 2020, Zhi et al. 2020)

Sulfate radical-based AOPs technology have been widely studied for the degradation of target pollutants (Cai et al. 2015, Ghanbari and Moradi 2017, Fang et al. 2018). The generation of $SO_4^{\bullet-}$ radicals usually occurs during the activation of persulfate (PS) or peroxymonosulfate (PMS) via UV photolysis, heat, ultrasound or transition metals (Jaafarzadeh et al. 2017, Ghanbari and Moradi 2017, Bu et al. 2018, Liu et al. 2019). Furthermore, the electrochemical activation of sulfate free radicals with higher oxidative potential has attracted research interest due to the simplicity, adaptability and outstanding performance (Bu et al. 2019, Wang et al. 2020).

A few sulfate radical-based AOPs using different activation approaches have been assessed for the degradation of NAs, such as zero valent iron ($S_2O_8^{2-}$/ZVI), catalyst-free thermally activated PS and UV/PS (Drzewicz et al. 2012, Xu et al. 2016, Fang et al. 2018).

The main objectives of this chapter were to study the electrochemical activation of PMS at the surface of different electrode materials; investigate the removal performance of 5-Phenylvaleric Acid (PVA) degradation as NA model compound, determine the mineralization of dissolved organics, and examine the significant effects of various operating parameters on the oxidation process, such as electrode material, PMS anion concentration and current density. The role of $SO_4^{\bullet-}$ and $^{\bullet}OH$ in the EO-PMS process by using scavengers was also investigated.

2.2. Materials and methods

2.2.1 Chemical materials

5-phenylvaleric acid (PVA, $C_{11}H_{14}O_2$) was a model compound provided by Sigma-Aldrich (St. Louis, MO, USA). Figure 2.1 shows the structure of PVA. Analytical grade methanol (MeOH) (HPLC grade, Fisher Chemicals, Canada) tert-butyl alcohol (TBA) (99.5%, ACROS Organics, Fisher Scientific, Canada), potassium monopersulfate triple salt ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$), sodium sulfate (≥ 99%, Sigma-Aldrich, Canada) were used during the experiments. Analytical grade sulfuric acid, sodium bicarbonate ($NaHCO_3$) and sodium hydroxide (NaOH) were purchased from Fisher Scientific Canada (Edmonton, Alberta). MilliQ water (R > 18 MΩ cm, Millipore Corporation) was used for the preparation of all synthetic solutions.

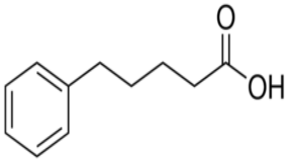

Figure 2.1 Structure of PVA

2.2.2 Experimental apparatus and procedure

All treatment experiments were performed in an open, undivided cylindrical glass reactor of 250 mL capacity and 6 cm diameter with the solution constantly stirred using a PTFE magnetic bar during treatment to enhance the mass transport towards the electrodes and keep homogenization of the solution. Different electrode materials with rectangular shape and effective area of 25 cm^2 were used. Anode materials: Pt, DSA, graphite plate and BDD mesh and cathodes: carbon felt, stainless steel mesh, graphite plate, graphite felt were investigated. In all cases, the two electrodes were placed and fixed in the center of the glass reactor parallel to each other at electrode distance of approximately 1.2 cm in order to minimize the resistance of the electrolysis medium while maintaining enough space for effective mass transport in the area between electrodes and prevent any gas accumulation. A triple output DC power supply (9130, B&K Precision, California, US) was used to deliver a stable current and the changes in voltage were monitored and recorded. Electrical connections were made to the electrodes with alligator clips. A control experiment with an identical setup of the reactor was run without electrical power in parallel with electrodes to ensure that any removal arising from adsorption or volatilization was excluded.

A stock solution of PVA was prepared in deionized water and the initial concentration (C_0) was kept at 50 mg/L and been buffered with 5mM $NaHCO_3$ solution (pH=8) to simulate the concentration and the pH of NAs in real OSPW (Kannel and Gan 2012, Fang et al. 2018).

Except otherwise stated, the reactor was operated in batch mode with 200 mL of synthetic NA acid solution under fixed current (Galvanostatic) conditions. 50 mM sodium sulfate (Na_2SO_4) was added as supporting electrolyte to ensure adequate conductivity of mixed solution. After PMS powder was added into the reactor and thoroughly mixed by a magnetic stirrer, the electrochemical reactions were initiated by applying the current for a total period of 4 hours. All samples were taken and then filtered through a 0.45 μm filter at predetermined time intervals which then been kept in LC vials containing 50 μL methanol (to quench the oxidation reaction) for the subsequent analysis.

2.2.3 Instrumental and analytical methods

The samples were filtered using a 0.45 μm nylon filter, and the pH value of sample was measured by a pH meter (AR 50, Fisher Scientific). The concentrations of the NA model compounds were analyzed by Ultra-performance Liquid Chromatography Mass Spectrometry (UPLCMS, Waters, USA) equipped with a C18 column of (1.7 μm, 2.1 x 50 mm) (Waters, USA) under negative electrospray ionization (-ESI) mode. Details of UPLC-MS analysis method were reported in other study (Shang et al. 2013). A TOC analyzer (Shimadzu, TOC-V CHS/CSN) was used to determine the total organic carbon (TOC) concentrations in the samples.

2.3. Results and discussion

2.3.1 Comparison of PVA degradation in the presence and absence of PMS at CF and SS cathodes

The preliminary experiments were conducted by comparing the degradation of PVA by electrochemical oxidation (EO) alone and combined EO-PMS system using two different cathodes, and Pt was used as the anode (Fig. 2.2). The results showed that combined electrochemically activated PMS and electrochemical oxidation achieved higher degradation efficiency and increased the rate of PVA degradation. For stainless steel cathode, the removal efficiency after 2 hours increased from around 45% using EO technique alone to almost 80% in the presence of PMS. Moreover, the electrochemical activation of PMS process using carbon-felt cathode showed faster degradation compared to applying the EO alone using the same cathode material, with the removal rate roughly 1.5 higher when adding PMS. Fig. 2.3 clearly indicates that the mineralization efficiency of PVA solution after 4 h via electro-activated PMS oxidation process using stainless steel and carbon-felt cathodes (13.6% and 25.1% respectively) was higher than EO process alone in the absence of PMS (only 6.6% and 7.6%, respectively). The explanation is that during EO process the PVA removal was mainly due to the direct electro-oxidation on the anode and the indirect oxidation by hydroxyl radicals M($^{\bullet}$OH) which are formed from water oxidation via Eq. (2.1) and Eq. (2.2), where M represents the metal surface of the anode (Sirés et al. 2014, Martínez-Huitle et al. 2015). While for electrochemical activation of PMS, the increase in removal efficiency could be interpreted with production of strong oxidant especially sulfate radicals ($SO_4^{\bullet-}$) via reduction of monosulfate anions by accepting an electron on cathode surface (Eq. (2.3)), and then both $SO_4^{\bullet-}$ and $^{\bullet}$OH may mineralize the organic pollutants (Liu et al. 2019).

$$M + H_2O \rightarrow M\,(^{\bullet}OH) + H^+ + e^- \quad (2.1)$$

$$M\,(^{\bullet}OH) + \text{organics} \rightarrow M + \text{oxidation products} \quad (2.2)$$

$$HSO_5^- + e^- \rightarrow OH^- + SO_4^{\bullet-} \quad (2.3)$$

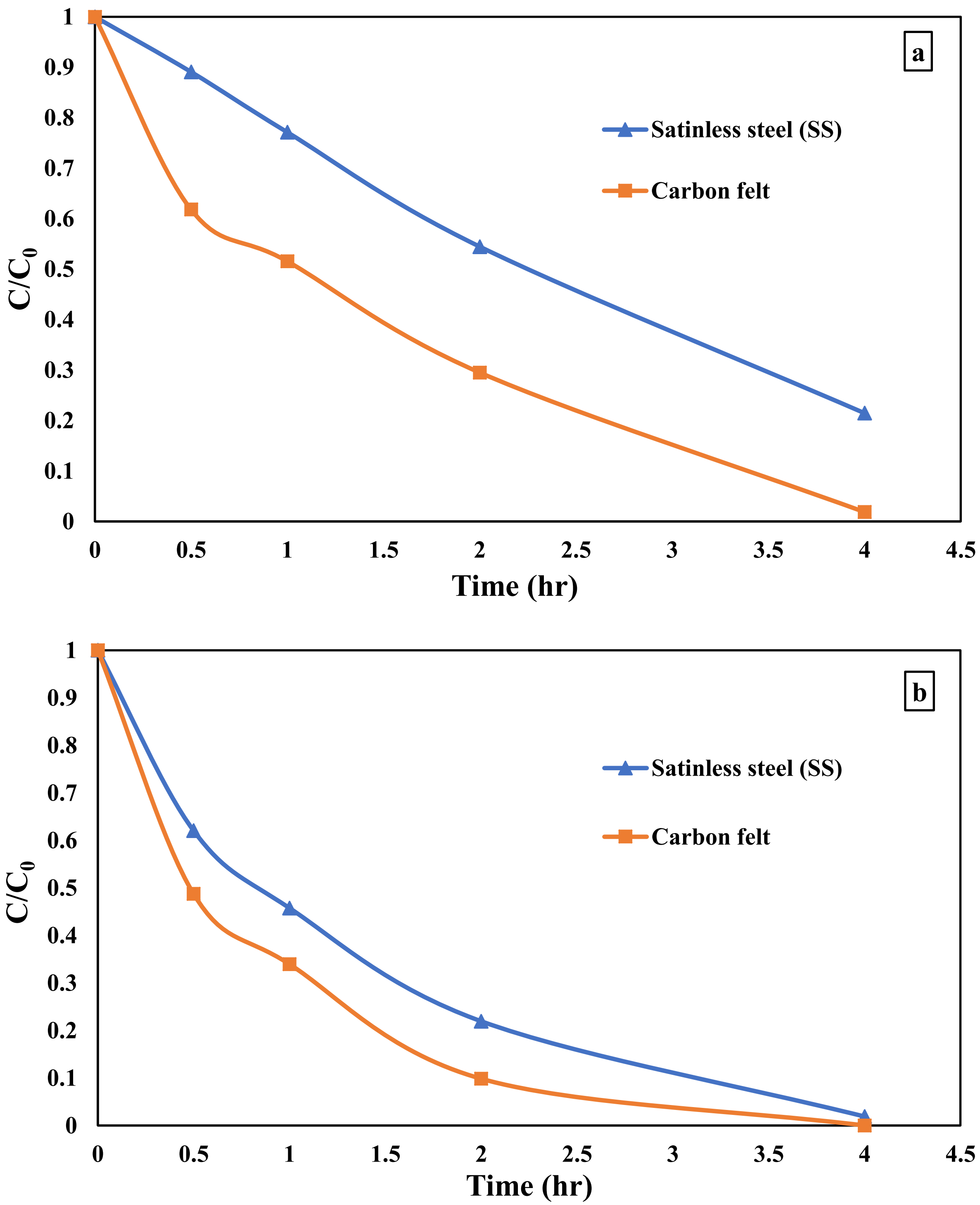

Figure 2.2 The effect of PMS addition on the degradation of 5-Phenylvaleric Acid (PVA) by EO using two different cathodes (stainless steel, carbon felt): **(a)** Absence of PMS, **(b)** Presence of PMS. (PMS = 4 mM, Pt anode, current (I) = 250 mA).

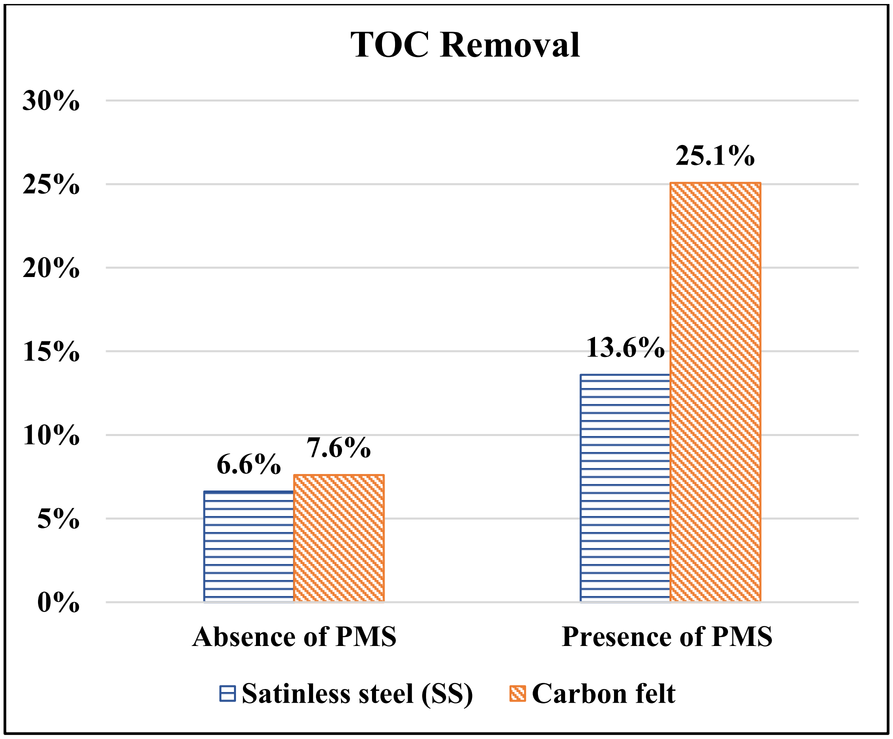

Figure 2.3 The effect of PMS addition on the mineralization of organic carbon.

2.3.2 Effects of cathode material

Combining electrochemically activated peroxymonosulfate with advanced electrochemical oxidation can achieve higher degradation efficiency. The influence of cathode materials on the degradation rate of PVA was studied. The anode was platinum and different cathodes have been applied to PVA removal by electrolysis and electrochemical activation of PMS.

As shown in Fig. 2.4 and Fig. 2.5, the carbon felt (CF) electrode not only achieved the faster rate of degradation of PVA, but also the highest rate of TOC mineralization among the cathodes. At CF cathode, almost 90% of PVA was removed after 2 hours, while the TOC removal efficiency reached around 25% at the end of the process. However, all of other three cathodes - graphite felt, graphite plate and stainless steel had close range of degradation rate compared to each other during the first half of the treatment process as showed in Fig. 2.3. In addition, the % TOC mineralization obtained by stainless steel and graphite felt were 12.2% and 22.2%, respectively (Fig. 2.5), whilst graphite plate removal efficacy was negligible (result not shown). This may be attributed to the good electro-activation and electro-catalytic properties of carbon-felt, as PMS has ideally been activated at its surface beside the formation of hydrogen peroxide (H_2O_2) on the CF cathode that contributed to the oxidation of PVA. Therefore, in this case the oxidation rate was accelerated when CF was used as cathode. The cathode materials play an important role in PMS activation and enhancing the degradation efficiency. Among all cathode materials, CF was considered as the best cathode material for the current electrochemical investigation, and it was selected for further studies.

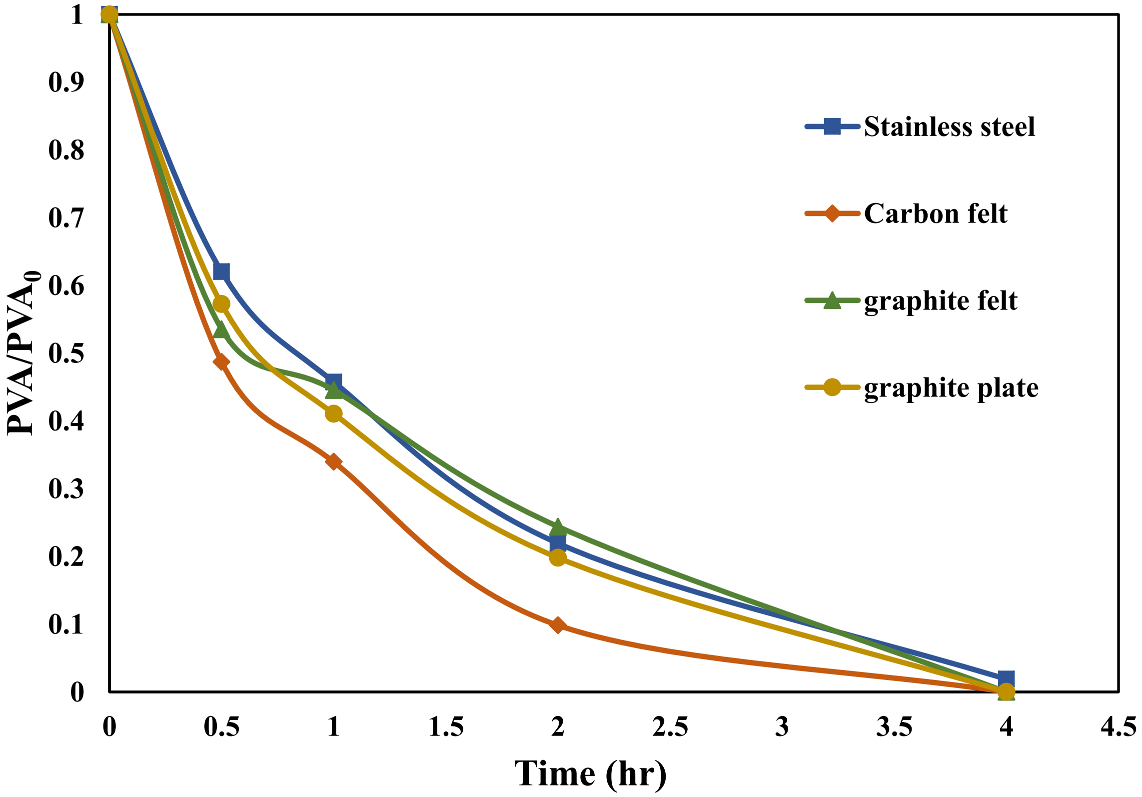

Figure 2.4 The effect of cathode material on the degradation of 5-Phenylvaleric Acid (PVA). (PMS = 4 mM, Pt [anode], current (I) = 250 mA).

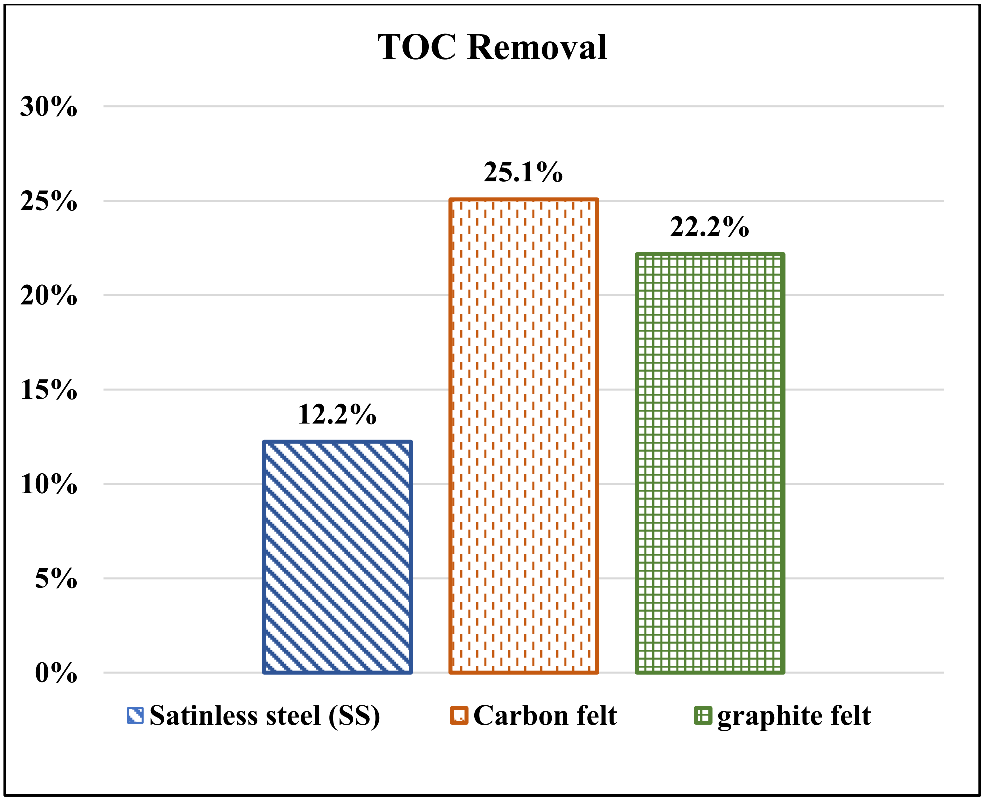

Figure 2.5 The effect of cathode material on the mineralization of organic carbon.

2.3.3 Effects of anode material

The PVA degradation by combined EO-PMS process using different anode materials was investigated using CF as cathode. The experiments were run at pH 8.2 value of PVA solution, which is similar to the pH value of real OSPW. The studied anodes were DSA, BDD, graphite plate, and Pt. The anode material effect on the oxidation of PVA can be seen in Fig. 2.6. Only 60 min was enough for BDD/CF cell in the presence of PMS to remove completely 42.5 mg/L of PVA, while Pt/CF cell needed 4 hours for full degradation. This is because Pt anode has a poor oxidation power and produces much lower active radicals of $^{\bullet}$OH than the BDD anode that has higher and great ability of $^{\bullet}$OH production (Sirés et al. 2005, Brillas et al. 2009, Outran et al. 2013).

However, a slow but complete destruction of PVA was achieved using the Pt anode. Both DSA and graphite plate anodes obtained degradation efficiency of roughly 90% over 4 hours compared to the other tasted anode materials. The results of TOC mineralization (Fig. 2.7) were in agreement with oxidation power of anodes. The maximum efficiency of TOC removal was obtained by BDD anode (96.8 %), and Pt reached only 25%, which is higher than the efficiency obtained with DSA and graphite plate anodes. This can be explained by the generation of high concentration of highly reactive and weakly (physically) adsorbed $^{\bullet}OH$ on the surface of BDD electrode. Meanwhile, $^{\bullet}OH$ at the Pt anode are strongly adsorbed (chemisorption) on the surface and are less reactive to perform oxidation (Jeong et al. 2009, Chaplin et al. 2014). The nature of the anode material has a significant effect on EO process efficiency and electro-generation of $^{\bullet}OH$. Pt and BDD are the most commonly used anodes; however, the BDD anode is the most effective in terms of complete degradation and mineralization of organic compounds. Nevertheless, although of the high oxidation rates, the cost of BDD anodes is relatively high. For the further studies, Pt was selected as an optimum anode and was used in the following experiments to clearly see the effect of PMS electro-activation and the generation of sulfate radicals.

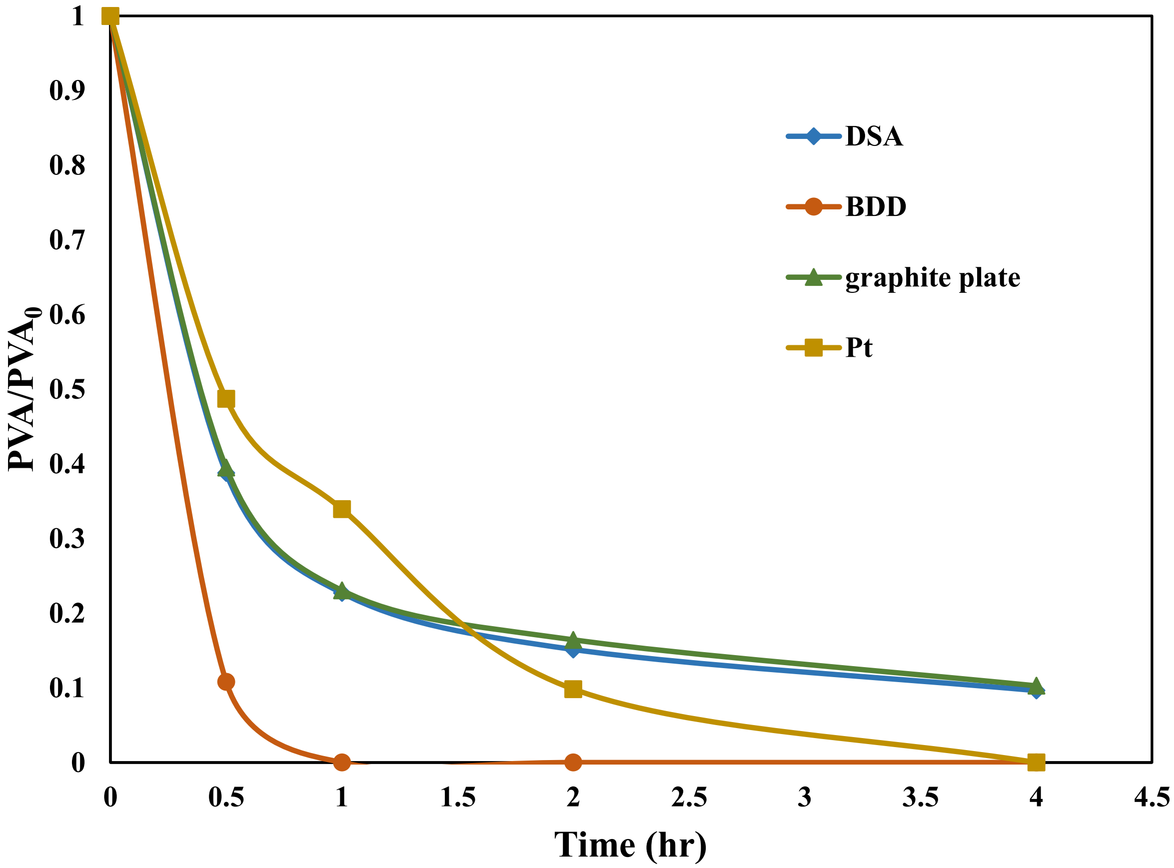

Figure 2.6 The effect of anode material on the degradation of 5-Phenylvaleric Acid (PVA). (PMS = 4 mM, carbon felt cathode, current (I) = 250 mA).

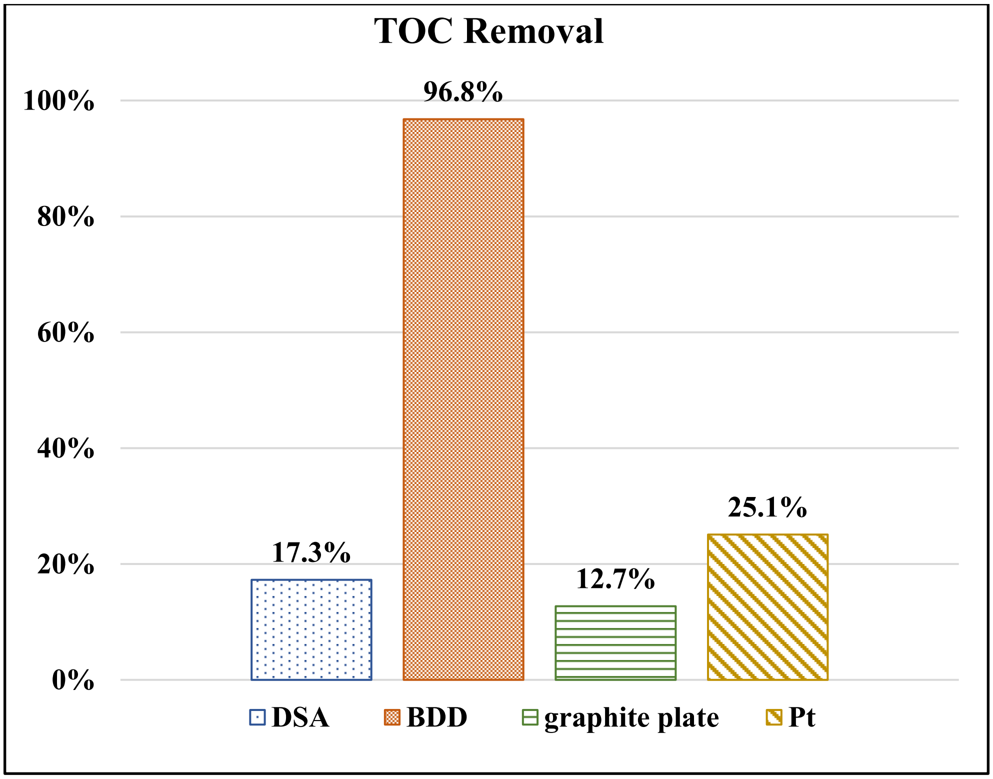

Figure 2.7 The effect of anode material on the mineralization of organic carbon.

2.3.4 The effect of initial PMS concentration

As a source of $SO_4^{\bullet-}$, the PMS has a significant role in the EO-PMS process and the concentration of PMS usually has an obvious impact on the removal of pollutants. Thus, some experiments were conducted using different PMS concentrations to evaluate the effect of PMS dosage on the degradation of PVA by the combined EO-PMS technique and the results are depicted in Fig. 2.8. It can be clearly seen that the removal efficiency and the degradation rate of PVA remarkably accelerated as the initial concentration of PMS increased. The PVA was totally removed within around 4 h and 1h when the concentration increased from 1 mM to 4 mM, respectively. This is because at low PMS concentration (1mM) there was insufficient generation of oxidants. As the PMS concentration increased further (2 mM and 4 mM), there was higher production of strong oxidants of $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals for the PVA degradation. However, further increase of PMS concentration to 10 mM caused a slightly decrease in the removal rate by almost 9%. This phenomenon could be probably due to the unfavorable scavenging reaction between excess PMS and $SO_4^{\bullet-}$ / $^{\bullet}OH$ resulting in the production of lower activity free radicals ($SO_5^{\bullet-}$, $HO_2^{\bullet}$) as described in Eqs. (2.4), (2.5) and (2.6) (Li et al. 2019, Zhang et al. 2020, Wang et al. 2020).

$$SO_4^{\bullet-} + HSO_5^{-} \rightarrow SO_5^{\bullet-} + HSO_4^{-} \quad (2.4)$$

$$SO_4^{\bullet-} + HSO_5^{-} + H_2O \rightarrow HO_2^{\bullet} + 2SO_4^{-} + 2H^{+} \quad (2.5)$$

$$^{\bullet}OH + HSO_5^{-} \rightarrow SO_5^{\bullet-} + H_2O \quad (2.6)$$

Moreover, further investigation was made by measuring the TOC removal efficiency after 4 h. Fig. 2.9 illustrates that the TOC mineralization noticeably improved with an increase of PMS concentration. The percentage removal of 12%, 14.3% and 25.1% were achieved at PMS concentration of 1 mM, 2 mM and 4 mM, respectively. Whereas at 10 mM PMS the mineralization slightly dropped to around 19%, which is in consistent with our previous obtained results above. Thus, the initial 4 mM PMS concentration was chosen as the optimal concentration and was used in later experiments of PVA destruction to investigate the other optimum reaction conditions.

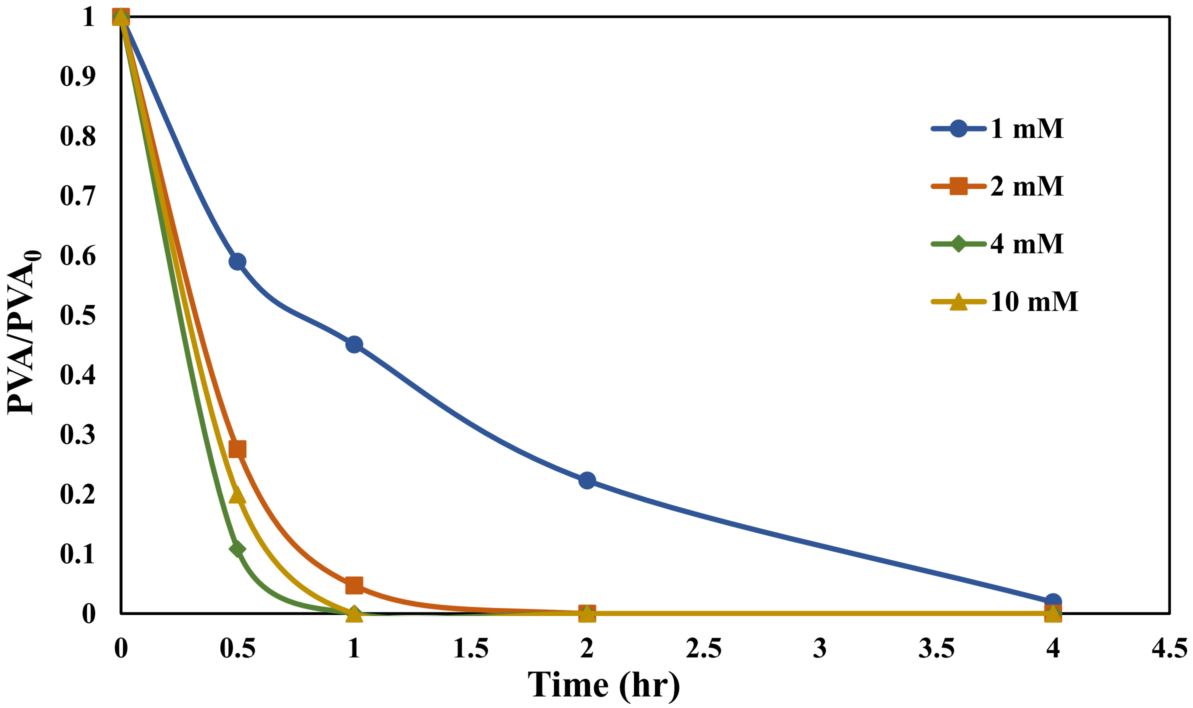

Figure 2.8 The effect of PMS concentration on the degradation of 5-Phenylvaleric Acid (PVA) (Pt anode, carbon felt cathode, current (I) = 250 mA).

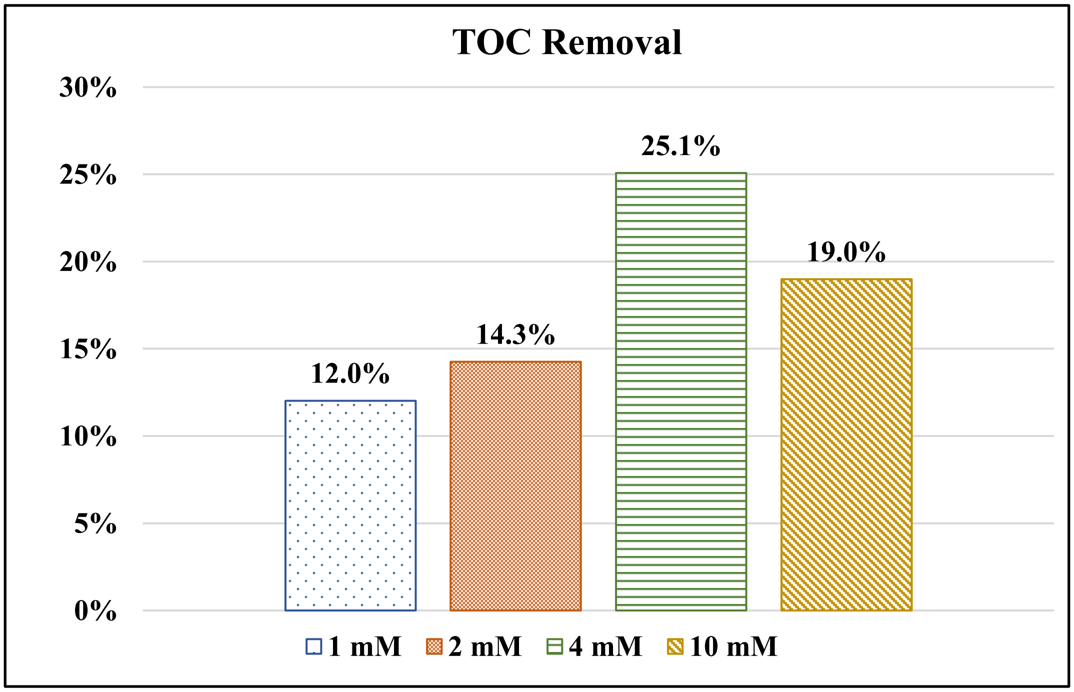

Figure 2.9 The effect of PMS concentration on the mineralization of organic carbon.

2.3.5 The effect of applied current on electro-activated PMS oxidation

It is well known that the current density plays a crucial role in most electrochemical processes because it controls the rate of electrode reactions. In this study, experiments with electric current ranging from 25 to 400 mA were performed and the results of PVA degradation were shown in Fig. 2.10. As the current increased, the degradation rate of PVA was significantly accelerated. The removal efficiency of PVA in 1 h went up from around 33% to 74%, when the electric current increased from 25 mA to 100 mA, and PVA was completely decomposed in 1 h at 250 mA electric current. The increase of current accelerates the direct oxidation of PVA and facilitates the generation of reactive oxygen species (ROS) as well as electrochemical activation of PMS. The increased current would lead to faster and more generation of $^{\bullet}OH$ at the anode surface (Eq. (2.1)) and more $SO_4^{\bullet-}$ via electron transfer reactions (Eq. (2.3)) (Li et al. 2017, Liu et al. 2018).

The degradation of PVA by electro-activated PMS oxidation clearly followed a pseudo first order kinetics model with rate constant (k) increasing from 0.36 h^{-1} to 4.45 $h^{-1}$when the electric current increased from 25 to 250 mA, respectively (Fig. 2.11). However, the further raising of electric current up to 400 mA reduced the removal rate to about 69% during the first hour. This phenomenon could be likely explained with the occurrence of side reactions of cathodic hydrogen gas evolution (Eq. (2.7)) when higher current was applied, which compete for electron during the activation process and generation of sulfate radicals (Eq. (2.3)) (Liu et al. 2018, Bu et al. 2018).

$$2H^+ + 2e^- \rightarrow H_2 \quad (2.7)$$

In addition, the current oversupply would lead to a decrease of the current efficiency and an increase of the energy cost. Therefore, among the studied electric currents, 250 mA was found to be the optimum current and was selected for the subsequent work using combined EO-PMS process.

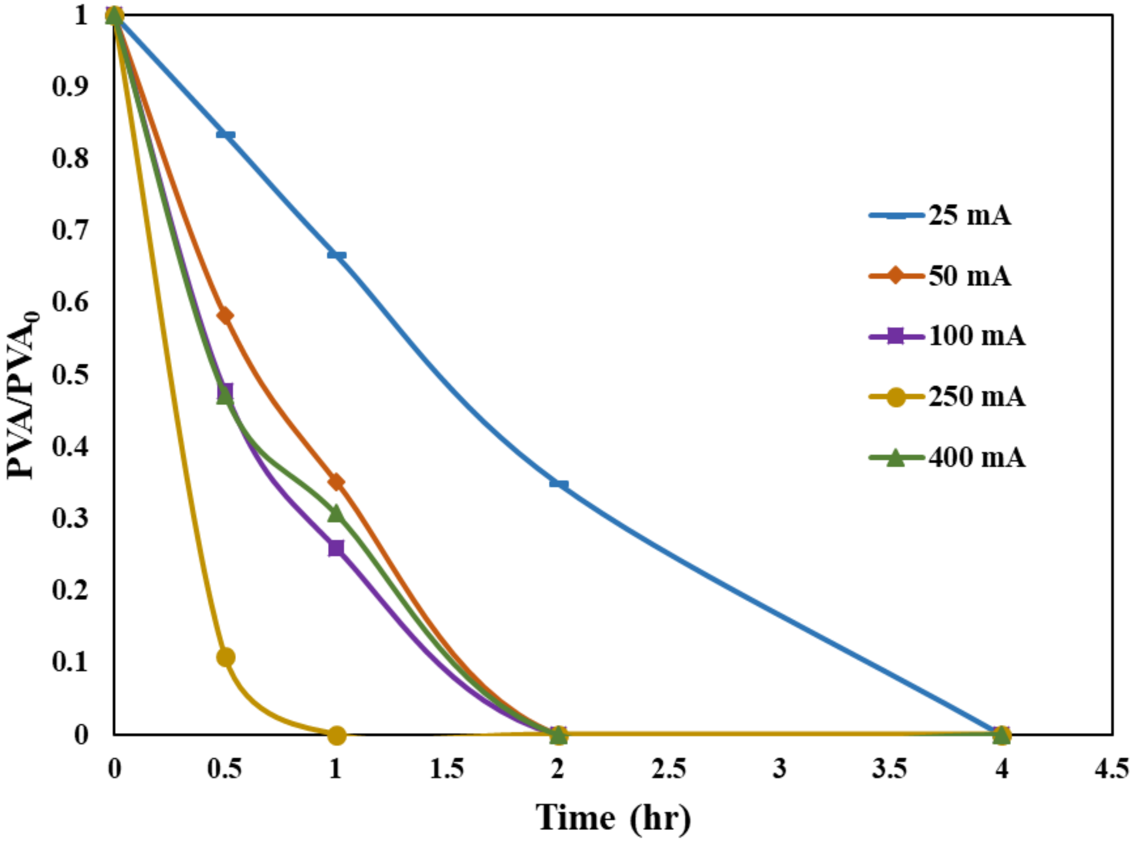

Figure 2.10 The effect of current on the degradation of 5-Phenylvaleric Acid (PVA). (PMS = 4 mM, Pt anode, carbon felt cathode).

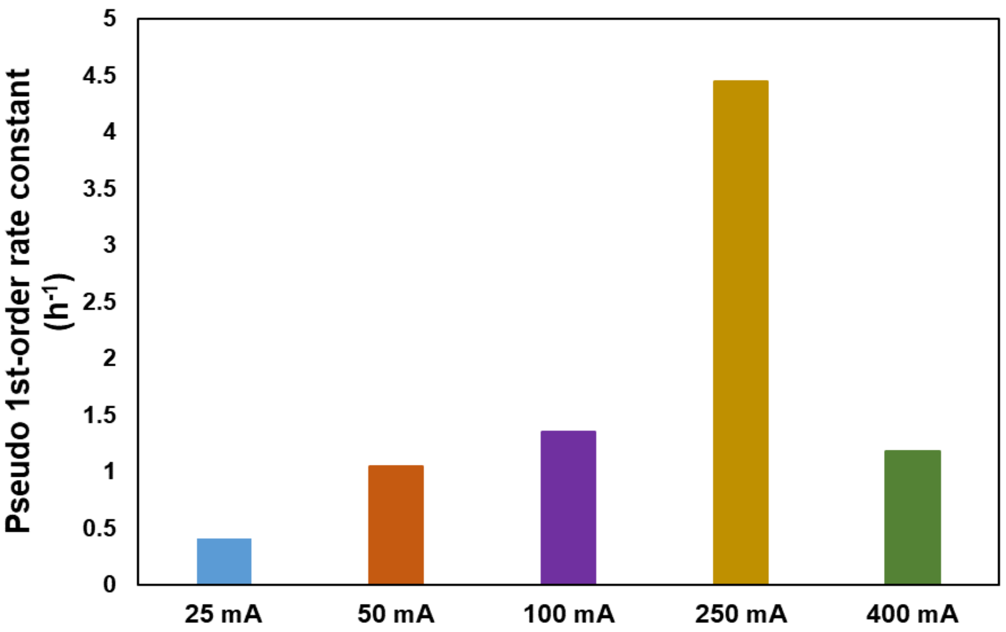

Figure 2.11 Corresponding reaction rate constants at different currents for PVA oxidation reported in Figure 2.9.

2.3.6 The quenching experiments

Generally, both $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals are the potential oxidizing species in PMS activated process. To clarify the contribution of $^{\bullet}OH$ and $SO_4^{\bullet-}$ to the degradation of PVA during EO-PMS process, scavenger experiments were conducted by adding methanol (MeOH) and tert-butanol (TBA) to the reaction mixture. TBA is considered as an effective quencher for $^{\bullet}OH$, whereas MeOH is capable of scavenging both $^{\bullet}OH$ and $SO_4^{\bullet-}$. From the result shown in Fig. 2.12, it can be clearly seen that the PVA removal efficiency decreased in the presence of TBA from 89.2% to 53.3% (30 min) and from 100% to 70.9% (60 min). In the presence of MeOH, PVA removal ratio remarkably declined from 89.2% to 41.9% and from 100% to 62.7% after reaction for 30 min and 60 min, consecutively. This indicating that $SO_4^{\bullet-}$ was generated during PMS activation process, and both $^{\bullet}OH$ and $SO_4^{\bullet-}$ played an important role on PVA degradation in EO-PMS process.

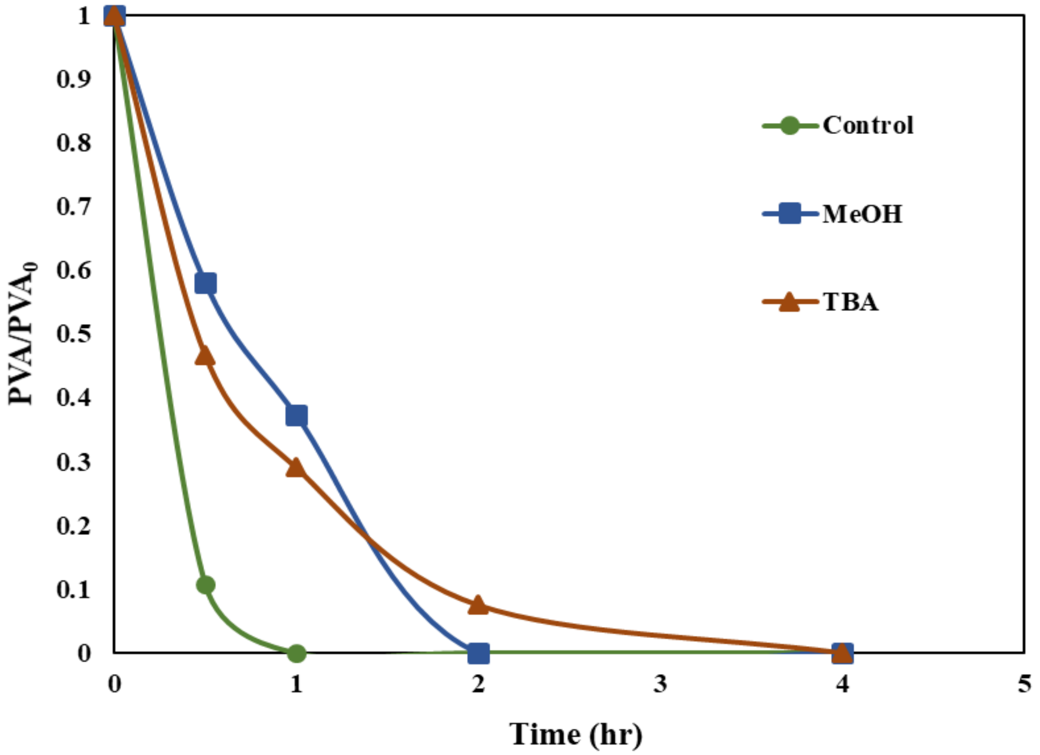

Figure 2.12 Effect of radical scavengers on the degradation of 5-Phenylvaleric Acid (PVA). (PMS = 4 mM, Pt [anode], carbon felt [cathode], current (I) = 250 mA).

2.4. Conclusions

In this study, coupling peroxymonosulfate (PMS) and electrolysis was verified to be an effective method and the process showed high removal efficiency of NA model compound (PVA), in which the electrochemical oxidation was enhanced by the addition of PMS. The effect of cathode material, anode material, PMS concentration and applied current was investigated for the PVA degradation. The findings from our experiments indicate that the removal efficiencies were promoted with the increase in PMS concentration and applied current. However, the excessive addition of PMS and at higher current had a negative influence on PVA oxidation. The results also demonstrate that the complete removal of 50 mg/L PVA can be readily achieved within 1 h under optimal conditions: carbon felt (cathode), Pt (anode), PMS= 4mM, I= 250mA, and pH_0= 8. Radical quenchers including MeOH and TBA were used to show the main oxidizing agents and both $SO_4^{\bullet-}$ and $^{\bullet}OH$ were found to be the primary reaction oxidants for the PVA degradation.

All the results confirmed that the combination of electrochemical oxidation and electro-activated PMS process (EO/PMS) could be a promising and efficient technology for the treatment of recalcitrant NA compounds in OSPW.

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3. DEGRADATION OF RECALCITRANT ORGANICS IN REAL OIL SANDS PROCESS WATER BY COMBINED ELECTROOXIDATION AND ELECTROCHEMICALLY ACTIVATED PEROXYMONOSULFATE (EO-PMS)

3.1 Materials and methods

3.1.1 OSPW and Chemicals

Raw OSPW was collected from an oil sands tailing pond in Fort McMurray, Alberta, Canada, and stored in a cold storage room at 4°C. 5-phenylvaleric acid (PVA, $C_{11}H_{14}O_2$) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Dichloromethane (HPLC and Optima grades), sodium hydroxide, sulfuric acid were obtained from Fisher Scientific (Ottawa, ON, Canada).

3.1.2 Experimental apparatus and procedure

All oxidation experiments were conducted using an open, undivided cylindrical glass reactor of 250 mL capacity and 6 cm diameter, constantly stirred with PTFE magnetic bar to maintain a homogenized solution and enhance the mass transport of substance towards/from the electrodes surface. Different anode materials with 25 cm^2 effective area were used, while the cathode was carbon felt of similar surface area and it was the same during all experiments. The electrodes were fixed in the center of the reactor (parallel to each other) at an electrode distance of 1.2 cm to ensure effective mass transport. A triple output DC power supply (9130, B&K Precision, California, US) was used to deliver a stable current and continuously monitor voltages. Electrical connections were made to the electrodes with alligator clips.

Except otherwise stated, all experiments were performed at room temperature in batch mode under fixed current (Galvanostatic) conditions with 200 mL of real OSPW without addition of any chemical since its conductivity was high enough for good electrical conduction. PMS ($KHSO_5$) powder was added into the reactor and thoroughly mixed by a magnetic stirrer, before the electrochemical reactions were initiated by applying the current of 250 mA for a total period of 240 min. At the end of the experiment (4 h), a sample of the solution was collected and filtered through a 0.45 μm filter, before 450 μL of filtered sample were transferred and quenched immediately with 50 μL methanol in LC vial for subsequent analysis.

The general current efficiency (GCE) for the different anode materials was calculated using the following equation formula (Panizza and Cerisola 2009):

$$\mathrm{GCE} = \frac{(\mathrm{COD_0} - \mathrm{COD_f})\mathrm{F}.\mathrm{V_r}}{8.\mathrm{I}.\Delta\mathrm{t}} \text{ x } 100\% \qquad (3.1)$$

where, COD_0 and COD_f represent the initial and final COD (g/L), F is Faraday's constant (96,485 C/mol), V_r is the reactor volume (L), I refer to the applied current (A), while Δt is the time (s), and 8 represents the equivalent mass of oxygen (32 g O_2 per mol/4 e^-).

Also, the specific energy consumption (SEC) per g of NA removed was calculated using the equation below (Panizza and Cerisola 2009):

$$\mathrm{SEC} = \frac{\mathrm{I}\,.\,\mathrm{U}.\mathrm{t}}{(\mathrm{NA_0} - \mathrm{NA_f})\,.\,\mathrm{V_r}} \qquad (3.2)$$

where, I is the current (A), U is voltage (V), t is time of the reaction (h), NA_0 and NA_f represent the initial and final classical NA concentrations (g/L), while V_r is the reactor volume (L).

3.1.3 Instrumental and analytical methods

The samples were filtered using a 0.45 µm nylon filter, and the pH value of the samples were measured using a pH meter (AR 50, Fisher Scientific). The NA concentration decay was analyzed using ultra-performance liquid chromatography time-of-flight mass spectrometry (UPLC TOF-MS). A Waters UPLC equipped with Phenyl BEH column (Waters, MA, USA), coupled with a high-resolution time-of-flight mass spectrometry TOF-MS (Synapt G2, Waters, MA, USA) operating in negative electrospray ionization mode and using myristic acid-1-^{13}C as internal standard was used to perform the chromatographic separation. Detailed descriptions of the sample analysis, chromatographic separation and data acquisition method using UPLC TOF-MS have been reported elsewhere (Huang et al. 2018) and can be found in the Appendix A. The mineralization of organic constituents of the OSPW was analyzed using a Shimadzu VCSH total organic carbon (TOC) analyzer (Shimadzu, TOC-V CHS/CSN). Chemical oxygen demand (COD) was determined using HACH COD reagent kits (TNT821, LR, Germany) and DR3900 spectrophotometer (HACH, Germany) following the manufacturer's instructions. The aromatic hydrocarbons in the treated solutions were measured by synchronous fluorescence spectra (SFS) using a Varian Cary Eclipse fluorescence spectrometer (Mississauga, ON Canada). Excitation and emission wavelengths ranged from 200 to 600 nm and from 218 to 618 nm, respectively. The spectra were recorded at scanning speed of 600 nm/min and the photomultiplier (PMT) voltage was at 800 mV.

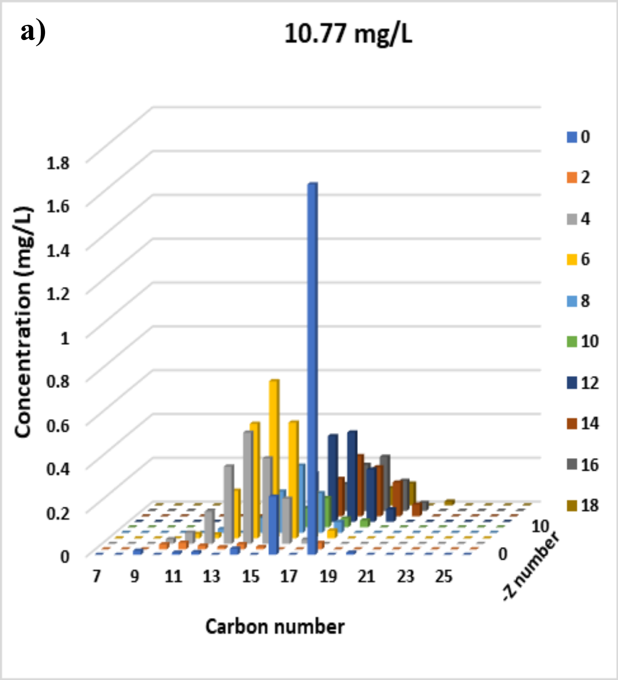
3.2 Results and discussion

3.2.1 Oxidation of OSPW NAs by coupling electro-oxidation and electrochemical activated PMS

The removal of NAs, especially the classical NAs has been considered as a main parameter to determine the efficiency of different treatment methods applied for OSPW remediation. This is due to their higher relative abundance combined with higher hydrophobicity (make them more attachable to the aquatic organisms' cell membrane) and their acute toxicity. The reduction of the concentration of different classes of NAs (O_x-NAs) after 4 h of treatment by combined system of electrochemical oxidation and electro-activated PMS (EO-PMS) process for real OSPW treatment was studied using different anode materials and carbon felt as a cathode. The studied anode were Pt, DSA, BDD and graphite plate. The initial concentration of classical NAs (O_2-NAs) in the raw OSPW sample was 10.77 mg/L, which was the highest among the other classes. Fig. 3.1 illustrate the concentration of classical NAs (O_2-NAs) before and after the treatment of raw OSPW using EO process alone and combined EO-PMS system with various anode materials. From Fig. 3.1b and Fig. 3.1c, it is obvious that the improvement in the removal efficiency performance as a result of adding PMS to EO system compared to applying only EO using the same anode material (Pt), with the concentration of classical NAs reduced to only 3.37 mg/L (68.7%) (Fig. 3.1b) and to 2.25 mg/L (79.2%) (Fig. 3.1c), respectively. This could be interpreted by the production of both free $^{\bullet}OH$ and strong oxidant of $SO_4^{\bullet-}$, which can rapidly oxidize the NAs. Moreover, among the other studied anode materials of DSA, BDD and graphite plate, the decay of the concentration of (O_2-NAs) can be clearly seen, which decreased to 2.58, 1.25 and 1.10 mg/L that accounted for removal rates of 76%, 88.4% and 89.7%, respectively (Figs. 3.1 d,e and F).

As mentioned earlier, NAs include also oxidized NAs that has oxygen atoms more than two in their molecular structure (O_x; X > 2). Although, some of these groups already existed in the NA mixture, they can be generated also as products from the oxidation of classical NAs (Abdalrhman et al. 2019b). In contrast to the classical NAs, the concentration of oxidized NAs (O_4-NAs) was always higher than the amount of classical NAs in all cases after the oxidation process (Fig. 3.2), except in case of BDD anode where all the oxidized NAs were completely removed. This confirmed what was mentioned earlier that during the electrochemical oxidation, some of the classical NAs (O_2-NAs) were transformed into oxidized NAs (O_4 and O_6).

The initial concentration of oxidized O_4-NAs and O_6-NAs were around 6.58 and 0.068 mg/L, respectively (Fig. 3.2). For O_4-NAs, the removal rate after the treatment by combined EO-PMS using DSA and graphite plate anodes reached 52.5% and 79.1%, respectively (Fig. 3.2), while for BDD anode there were no O_4-NAs species detected. On the other hand, for O_6-NAs, there was remarkable increase in the concentration at the end of all conducted experiments, with an exception for BDD anode that showed 100% removal rate of O_6-NAs (Fig. 3.2). This indicating that these oxidized NAs are generated as products of the oxidation process. The difference in the oxidized NAs degradation behavior between graphite plate and DSA can be attributed to the difference in the oxidation mechanisms (Abdalrhman et al. 2019a). Moreover, the excellent performance of BDD anode was due to the formation of greater amounts of oxidants especially, weakly sorbed BDD ($^{\bullet}OH$) that rapidly oxidized the NAs (Ganiyu and Gamal El-Din 2020).


a)
10.77 mg/L
Concentration (mg/L)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
7
9
11
13
15
17
19
21
23
25
Carbon number
0
10
-Z number
0
2
4
6
8
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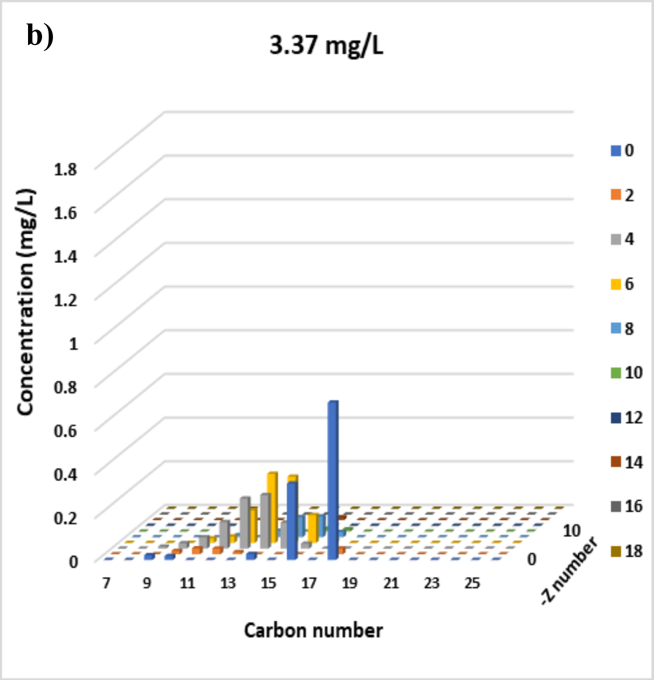
12
14
16
18


b)
3.37 mg/L
Concentration (mg/L)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
7
9
11
13
15
17
19
21
23
25
Carbon number
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10
-Z number
0
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4
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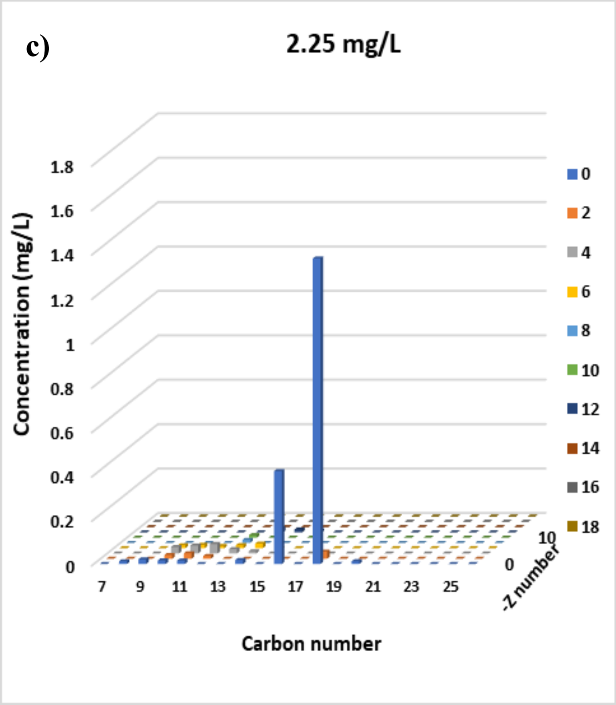
16
18


c)
2.25 mg/L
Concentration (mg/L)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
7
9
11
13
15
17
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Carbon number
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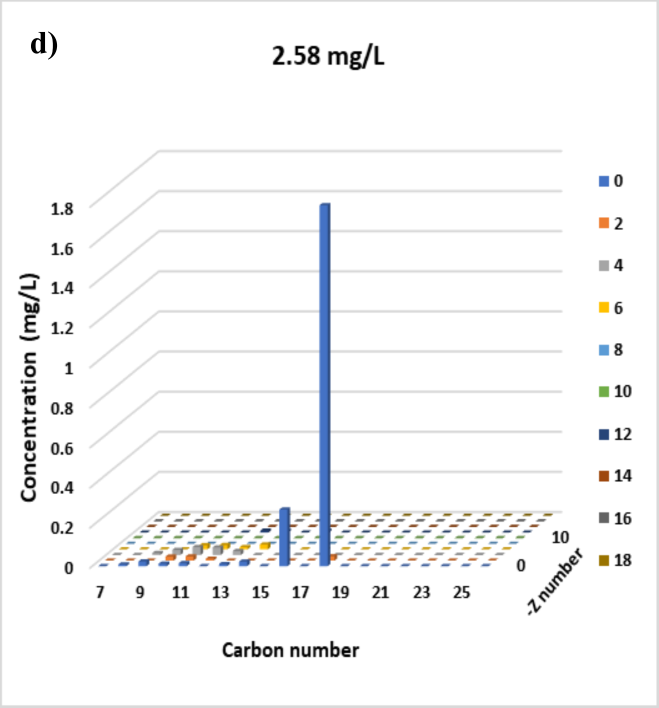
d)
2.58 mg/L
Concentration (mg/L)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
7
9
11
13
15
17
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Carbon number
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-Z number
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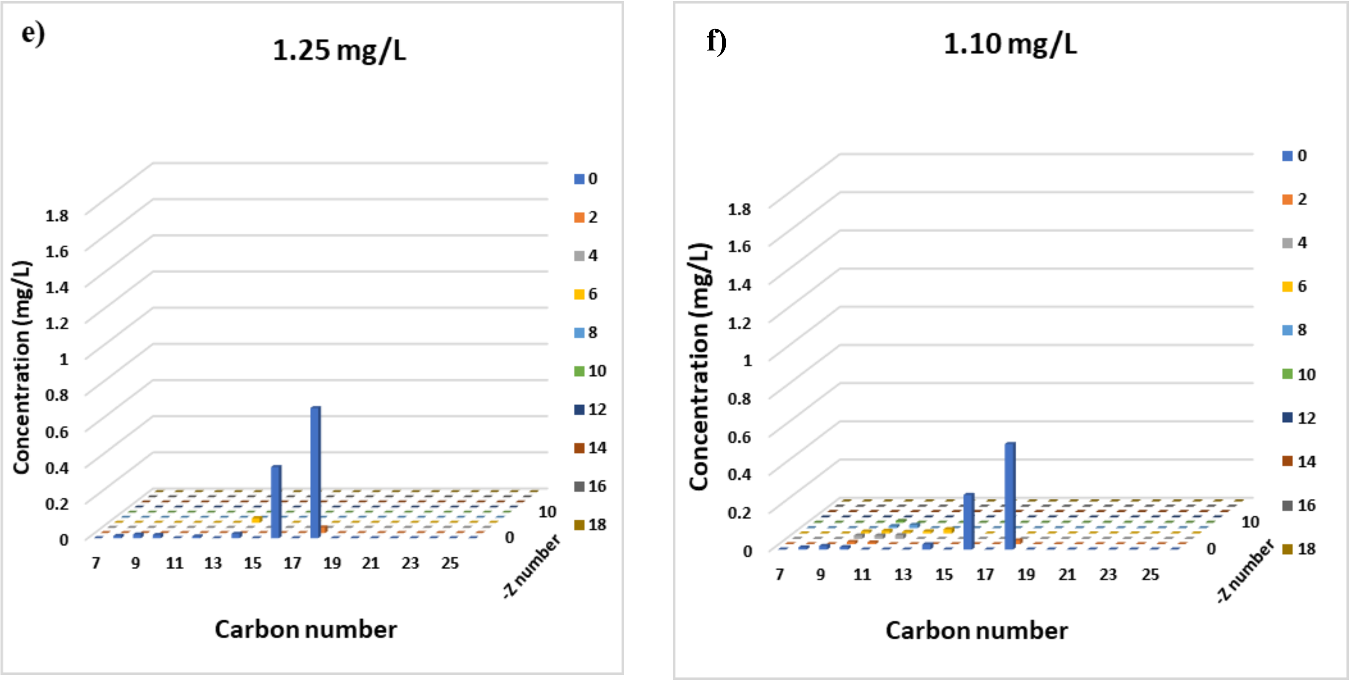


Figure 3.1 Distribution of classical NAs (O_2) in the OSPW (a) before the treatment, and after applying (b) EO only (Pt), EO-PMS with (c) Pt, (d) DSA, (e) BDD, and (f) graphite plate.

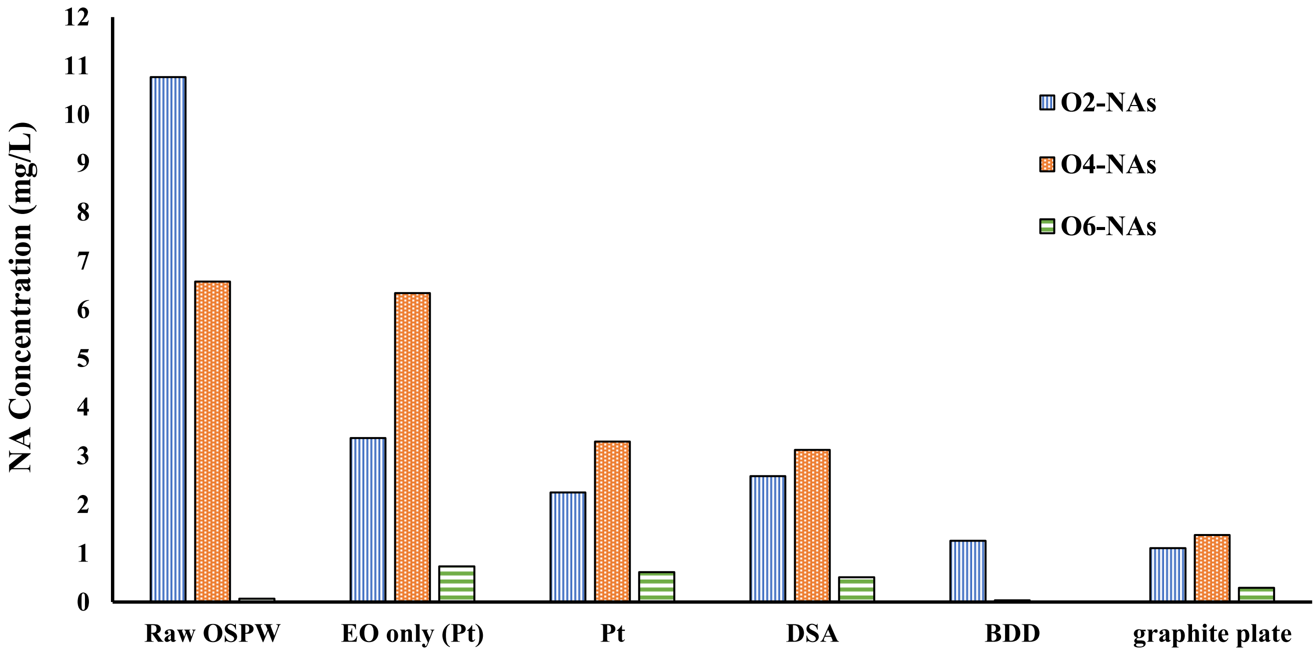


Figure 3.2 Concentration of classical-NAs (O_2) and oxidized NAs (O_4, and O_6) in raw OSPW and treated OSPW after using EO only and combined EO-PMS treatment processes.

3.2.2 COD & TOC removal analysis

The mineralization of the OSPW was evaluated by measuring the COD and TOC removal efficiency after electrolysis for 4 h. Fig. 3.3 and Fig. 3.4 show the effect of applying electro-oxidation (EO) alone and with electrochemical activated PMS (EO-PMS) using different anode materials on the removal of COD and TOC in OSPW. As can be seen clearly in Fig. 3.3, the COD reduction was low (less than 20% removal) in the case of EO alone and EO-PMS using Pt and DSA anodes, while graphite plate achieved almost 35% COD removal. This partial removal of COD indicated incomplete mineralization of dissolved organics in the OSPW. This behavior was expected due to the classification of these anodes as active anode materials and they cannot be effective in mineralizing NAs (Sirés et al. 2014, Abdalrhman and Gamal El-Din 2020). On the other hand, using inactive anodes such as BDD could achieve complete mineralization of the OSPW, which reached a COD reduction of more than 85% in this study when BDD was used as an anode in EO-PMS oxidation process (Fig. 3.3). Moreover, this trend of low COD removal was similar to that of TOC results (Fig. 3.4). The low removal of both COD and TOC may be explained by the assumption that the NAs degrade into simple organic compounds, which still contribute to the COD and TOC of the OSPW samples. For graphite plate, some particles from the electrode surface dissolved within the solution that resulted in low TOC removal. However, further investigation and experiments are needed to study the mechanism of the NA degradation pathways.

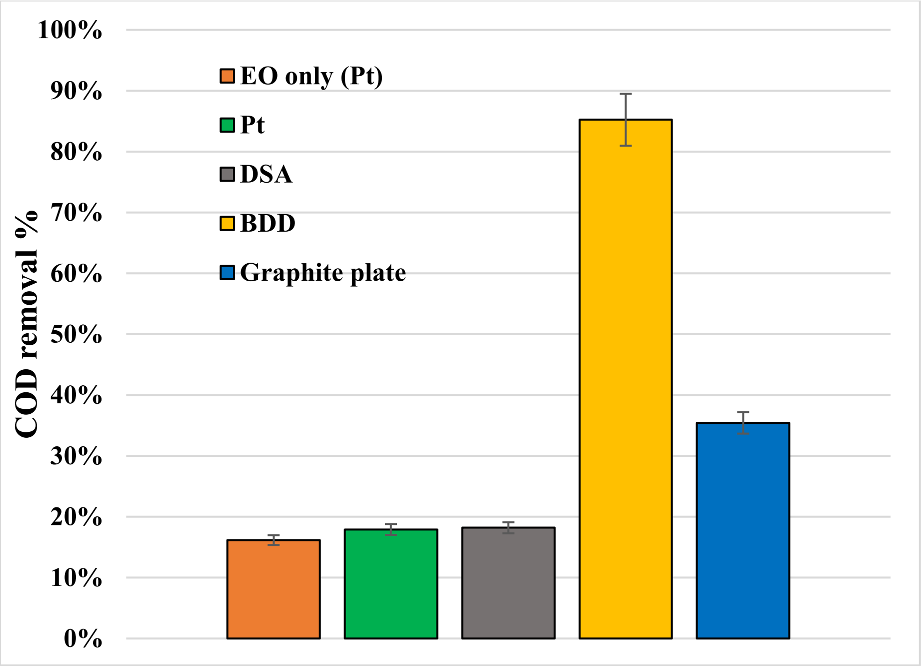


Figure 3.3 The effect of EO process only and combined EO-PMS with different anode materials on the COD removal of OSPW.

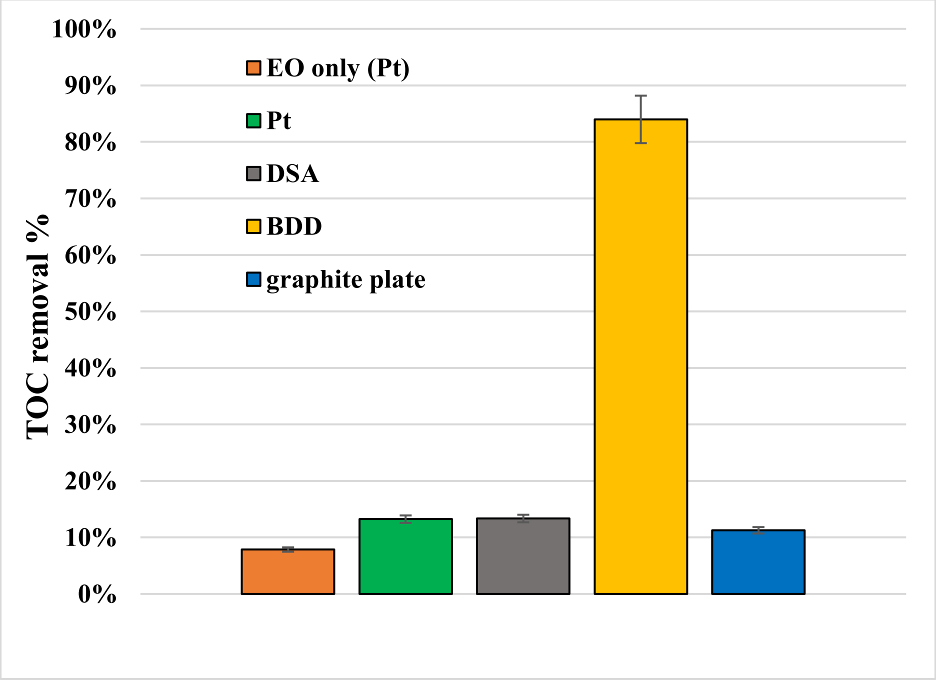


Figure 3.4 The effect of EO process only and combine EO-PMS with different anode materials on the TOC removal of OSPW.

3.3.3 Synchronous fluorescence spectroscopy (SFS) analysis for aromatics reduction

The aromatic compounds in OSPW are considered as one of the major organic fractions in the matrix of OSPW, which contribute significantly to the acute toxicity and estrogenic effects of OSPW, although they have relative lower concentrations compared to aliphatic NAs.

In this study, synchronous fluorescence spectroscopy (SFS) analysis was carried out to investigate the removal of aromatic compounds in the treated OSPW at the end of the experiment. As depicted in Fig. 3.5, the SFS spectra for the raw and treated OSPW displayed three (3) distinct peaks maximum; at 273 nm (O_I), 311 nm (O_{II}) and 325 nm (O_{III}) which are assigned to single-ring aromatics, two fused aromatic rings, and three fused aromatic rings, respectively. The single-ring aromatics were the predominant compounds in OSPW as showed by the highest peak at 273 nm, which is similar to the previous studies (Ganiyu and Gamal El-Din 2020). The removal efficiency of aromatics was studied during EO process and combined EO-PMS at different anode materials (Pt, DSA, BDD and graphite plate) after 4 h of electrolysis. As can be clearly seen in Fig. 3.5, there was a high reduction of all three classes of aromatics, with relatively complete removal of aromatic compounds with two and three rings (O_{II}, O_{III}). This can be attributed to the huge production of oxidants that have higher reactivity towards aromatic compounds with increased number of aromatic rings. In addition, the aromatics with single-ring could be formed from the degradation of the double and triple fused rings during the treatment. Previous studies that used ozonation, UV/chlorine, UV/H_2O_2 and ferrate (VI) showed that aromatics with single-ring are the most persistent fraction for oxidation (Shu et al., 2014; Zhang et al., 2015; Abdalrhman et al., 2019b). Moreover, EO-PMS process with BDD anode completely degraded all of the three different aromatic species. Since it was able to degrade the most persistent part of single-ring aromatics, it can be assumed that EO-PMS is more effective for the degradation of the aromatic fraction.

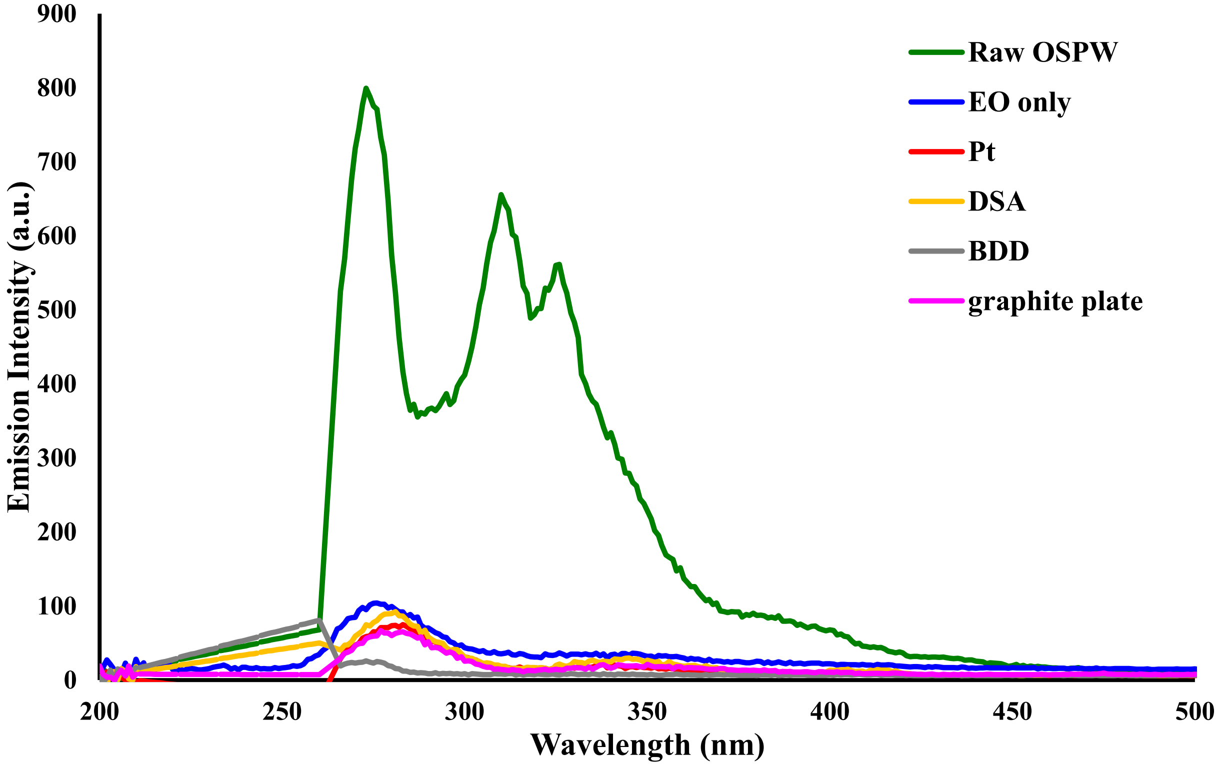


Figure 3.5 Synchronous Fluorescence Spectra of raw OSPW (green) and treated OSPW by EO only (Blue) and combined EO-PMS using: Pt, DSA, BDD and graphite plate anodes (Red, yellow, gray and pink, respectively).

3.3.4 Toxicity

The presence of NAs in the OSPW has been widely stand for acute toxicity towards the organisms such as fish, plant, mice, and other organisms. The Microtox® bioassay is a simple, reliable and fast approach for determining toxicity of OSPW, because it has shown a high correlation to other animal-based toxicity assay (Holowenko et al. 2001, Zhang et al.

2016). Microtox® bioassay was used to study the reduction in toxicity to *V. fischeri* after different treatments though bioluminescence inhibition. As shown in Fig. 3.6, the initial inhibition level of the raw OSPW was around 45%. The use of EO only process resulted in remarkable reduction of toxicity, with the inhibition effect decreasing to less than 6% (Fig. 3.6). On the other side, the combined EO-PMS experiments with four examined anode materials showed a contrast in the results in terms of toxicity when 4 mM of PMS was added to the system. For DSA and graphite plate anodes, the inhibition levels were reduced to 25.1% and 29.9%, respectively. While in case of Pt and BDD anodes, the inhibition effects increased to reach roughly 58.6% and 57.1%, respectively. This high level of toxicity after the treatments may be due to the remaining sulfate precursor (PMS) as well as the formation of chlorinated byproducts especially with BDD anode. Moreover, the residual concentration of sulfate ions in the treated OSPW was measured to be around 3215 mg/L, which is very high. However, additional treatment may be needed to ensure a complete detoxification, and more comprehensive studies should be carried out to fully assess the impact of combined treatment on OSPW toxicity removal.

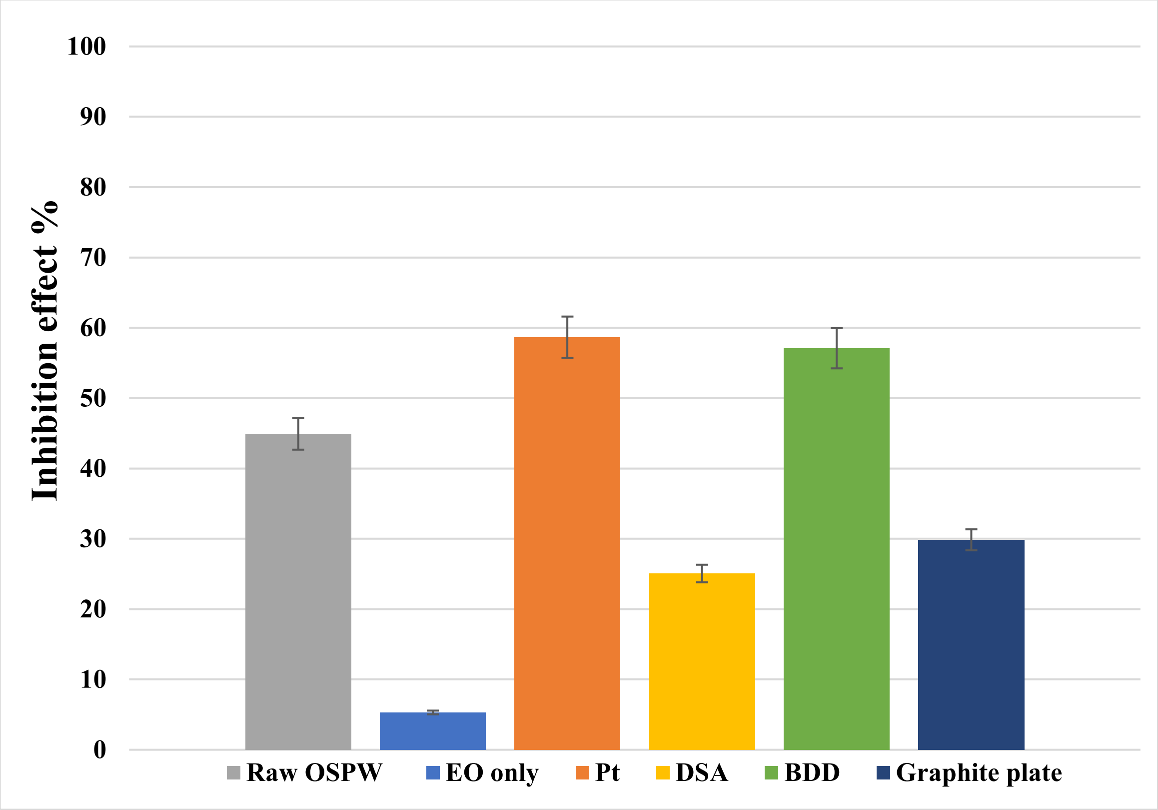
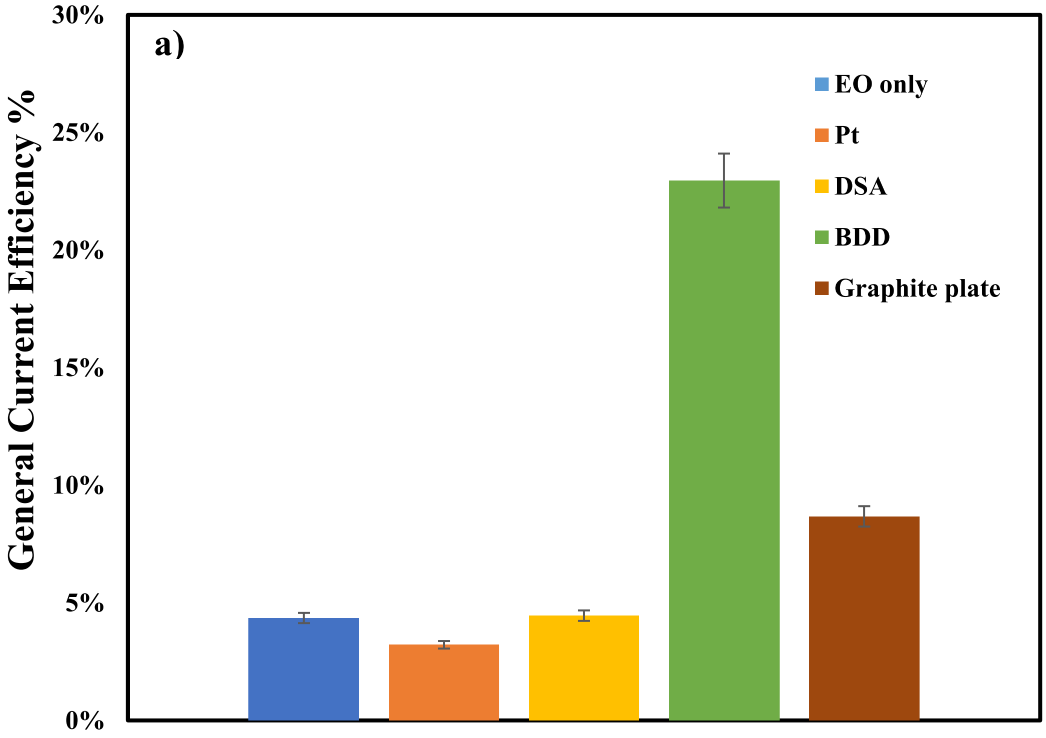


Figure 3.6 The effect of EO only and combined EO-PMS on the toxicity of the OSPW towards *Vibrio fischeri*.

3.2.5 Current efficiency and energy consumption

The comparison between the removal performances of different anode materials can be evaluated using the current efficiency and the specific energy consumption parameters. The general current efficiency (GCE) determines the electrical charge consumed for the oxidation of organics as percentage of the total charge supplied during electrolysis and can be calculated using Eq. (3.1). As shown in (Fig. 3.7a), the current efficiency in all cases was less than 10% (EO only and combined EO-PMS/ Pt, DSA, and graphite plate); while for BDD, it reached around 22%. This can be attributed to the surface nature of the anode and the different in the oxidation behavior.

The specific energy consumption (SEC) represents the amount of energy that consumed (kWh) for every g of NAs removed, which can be calculated using Eq. (3.2). As can be depicted in (Fig. 3.7b), low SEC can be achieved using combined EO-PMS with anode materials of graphite plate, Pt, DSA and BDD. On the other side, EO oxidation process alone with Pt anode showed higher SEC compared to the combined system of EO-PMS. This behavior was different from the case of GCE, but it can be explained by considering that the COD removal is used for estimating GCE and not NA removal (Eq. (3.1)).



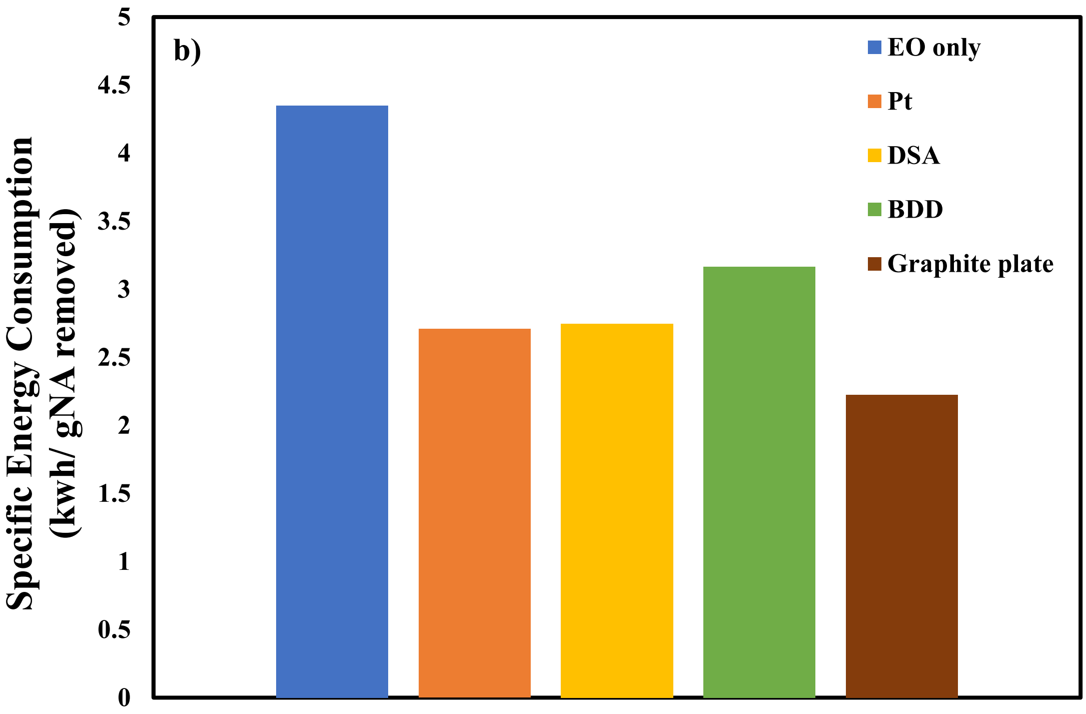


Figure 3.7 (a) General current efficiency and (b) specific energy consumption for the treatment of OSPW by using EO only and combined EO-PMS using Pt, DSA, BDD and graphite plate anodes.

3.3 Conclusions

This study concludes that the use of combined system of electro-oxidation and electro-activated PMS (EO-PMS) exhibited a good performance on the removal of NAs from OSPW. Combined EO-PMS process using Pt, DSA, BDD, and graphite plate anodes was able to reduce the COD, TOC, classical and oxidized NAs as well as aromatics in OSPW when the applied current was 250 mA and carbon felt used as cathode for 4 h treatment time. However, applying EO only showed lower degradation and removal compared when adding PMS to the system using the same Pt anode. This could be attributed to the production of both free $^{\bullet}OH$ and strong oxidant of $SO_4^{\bullet-}$ in the presence of PMS, which can highly oxidize the NAs and organic compounds. Moreover, DSA, BDD and graphite plate anodes achieved maximum reduction of 76%, 88.4% and 89.7% of classical NAs (O_2-NAs) concentration, respectively. When compared to the other anodes, only BDD completely removed all the oxidized NAs (O_4-NAs and O_6-NAs) and was able to mineralize the organics in OSPW. The reduction of both COD and TOC were relatively low when using Pt, DSA and graphite plate anodes. This shows that during the combined EO-PMS process, the degradation products had smaller organic molecules, which still contributed to both COD and TOC in treated OSPW. All anode materials were able to remove the three classes of aromatic compounds, specifically with complete removal of aromatics that have two and three rings. While the highest removal of single ring aromatics was achieved by BDD anode. The combined system of EO-PMS presents an efficient technology for the degradation of NAs and has a great potential to be attractive for wastewater treatment in oil sands industry due to its flexibility and high effectiveness at removing constituents of concern from OSPW as part of reclamation options.

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4. CONCLUSIONS AND RECOMMENDATIONS

4.1 Thesis overview

The oil sands reserves located in Northern Alberta, Canada, are considered the third largest oil reserves in the world and represent a significant economic asset and one of the main contributors to the country's economy. However, they are attracting many concerns and attention because of the large amounts of water consumed and, subsequently, large volumes of oil sands process water (OSPW) generated.

OSPW is a complex mixture of suspended solids, salts, inorganic compounds, dissolved organic compounds and trace metals that is generated during the surface extraction of minable bitumen. Currently, the treatment of OSPW is considered a major challenge facing the oil sands industry. Moreover, NAs in OSPW have attracted increasing attention due to their acute toxicity associated with complexity and persistently, which are great hazards towards several organisms. Therefore, the development of efficient and effective technique is extremely needed for possible remediation of organic constituents (especially NAs) in OSPW.

However, as previously discussed in Section (1.3.4), most of the current proposed treatment methods have some major drawbacks such as high cost (physical and chemical processes), very slow rate (biodegradation), or have technical restrictions (Fenton and UV-based AOPs) and therefore, the need of highly effective and efficient treatment option is urgent.

In this context, electro-oxidation (EO) has been considered a promising and efficient approach for degrading persistence organic compounds in industrial wastewater such as

OSPW. Despite that, few studies have reported the use of electrochemical- oxidation for OSPW remediation.

In recent years, sulfate radicals ($SO4^{\bullet-}$)-based AOPs technology have been widely studied for the degradation of various types of recalcitrant organic compounds. The electrochemical activation of sulfate free radicals has attracted research interest due to the simplicity, adaptability and outstanding performance. However, no study has reported the synergistic effect of coupling electro-oxidation and electrochemically activated peroxymonosulfate (EO-PMS) on the degradation of NAs and OSPW treatment.

The purpose of this research was to investigate the applicability and effectiveness of using combined EO-PMS process for the treatment of OSPW. The removal of recalcitrant organic compounds in OSPW by EO-PMS was evaluated with special focus on NAs; which are considered the main complex and toxic organics in OSPW. This research was conducted in two stages. The first stage, the electrochemical activation of PMS at the surface of different electrode materials, investigated the removal performance of 5-Phenylvaleric Acid (PVA) degradation as NA model compound and determined the mineralization of dissolved organics. In the second stage, the treatment of real OSPW by combined EO-PMS process using different types of anode materials was investigated and compared.

4.2 Conclusions

The results obtained in this research show the capability of EO-PMS in degrading the recalcitrant organics in OSPW effectively. This study has shown that EO-PMS can be successfully applied for OSPW treatment. The main conclusions of each chapter are listed below:

Chapter 2: Degradation of synthetic naphthenic acid solution (PVA)

- Coupling peroxymonosulfate (PMS) and electrolysis was verified to be an effective method and the process showed high removal efficiency of NA model compound (PVA), in which the electrochemical oxidation was enhanced by the addition of PMS.

- The effect of cathode material, anode material, PMS concentration and applied current was investigated for the PVA degradation.

- The removal efficiencies were promoted with the increase in PMS concentration and applied current. However, the excessive addition of PMS and at higher current had negative influence on PVA oxidation. The degradation of PVA by EO-PMS followed pseudo-first order kinetics model.

- It was found that a complete removal of 50 mg/L PVA can be readily achieved within 1 h under optimal conditions: carbon felt (cathode), Pt (anode), PMS= 4 mM, and I= 250 mA.

- The use of radical quenchers showed that both $SO_4^{\bullet -}$ and $^{\bullet}OH$ were found to be the primary reaction oxidants for PVA degradation.

- The findings of this study confirm that the combination of electrochemical oxidation and electro-activated PMS process (EO-PMS) could be a potential and promising treatment for NA degradation and can be used in the further design for OSPW reclamation.

Chapter 3: Degradation of recalcitrant organics in real oil sands process water by combined electrooxidation and electrochemically activated peroxymonosulfate (EO-PMS)

- Combined EO-PMS process using Pt, DSA, BDD, and graphite plate anodes was able to reduce the COD, TOC, classical and oxidized NAs as well as aromatics in OSPW when the applied current was 250 mA and carbon felt used as cathode for 4 h treatment time.

- Applying EO only showed lower degradation and removal of NAs compared when adding PMS to the system using the same Pt anode. This could be attributed to the production of both $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals in the presence of PMS, which can highly oxidize the NAs and organic compounds.

- DSA, BDD and graphite plate anodes achieved maximum reduction of 76%, 88.4% and 89.7% of classical NAs (O_2-NAs) concentration, respectively. Compared to other anodes, only BDD completely removed all the oxidized NAs (O_4-NAs and O_6-NAs) and was able to mineralize the organics in OSPW.

- The reduction of both COD and TOC were relatively low when using Pt, DSA and graphite plate anodes. This shows that during the combined EO-PMS process, the degradation products had smaller organic molecules, which still contributed to both COD and TOC in treated OSPW.

- All anode materials were able to remove the three classes of aromatic compounds, specifically with complete removal of aromatics that have two and three rings.

- The combined system of EO-PMS presents an efficient technology for the degradation of NAs and has a great potential to be attractive for wastewater treatment in oil sands industry due to its flexibility and high effectiveness at removing constituents of concern from OSPW as part of reclamation options.

4.3 Recommendations

The recommendations for future works may include the following:

- Future experiments should examine the significance of dissolved oxygen on EO-PMS process and its effect on OSPW treatment.
- In addition, it is recommended to study the impact of others sulfate radical precursor compounds and compare their performance in the aspects of activation on the electrode surface and production of sulfate radicals.
- More comprehensive studies should be carried out to evaluate the effect of the residual concentration of sulfate ions in the treated OSPW after using combined EO-PMS process. Additional treatment may be needed to ensure a complete removal of OSPW toxicity and decrease the amount of sulfate ions residual.
- Also, it is recommended to determine the possible hazardous by-products production in the presence of halide ions (i.e., chlorinated and brominated organic compounds) in OSPW. Applying pretreatment processes may be needed.
- Lastly, all the discussed EO-PMS experiments in this research were conducted by using batch reactors that are simple, and easily to operate and control. However, reactor design must be also considered, especially for large-scale applications, where huge volumes of stored OSPW are waiting for the treatment. Thus, the use flow-

through reactors are more relevant, and can promote the mass transfer to electrode surface, which might affect the system's ability to effectively activate PMS and subsequently degrade the contaminates. Therefore, the performance of using flow-through reactor can be investigated, besides optimizing the reactor conditions.

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APPENDIX A. EXPERIMENTAL METHODOLOGY

Ultra-performance liquid chromatography time-of-flight mass spectrometry (UPLC TOF-MS)

The ultra-performance liquid chromatography time-of-flight mass spectrometry (UPLC TOF-MS) was used to measure the concentration of NA. The analysis of the sample was carried out using a high-resolution time-of-flight mass spectrometry TOF-MS (Synapt G2, Waters, MA, USA) on mode of negative electrospray ionization and the used internal standard was myristic acid-1-13C. The chromatographic separation was performed by using Waters UPLC Phenyl BEH column (Waters, MA, USA). A mixture of 500 µL OSPW sample, 400 µL methanol and 100 µL of 4.0 mg/L internal standard (myristic acid-1-13C) was injected into the instrument. The temperature of instrument column was set at 50 ºC while for the sample it was 10 ºC. For the mobile phases, (A) a 10 mM of ammonium acetate was in water and (B) 10 mM ammonium acetate in mixture of 50/50 methanol/acetonitrile at flow rate of 100 µL/min. The elution gradient was as follow: 1% B during 0–2 min; then during 2–3 min it increased to 60% B before reached 70% B during 3–7 min; and went up to 95% B between 7–13 min; then dropped to 1% B over 13–14 min, and the 1% B was kept until 20 min to equilibrate the column with 100 µL/min flow rate. The acquisition process of the data was accomplished using MassLynx (Waters, MA, USA) and TargetLynx (Waters, MA, USA) was used to complete the data extraction from the spectrum. The identification 222 of classical NAs (O_2) and oxy-NAs was made using the empirical formula $C_nH_{2n+z}O_x$ (x=2, 4, 6) where n ranged from 7 to 26 and z from 0 to -18.

APPENDIX B. SUPPORTING FIGURES

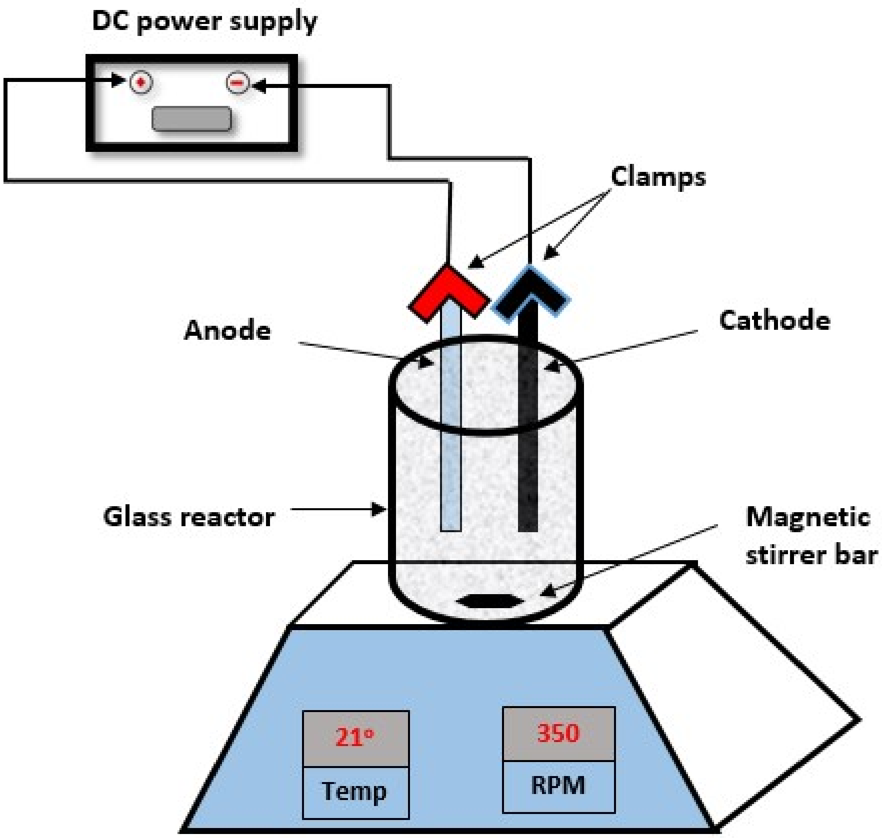

Figure B1 Schematic diagram of the experimental set up.