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Oxidation of 2,4-D using iron activated persulfate and peroxymonosulfate

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Oxidation of 2,4-D using iron activated persulfate and peroxymonosulfate

by

Guyu Shi

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Major: Civil Engineering (Environmental Engineering)

Program of Study Committee:
Say Kee Ong, Major Professor
Roy R. Gu
Michael Thompson

Iowa State University

Ames, Iowa

2015

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NOMENCLATURE

AOPs	Advanced Oxidation Processes
PS	Persulfate
PMS	Peroxymonosulfate
BFO	Bio-exponential first-order
AAFO	Availability-adjusted first-order

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ABSTRACT

This study reviews the application of sulfate free radicals for the oxidation of organic pollutants in surface water and groundwater. Sulfate free radicals can be generated from persulfate and peroxymonosulfate (PMS) using various activation methods. Activation methods include heat, transition metals, and ultra-violet light. Experiments were conducted to investigate the oxidation of 2,4-dichlorophenoxyacetic acid (2,4-D) by sulfate free radicals generated by the activation of persulfate anion or peroxymonosulfate using ferrous ions. 2,4-D was found to be rapidly oxidized within minutes but plateaued to a asymptotic concentration. The optimal molar ratio of persulfate:Fe²⁺ or peroxymonosulfate:Fe²⁺ for the oxidation of 2,4-D was found to be 1:1. The plateauing of 2,4-D concentration in the oxidation process may be due to the rapid conversion of Fe²⁺ to Fe³⁺ by the sulfate radicals generated which in turn slowed the activation process. Sequential addition of Fe²⁺ at different times resulted in further 2,4-D oxidation which indicates that Fe²⁺ may be limiting in the activation process. A bi-exponential first-order model provided the best fit of the experimental data with R² values greater than 90%. Ferrous ion can be used as a low cost material to activate persulfate or peroxymonosulfate for the removal of 2,4-D and other organic compounds in contaminated groundwater and drinking water.

CHAPTER I

INTRODUCTION

1.1. Introduction

Advanced chemical oxidation is a treatment technology that has the potential to completely destroy harmful organic contaminants in water. It is also known as Advanced Oxidation Process (AOP) and has played a crucial and important role in water and wastewater treatment, and remediation of contaminated sites. In AOPs, the reactions follow a specific oxidation pathway, which includes the formation of free radicals. In this study, sulfate free radicals ($\text{SO}_4^{\bullet-}$) generated from persulfate ($\text{S}_2\text{O}_8^{2-}$) and peroxymonosulfate will be investigated.

Persulfate has recently been studied as an oxidant alternative for treating organic contaminants in aqueous system due to its high aqueous solubility and stability, relatively low cost and benign end products. In addition to persulfate, peroxymonosulfate (PMS), a powerful oxidant for a wide variety of industrial and consumer applications, is also being promoted as an oxidant for removal of hazardous contaminants.

There are several activation methods for the generation of sulfate free radicals from persulfate and peroxymonosulfate. The methods used include:

- Heat activation
- Metals activation using transition metals, zero-valent iron or metal chelates
- UV activation
- Cavitation activation using ultrasound
- Alkaline activation

- Hydrogen peroxide activation

Sulfate free radical oxidation has several advantages over other oxidizing agents such as ozone or hydrogen peroxide systems. Persulfate and peroxymonosulfate themselves are fairly stable and can be purchased in solid forms. Another advantage is that sulfate free radicals generated are relatively more stable than hydroxyl radicals and therefore can be transported to relatively greater distances or remain in solution longer than hydroxyl radicals. Another important aspect is that sulfate radical oxidation can oxidize a broad range of organic contaminants. Much work have been done on sulfate radicals oxidation of a range of common pollutants such as benzene, toluene, trichloroethylene, and methyl tert-butyl ether. However, the amount of work done on the sulfate radical oxidation of pesticides and herbicides are limited.

1.2. Objectives

The primary objective of this study was to investigate the oxidation of 2,4-dichlorophenoxyacetic acid (2,4-D) using iron activation of peroxymonosulfate and persulfate.

The specific objectives are:

- 1) Investigate the effects of molar concentrations of oxidant and iron on 2,4-D degradation
- 2) Model 2,4-D degradation kinetics
- 3) Compare the oxidizing potential of persulfate and PMS for 2,4-D degradation.

CHAPTER II

LITERATURE REVIEW

Abstract

Persulfate and peroxymonosulfate are novel oxidants that can generate sulfate free radicals, a powerful oxidizing agent ($E^0 = 2.6 \text{ V}$), by using the appropriate activation method. In this review, the basic reaction mechanisms and factors affecting persulfate and peroxymonosulfate activation were discussed. The activation methods used include heat, transition metals such as Fe^{2+} , Co^{2+} , chelated iron, and UV. In particular, iron activation is a relatively promising method due to its low cost, availability, transportability and reactivity at ambient temperature. Based on work done by various researchers, sulfate free radicals were found to degrade various compounds such as BTEX, TCE, and phenol in aqueous and soil slurry matrices. Some of the important factors affecting contaminant degradation are: persulfate:activator ratio, pH, temperature, and catalysts. This review found that activated persulfate and peroxymonosulfate can be effective in oxidizing organic compounds in wastewater, groundwater and in soil slurries. Further research requires a better understanding of the interactions between the persulfate/peroxymonosulfate and the activator and the degradation kinetics of persulfate and peroxymonosulfate.

Key Words: persulfate, peroxymonosulfate, sulfate radical, ISCO, AOTs

2.1. Introduction

In past two decades, advanced oxidation processes (AOPs) have been developed for the oxidation of recalcitrant organic compounds in industrial wastewaters, contaminated

groundwater, surface waters, and contaminated sites. The two more common AOPs are Fenton's agent and the generation of hydroxyl radicals using ozone. Fenton's reagent, the use of Fe^{2+} to activate the generation of hydroxyl radicals ($\text{HO}\cdot$) from hydrogen peroxide ($E^0=2.70\text{ V}$), has the potential to degrade a wide range of organic contaminants. Hydroxyl and other superoxide radicals can be generated from ozone using ultraviolet light and the appropriate activation chemicals such as hydrogen peroxide, and hydroxide (OH^-). Even though much advances have been made in understanding the chemistry of hydrogen peroxide and ozone in different media, researchers have observed that hydroxyl radicals generated from hydrogen peroxide and ozone are highly reactive but short-lived and under certain circumstances such as at contaminated sites or for certain recalcitrant compounds, these AOPs are not sufficiently effective without adding large amounts of the oxidizing agents.

In recent years, researchers have explored other oxidizing agents such as permanganate and persulfate as suitable oxidizing agents. These oxidizing agents themselves are not as powerful as hydrogen peroxide and ozone but can remain in solution longer than both hydrogen peroxide and ozone. However, when permanganate and persulfate are activated, they generate free radicals which can be as powerful as that of hydroxyl radicals. These radicals are known to remain in aqueous solution relatively longer than hydroxyl radicals, allowing them to be transported further and therefore be more effective in oxidizing organic compounds. The purpose of this chapter is to conduct a literature review on sulfate radicals generated from sulfate compounds, different activation methods, and their reactions with various organic compounds.

2.2. Sulfate Radical Chemistry

2.2.1 Radicals formation using persulfate

Persulfate anion itself is a strong two-electron oxidizing agent with a redox potential of 2.01 volts. Reduction of the persulfate anion results in the production of two sulfate anions as shown in eq. 1.



Oxidation reactions with persulfate anion in water are kinetically slow (House, 1962). Most oxidation studies are focused on the oxidation of sulfate free radicals generated by activating the persulfate anion. Sulfate free radicals are very strong oxidizing agents with a redox potential of 2.6 volts. The activation reaction of persulfate with the formation of sulfate free radicals can be described by eq. 2 and eq. 3.



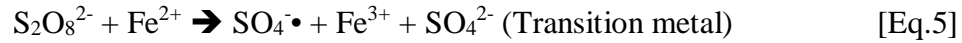
As shown above in eq. 2b, the O-O bond in the persulfate is ruptured by activation producing the sulfate free radicals. The sulfate free radical accepts a single electron to produce sulfate anion as shown below:



2.2.2. Sulfate free radicals activation

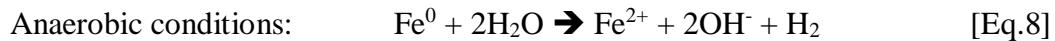
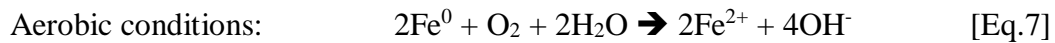
The two common methods used in the activation of persulfate are thermal activation and transition metal activation. For eq. 2a and b above, the initiator or activator used is by providing sufficient heat (Huang et al., 2002; Huang et al., 2005; Liang et al., 2003; Liang et al., 2008c; Johnson et al., 2008; Tsitonaki et al., 2008; Waldemer et al., 2007; Tan et al., 2012) or by use of

transition metal ions (Chen et al., 2012; Liang et al., 2004a, 2004b; Crimi et al., 2007; Killian et al., 2007; Cao et al., 2008; Liang et al., 2008a; Romero et al., 2010) as presented below:



Eq. 6 shows that Fe^{2+} is also an intrinsic scavenger of sulfate radicals, removing sulfate radicals from further reaction.

Recently, zero-valent iron has been used as a possible metal for the activation of persulfate (i.e., Sun et al., 2012; Oh et al., 2009, 2010). A reason for using zero-valent iron is that it provides ferrous ion through the reaction as shown below (Sun et al., 2012):



Another reaction is the direct reaction of persulfate and zero-valent iron which releases ferrous ion as shown by the following:



The residual ferric ion (eq. 10) can react with the applied zero-valent iron to produce more ferrous ion as shown below (Oh et al., 2009):



Besides the use of ferrous ions, other transition metals can be used. These metals include Cu (I) and Ag (I) (House, 1962).

Another activation method used is the application of UV irradiation at a wavelength of 254 nm (Gao et al. 2011):



Other novel activation methods studied include the application of ultrasound (Chen et al., 2012 and Li et al., 2013) and microwave irradiation (Yang et al., 2009). These reaction equations are the same as heat and UV activation.

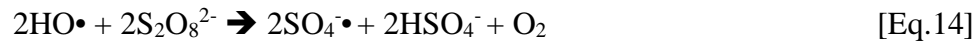
Cavitation caused by ultrasonic irradiation results in high energy implosions of tiny gas bubbles which in turn can act as activators for sulfate radicals generation. The mechanism of activation for microwave irradiation is most probably due to thermal activation from the increased energy of the water molecules subjected to microwave irradiation.

Persulfate in alkaline conditions has shown to generate sulfate radicals plus the generation of hydroxyl radicals as shown below (Liang et al., 2007b):



Eq. [12] shows that sulfate free radicals react with water to produce hydroxyl radicals which in turn participate in the degradation of organic compounds. Eq. [13] shows sulfate free radicals reacting with hydroxyl ions (high pH condition) to produce hydroxyl radicals (Liang et al. 2004). Generally, lime is used to raise the pH of the aqueous solution.

Hydroxyl radicals generated from hydrogen peroxide can be used to generate sulfate free radicals as shown by the reaction below (House, 1962):



Block et al. (2004) reported that the use of hydrogen peroxide and persulfate probably resulted in a synergistic reaction of hydroxyl and sulfate radicals which could enhance the degradation of the contaminants. In addition, the decomposition of hydrogen peroxide would produce heat which in turn raise the temperature of the solution to thermally activate persulfate (Waldemer et al., 2007)

2.2.3 Radicals formation from peroxymonosulfate

Under normal conditions without activation, peroxymonosulfate (trade name: oxone) cannot generate sulfate free radicals. Under acidic and reducing conditions, peroxymonosulfate is reduced to hydrogen sulfate and water as shown in the following reaction:



But in the presence of different activators, peroxymonosulfate produces a sulfate radical ($\text{SO}_4^{\cdot-}$) and a hydroxyl radical ($\text{HO}\cdot$) by rupturing the O-O bond of peroxymonosulfate (H-O-O-SO_3^-) as shown below [Eq.16] (Kennedy, 1960):

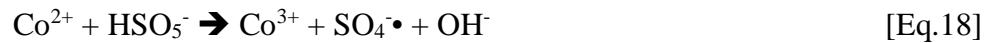


2.2.4 Sulfate radicals activation for peroxymonosulfate

As for persulfate activation, peroxymonosulfate can be activated into highly reactive radicals ($\text{SO}_4^{\cdot-}$ and $\text{HO}\cdot$) through hemolytic cleavage of the peroxide bond of HSO_5^- by photolysis (UV irradiation) or thermolysis (thermal activation) or directly into $\text{SO}_4^{\cdot-}$ via an electron transfer by a transition metal as shown in the following equation:



Transition metal activation of peroxymonosulfate was studied by several researchers, and they confirmed that cobalt (II) is the most efficient metal ion to activate peroxymonosulfate. The reaction of Co^{2+} and peroxymonosulfate is shown below:



Even though cobalt has been shown to have significant activation efficiency, the application of cobalt activation would result in secondary environmental pollution due to the toxicity of cobalt. Other transition metals that can be used include iron, manganese, nickel, and silver.

2.3. Specific Application of Persulfate Oxidation

2.3.1. Heat activation

Heat-activated persulfate has been well-documented through bench-, pilot- and full-scale studies. Persulfate can be activated by heating at temperatures ranging from 35°C to 130°C (House, 1962; Huang et al., 2002; Tsitonaki, 2008). Examples of thermal activation studies of persulfate oxidation of various pollutants are presented in Table 2.1. Some of the more significant work are summarized below. Work done by Kolthoff et al. (1951) found that thermal activation of persulfate was effective for a solution pH greater than 2. They indicated that persulfate would decompose at $\text{pH} < 2$ without producing sulfate radicals resulting in ineffective degradation of target contaminants. This observation was supported by the work of Liang et al. (2007b).

Huang et al. (2002) found that increasing the temperature of the solution or the oxidant concentrations over a pH range of 2.5 – 7 and ionic strength of 0.11 - 0.53 M resulted in an increase in reaction rates for MTBE. In another study, Huang et al. (2005) tested the degradation of 59 VOCs using sodium persulfate at different doses of 1 g/L and 5 g/L, and at temperatures of 20°C, 30°C, and 40°C and found that the persistent contaminants such as chlorinated alkanes require a higher activation temperature for the same persulfate dose and percent removal. Based on the percent removal, Huang et al. (2005) reported that the optimal degradation rate for his study was at 40°C and a dose of 5 g/L. Liang et al. (2003) applied thermally activated persulfate at a concentration of 4.6 mM and obtained 100 % degradation of TCE and TCA at 40°C and 50°C, respectively. In a separate experiment, Liang et al. (2007b) reported that persulfate at a concentration of 23 mM was able to oxidize TCE (0.46 mM) at low temperatures ranging from 10 to 30°C. They also found that both high temperature and low pH have a synergistic effect resulting in an increased rate of radical generation. In addition, Liang et al. (2006) found that

Table 2.1 Examples of heat activated persulfate oxidation

Contaminant	Temperature	Media	pH	Contaminant Conc.	Persulfate Conc.	% Removal	Reference
59 VOCs	20 - 40°C	Aqueous	2.1-6.8	0.6-2 µM	5 g/L	At 40°C, 37 of 59 VOCs >90%, halogenated ethanes, <20%	Huang et al., 2005
TCE and 1,1,1-TCA	40 - 60°C	Aqueous and soil	6	0.46 mM	4.6 mM	100% TCE at 40°C; 100% TCA at 50°C	Liang et al., 2003
MTBE	20 - 50°C	Aqueous	7	0.06 mM	31.5 mM	10% at 20°C 87% at 40°C	Huang et al., 2002
PCE, TCE, cis-DCE, trans-DEC	30 - 70°C	Aqueous	3.7-8.7	45 µM	450 µM	55 - 93% for PCE, 80 - 90% for TCE	Waldemer et al., 2007
16 PAHs	70°C	Soil	Low pH	7-2036 mg/kg	0.0357 g/mL	2-3-rings PAHs: 80%; 4-ring PAHs: 0-75%; 5-6-ring PAHs: 0-50%	Cuyppers et al. 2000
TCE	10 - 30°C	Aqueous	7	0.46 mM	23 mM	92 - 100%	Liang et al., 2007b
Diuron	50 - 70°C	Aqueous	5.5-8.1	0.0375 mM	0.375 mM	35% - 55%	Tan et al., 2012

chloride ion concentration of 0.3 M at 20°C resulted in a lower degradation efficiency of TCE as compared to a chloride ion concentration of 0.2 M.

Johnson et al. (2008) conducted batch studies to analyze persulfate persistence/decomposition for concentrations of 0.1, 1.0, 10, and 100 mM at 30, 50, and 70°C and found that persulfate was decomposed at 70°C. Presence of soil in the aqueous solution resulted in a higher persulfate decomposition rate at 70°C than without soil present (Cuyper et al. 2000). Tan et al. (2012) compared heat activated persulfate oxidation and Fe²⁺-catalyzed activated persulfate of diuron and found that heat-activated persulfate had better diuron removal than Fe²⁺-activated persulfate.

2.3.2. Transition metal activation

Metal activation of persulfate is also an effective method for persulfate activation but at ambient temperature. Fe²⁺ is the most commonly used metal activator (Liang et al., 2009b; Liang et al., 2013). Other transition metals that have been used to activate persulfate include Cu (I) and Ag (I) (House, 1962). These metals are not the most desirable due to their toxicity. Recently, studies were conducted using zero-valent iron as an activator for persulfate (Hussain et al., 2012; Oh et al., 2009, 2010; Kambhu et al., 2012). Results of the experiments showed that zero-valent iron and sequential addition of ferrous iron on persulfate oxidation gave higher removal of 10% than with the addition of ferrous iron alone. Table 2.2 provides a list of studies using iron or chelated iron as the activator.

Table 2.2 Examples of metal activated persulfate oxidation

Contaminant	Setup	Metal Conc.	pH	Contaminant Conc.	Persulfate Conc.	% Removal	Reference
PCE, TCE, cis-DCE, VC	Persulfate alone	0	6.6-8.4	60 ug/L	1 g/L	74% PCE, 86% TCE, 84% cis-DCE, 90% VC	Dahmani et al., 2005
PCE, TCE, cis-DCE, VC	EDTA- Fe ²⁺	250-861 mg/L	6.6-8.4	60 ug/L	1 g/L	68% PCE, 78% TCE, 69% cis-DCE, 65% VC	
PAHs	EDTA- Fe ²⁺	0.124 g/L	N/A	5 ug/L – 57 ug/L	5 g/L	75- 100%	Nadim et al. (2005)
TCE	Added all at once	2.27-13.65 mM	Initial: 5.0; Final: 2.5-3.0	0.45 mM	0.45 – 13.65 mM	10 - 70%	Liang et al., 2007a
TCE	Continuous addition (Aq.)	0.45–2.27 mM	Initial: 2.7; Final: 2.0-2.5	0.45 mM	9.1 mM	73-95%	
TCE	Pulse addition, gradual addition, thiosulfate	0.45–2.27 mM with thiosulfate	Initial: 5.0; Final: 2.0-2.5	0.45 mM	9.1 mM	84 - 92%	
TCE	Chelated Fe ²⁺	0.45–2.27 mM with chelate	Initial: 2.8-4.8; Final: 2.2-3.2	0.45 mM	9.1 mM	65 - 100%	Liang et al., 2004b

Table 2.2 continued

BTEX	Fe ²⁺ / citric acid	0.04-1.0M with 0.008-0.2 M CA	Initial: 5.5; Final: 2.0- 1.6	B:6.55, T:1.37, E:0.48 and X:0.73mM	0.1 M	50%	Liang et al., (2009a)
BTEX	Fe ²⁺	5 mM	Initial: 5.6; Final: 2.4	1 mM	5, 20 and 100 mM	80%	Liang et al. (2008b)
BTEX	Fe ²⁺ / citric acid	5 mM with 5mM CA	Initial: 5.6; Final: 1.7- 2.4	1 mM	100 mM	100%	
BTEX, PAHs	Sequential Fe ²⁺ addition	0.9 M	N/A	BTEX: 335.9 mg/kg PAHs: 5861 mg/kg	1.05 M	86% BTEX 56% PAHs	Killian et al., 2007
BTEX, PAHs	chelated	0.2M with 1M citric acid	N/A	BTEX: 427 mg/kg PAHs: 4259 mg/kg	2.1 M	99% BTEX 92% PAHs	
BTEX	Fe ²⁺ activation in different pH values	N/A	N/A	N/A	N/A	acidic 97.5%, neutral 95.8%, and basic 95.2%	Achugasim et al. (2011)
PAHs		N/A	N/A	N/A	N/A	acidic 26%, neutral 2.7%, and basic 46%	
TCE, DCE, VC	Fe ²⁺ (Soil)	3.58 mM	2.9-4.8	N/A	7.16 mM	Fe (2) promoted TCE degradation and decreased TCE adsorption	Liang et al., 2008a
Lindane	Fe ²⁺	0.108 mM	5.7	0.0172 mM	4.2 mM	96.20%	Cao et al., 2008
MTBE	Fe ²⁺	3.57 mM	6.99	11.39 mM	0.114 mM	100%	Chen et al., 2009

Table 2.2 continued

diuron	Fe ²⁺	0.72 mM	4-5	0.09 mM	2.1 mM	60-100%	Romero et al., 2010
p-chloroaniline (PCA)	copper	0.5 g/L	5-7	0.5 mM	2.5 mM	98.1%	Liang et al. (2013)
p-chloroaniline (PCA)	zero-valent iron	0.7 g/L	4	0.05 mM	2.5 mM	near 100%	Hussain et al. (2012)
2,4-dinitrotoluene (DNT)		5 g	6.2-6.4	50 mg/L	1.3 mM	100%	Oh et al. (2010)
PVA		1.3 mM	N/A	47.1–50.2 mg/L	1.3 mM	100%	Oh et al. (2009)
BTEX		1.19 cm ZVI candles	N/A	B:0.1, T:0.08, E:0.07 and X:0.07mM	10 mM	90%	Kambhu et al. (2012)

Liang et al. (2004a) found that a Fe^{2+} : TCE molar ratio of 15:1 resulted in an increase in 20% degradation of TCE as compared to a Fe^{2+} : TCE molar ratio of 5:1 for a $\text{S}_2\text{O}_8^{2-}$:TCE ratio of 20:1. Cao et al. (2008) showed that an increase of ferrous iron concentration from 0.108 to 3.32 mM for the activation of 4.2 mM persulfate resulted in an increase in the degradation of lindane. Chen et al. (2009) found that MTBE could be degraded effectively (100%) using $\text{S}_2\text{O}_8^{2-}$: Fe^{2+} molar ratios of between 1:0.031 and 1:0.31. They also conducted experiments with the addition of hydrogen peroxide (1.18 mM) and found that the first order reaction rate was four times higher than that without H_2O_2 . Complete diuron (0.09 mM) oxidation in a few minutes was observed by Romero et al. (2010) who used a persulfate concentration of 2.1 mM and a Fe^{2+} concentration of 0.72 mM. In addition, they pointed that bicarbonate in the solution may result in a lower rate of diuron degradation by persulfate.

To keep the iron in solution under neutral pH, several common chelates have been used, such as ethylenediaminetetraacetic acid (EDTA), citric acid, nitrilotriacetate (NTA), N-(2-hydroxyethyl) iminodiacetate, and hydroxylpropyl- β -cyclodextrins (Huling, 2006; Liang et al., 2007a). Dahmani et al. (2006) found that PCE, TCE and cis-DCE degraded at 74%, 86% and 84%, respectively by sodium persulfate alone while Fe^{2+} -chelated $\text{Na}_2\text{S}_2\text{O}_8$ (using EDTA as the chelating agent) resulted in PCE, TCE and cis-DCE degradation of 68%, 78% and 69%, respectively. In contrast, Liang et al. (2004b) studied the use of chelating agents to maintain ferrous ion activity as an activator for persulfate oxidation of TCE in aqueous and soil slurry conditions. They found that in the aqueous experiments the chelate: Fe^{2+} molar ratio should not be less than 1:5, otherwise the excess Fe^{2+} will complete for the sulfate free radical resulting in a reduced efficiency of TCE degradation. In addition, they indicated that the $\text{S}_2\text{O}_8^{2-}$: TCE molar ratio must be maintained at least at 10:1 when the chelate: Fe^{2+} : TCE molar ratio of 2:10:1 was

used. On the other hand for the same $S_2O_8^{2-}$:chelate: Fe^{2+} :TCE molar ratios used in aqueous experiments, the results for the soil slurry experiments showed TCE degradations and persulfate decomposition were slower than in aqueous system. In addition, they speculated that citric acid as a chelating agent could extract the ferrous ion from the soil used which then could be used to activate persulfate for the degradation of TCE. Work done by Crimi and Taylor (2007) showed that an excess of chelate to iron is necessary to control the availability of Fe^{2+} for successful treatment of BTEX. Other studies on the use of citric acid as chelating agent for iron-activated persulfate included a study by Liang et al. (2009a) where they used a Fe^{2+} : citric acid molar ratio of 5:3 with persulfate to oxidize BTEX in a scrubber solution and the work by Killian et al. (2007) for the oxidation of BTEX and PAHs at a manufactured gas plant site where better results were obtained with citric acid chelated Fe^{2+} as persulfate activator than the addition of iron (II) alone. Killian et al. (2007) showed that the percent removal of BTEX compounds were higher than the heavier molecular weight compounds. Similarly, Liang et al. (2008b) demonstrated that citric acid chelated Fe^{2+} was a suitable activator and a persulfate: citric acid: iron: BTEX molar ratio of 20:5:5:1 resulted in complete degradation of BTEX within 70 minutes.

Liang et al. (2004) compared different chelating agents such as EDTA, STPP, HEDPA, and citric acid and found that citric acid was the most effective agent to regulate ferrous ion activated persulfate for the degradation of TCE in both aqueous and soil slurries conditions at 20°C. In another study, Liang et al. (2008b) compared the effects of HPCD, EDTA, and citric acid as chelating agents and found that HPCD and EDTA were less suitable in maintaining available Fe^{2+} in the persulfate system. Iron-citrate complexes are probably more stable than EDTA complexes since citric acid is less sensitive to the presence of competing metals. Nadim et al. (2005) demonstrated that EDTA chelated Fe^{2+} activated persulfate (5 g/L sodium

persulfate) completely degraded 16 target EPA PAHs at a concentration of 1 µg/L at ambient temperature. Liang et al. (2009b) studied the pH dependence of persulfate activation by EDTA/Fe (III) for the degradation of TCE (0.3 mM) and found an optimum pH of 10 was needed for a EDTA:Fe(III) molar ratio of 1:1. A recent study by Achugasim et al. (2011) on the effects of pH showed that percent removal of BTEX was 97.5%, 95.8%, and 95.2% at acidic, neutral, and basic conditions and only 26%, 2.7%, and 46% of percent removal of PAHs for the same conditions.

An alternative method of sustaining Fe^{2+} availability was by adding a reducing agent such as thiosulfate to induce reducing conditions to convert Fe^{3+} to Fe^{2+} and making Fe^{2+} available to activate persulfate (Liang et al., 2004a). In their laboratory experiments, they achieved >98% TCE degradation in aqueous systems for a $\text{S}_2\text{O}_8^{2-}:\text{S}_2\text{O}_3^{2-}:\text{TCE}$ molar ratio of 20:5:1 within 20 min, and 60-96% after 42 hours in soil slurries at three levels of $\text{Fe}^{2+}:\text{TCE}$ molar ratio of 1:1, 5:1, and 10:1, respectively. It was shown that higher initial Fe^{2+} content resulted in higher TCE degradation in the soil slurry and that an increase in thiosulfate concentration resulted in a decrease in TCE degradation which may be due to excess Fe^{2+} present as induced by thiosulfate. These results suggested that a persulfate–thiosulfate redox couple can prolong the availability of Fe^{2+} and improve persulfate oxidation.

Liang et al. (2007a) investigated hydroxypropyl- β -cyclodextrin (HP- β -CD) as a means to increase the solubility of the contaminants and to form inclusion complexes with organic contaminants and Fe^{2+} which may effectively increase contaminant degradation due to direct sulfate radical interaction with the target compounds. In their studies, they found that PCE and TCE were oxidized by 92% using 9.1 mM of persulfate. One recommendation from their studies

was that the Fe^{2+} was to be added continuously instead of a single dose into the system in order to maintain a continuous rate of sulfate radical generation for the degradation of PCE and TCE.

Instead of using ferrous iron, another approach is to use zero-valent iron as a source of electrons and as a source of Fe^{2+} for the activation of persulfate. Hussain et al., (2012) used zero-valent iron (ZVI) as a persulfate activator and found that p-chloroaniline (PCA) was degraded by near 100% for a ZVI concentration of 0.7 g/L and 2.5 mM of persulfate at a pH of 4 and temperature of 50°C. Oh et al., (2010) compared zero-valent iron (ZVI) - activated persulfate (5 g of ZVI and 1.3 mM of persulfate) and ferrous-activated persulfate (5 g of ferrous iron and 1.3 mM of persulfate) for the degradation of 2,4-dinitrotoluene (DNT). They found that ferrous iron activated persulfate had a faster initial degradation rate than ZVI but ZVI was effective over a longer period of time than ferrous ion and gave a percent removal of 100%. In an earlier study, Oh et al. (2009) obtained complete degradation of polyvinyl alcohol in 2 hours using a persulfate:ZVI mole ratio of 1:1 (concentrations of 1.3 mM of persulfate and 1.3 mM of ZVI). An example of the application of ZVI and persulfate is the work by Kambhu et al. (2012) for remediation of groundwater. Kambhu et al. (2012) inserted into groundwater wells candles made of a mixture of persulfate and paraffin (ratio of 2.25:1) and candles of zero-valent iron. They found that the sulfate radicals produced from the slow release of persulfate and ferrous ions from the candles resulted in a decrease of benzene and benzoic acid by more than 90 percent in 7 days. The slow release persulfate and zero-valent iron candles seemed to be a promising technology for application of in situ chemical oxidation.

In addition of Fe^{2+} and correlatives, other metal ions were considered as activator. For instance, Liang et al. (2013) applied persulfate activated with copper oxidate for the degradation of p-chloroaniline (PCA). The results indicated that a higher copper oxidate dosage and

persulfate concentration cause more destruction of PCA at the optimal neutral pH. They suggest that copper possessed multiple characteristics including persulfate activation and good mineralization. But the secondary pollution has to be of concern due to the toxicity of copper ion in the solution.

2.3.3. Other novel activation methods

In recent years, some novel activation methods such as ultraviolet light activated persulfate (Gao et al., 2011; Lin et al., 2011, 2013;), copper activated persulfate (Liang et al., 2013), magnetite (or magnetite non-particles) activated persulfate (Usman et al., 2012; Fang et al., 2013), microwave activated persulfate (Yang et al., 2009), and ultrasound activated persulfate (Li et al., 2013; Chen et al., 2012) were developed. All of these technologies are summarized in Table 2.3 and have been shown to have potential for degradation of contaminants in soil and groundwater in laboratory experiments.

Gao et al. (2011) applied UV on persulfate for the degradation of sulfamethazine (SMT) at a pH of 11 and found that UV light (254 nm) in the presence of persulfate (0.5 mM) achieved 97% removal of SMT (0.02 mM initial concentration). It is probable that reactive sulfate radicals may generate hydroxyl radicals in alkaline condition which can rapidly degrade SMT and its intermediate oxidation products. Lin et al. (2011) used UV activated persulfate oxidation and obtained complete phenol degradation after 30 min of treatment in a solution with a persulfate:phenol ratio of 84:0.5 over a pH range of 3-11. In addition, Lin et al. (2013) applied UV/S₂O₈²⁻ for the degradation of polyvinyl alcohol (PVA). They found that the best degradation efficiency of PVA happened at pH 3 with a higher concentration of persulfate and lower initial concentration of PVA. They pointed that the bicarbonate and carbonate ions were formed under

Table 2.3 Other activation methods for persulfate oxidation

Activator	Contaminants	Intensity/ Conc. of activator	Contaminant Conc.	Persulfate Conc.	% Removal	Reference
ultraviolet light	sulfamethazine (SMT)	254 nm	0.02 mM	0.05–0.5 mM	97%	Gao et al. (2011)
	phenol	400–460 nm	0.5 mM	84 mM	100%	Lin, et al. (2011)
	polyvinyl alcohol (PVA)	365 nm	20 mg/L	1.00 mM	97%	Lin et al. (2013)
Magnetite	polycyclic aromatic hydrocarbons (PAHs)	(Fe ^{II} Fe ^{III} ₂ O ₄) with Fe ^{II} :Fe ^{III} ratio of 1:2	1369 ug/g	N/A	70-80%	Usman et al. (2012)
magnetite nonparticles	PCB28	1 g/L	2.5 uM	2 mM	95%	Fang et al. (2013)
Microwave	Azo dye acid Orange 7 (AO7)	MW furnace (800 W)	500 mg/L	50:1 of SPS/AO7	100% decolorization, 83-95% COD	Yang et al. (2009)
Ultrasound	TCA	400 kHz, 100 W	25.0 mg/L	3.76 mM	near 100%	Li et al. (2013)
	dinitrotoluenes	ultrasonic power intensity=126 W/cm ²	450 mg/L	2 wt%	TOC removal near 100%	Chen et al. (2012)
peroxymonosulfate (Another oxidant)	polychlorinated biphenyls (PCBs)	0.11-0.44 mM with 0.11-0.44 mM Fe ²⁺	0.0212 mM	None	32-99%	Rastogi et al., (2009)

alkaline conditions, which may inhibit the degradation of PVA. This result was supported by some previous studies (Huang et al., 2002; Liang, 2006, 2007; Waldemer et al., 2007). However, all of the UV activation has some limitations. The removal efficiency depends on persulfate doses and solution pH.

Based on use of iron, magnetite was also considered as activator. Usman et al. (2012) used magnetite ($\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$) to activate persulfate to degrade polycyclic aromatic hydrocarbons (PAHs) contaminated soils. Their results indicated that magnetite activated persulfate has 75-100% degradation efficiency of 16 PAHs compared to 15-20% degradation for Fe^{2+} activated persulfate and without iron activation. However, significant degradation was obtained depending on the molecular weight of PAHs and the soil matrix. Complete degradation only happened when the concentration of contaminants was very low. Recently, Fang et al. (2013) proposed a more creative method using magnetite nanoparticles (MNPs) to activate persulfate for the degradation of PCB 28. They proposed that a significant species, superoxide radicals ($\text{O}_2^{\cdot-}$) was generated in MNPs which can react with persulfate to produce sulfate radicals. The results indicated that increasing the pH and dissolved oxygen dose could increase the concentration of $\text{O}_2^{\cdot-}$ radicals generated by MNPs and Fe^{2+} adsorbed on MNPs surface could generate $\text{O}_2^{\cdot-}$ and OH^{\cdot} . Results of this study showed that a combination of PS/MNPs/ Fe^{2+} could achieve 95% of PCB 28 degradation within 120 mins. In addition, persulfate with commercial MNPs could achieve 60% degradation of PCB 28.

Microwave may be considered as thermal activation due to the generation of heat. Yang et al. (2009) developed a new oxidation-based approach applying degrade organic pollutants by microwave (MW)-activated persulfate oxidation. They investigate the function of MW – activated persulfate oxidation by using Azo dye acid Orange 7 (AO7) as a model compound (up

to 1000 mg/L) to compare with the heating model, and the result indicates that MW model has lower activation energy, shorter reaction time, and higher rate and selectivity of reaction than heating model. In addition, they enhanced the efficiency of MW by adding absorbing material – active carbon (AO) as catalyst. And the results indicated that AO-MW-APO has less reaction time than MW-APO. But for this method, Yang et al. group only focused on decolorization and COD removal and there were no details on the dye degradation and the pH for persulfate reactions.

Instead of microwave, ultrasound, a sonochemical activation, was used Li et al., (2013) for persulfate activation for the degradation of TCA. Their results indicated that near complete degradation of TCA was obtained for pH=7, an ultrasonic frequency 400 KHz and power of 100W, and a PS:TCA ratio of 10/1 at ambient temperature. Persulfate activated with ultrasonic irradiation is a potential method for the remediation of TCA-contaminated groundwater. Similarly, Chen et al. (2012) achieved near complete elimination of dinitrotoluenes in wastewater for an ultrasonic power intensity of 126 W/cm, pH at 0.2, temperature of 45°C, and persulfate concentration of 2% (wt/wt).

2.4. Specific Application of peroxymonosulfate Oxidation

Peroxymonosulfate is an alternative novel chemical oxidant for the generation of sulfate free radicals. Generally the salt form of peroxymonosulfate is present as potassium peroxymonosulfate, which is also called oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$). Oxone is inexpensive, water soluble, and a stable oxidizing reagent that is commercially available, but this reagent is insoluble in common organic solvents and buffering is needed due to its acidity (Kennedy, 1960). The oxone provides the strong oxidizing peroxymonosulfate (HSO_5^-) anion ($E^\circ = 1.44\text{v}$).

It is used as an alternative bleaching agent for chlorine in the paper and pulp industry as well as a cleaning and disinfection agent in pools and spas. Recently, peroxymonosulfate was reported to be an oxidant for the degradation of contaminants in aqueous system or soil system. Kennedy and Stock (1960) found that $\text{KHSO}_5\text{-KHSO}_4\text{-K}_2\text{SO}_4$ could oxidize the organic compounds based on free radicals in natural condition. But only a few organic compounds could be degraded since free radical generation did not occur without external activation. Recently, activated peroxymonosulfate was found to be more efficient as an oxidizing agent than hydrogen peroxide and persulfate in terms of radical generation (Rastogi et al., 2009).

2.4.1. Transition metal activation

As for persulfate, transition metals are also an effective method for the activation of peroxymonosulfate. Table 2.4 list the examples of Fe^{2+} as an activator for the generation of free radicals from peroxymonosulfate. For example, Dionysiou and Rastogi (2005) investigated Fe^{2+} activated PMS for degradation of chlorophenol and found that Fe^{2+} -PMS system was more effective for chlorophenol degradation in short term (duration = 2 hours) than PS system, but Fe^{2+} -PS system achieved higher TOC removal over a longer period (duration = 8 days) than PMS system. In addition, Rastogi et al., (2009) studied the degradation of PCBs and found Fe^{2+} -PMS system with 1:1 of molar concentration ratio was the optimum ratio for the degradation of PCB. Also, Wang and Chu (2011) applied Fe^{2+} -PMS for oxidation of xanthene dye Rhodamine B (RhB) in aqueous solution and found complete RhB removal in 90 min with an optimal Fe^{2+} :Oxone molar ratio of 1:1.

Table 2.4 Examples of Iron activation for peroxymonosulfate

Activator	Compounds	Contaminant Conc.	Iron Conc.	Peroxymonosulfate Conc.	% Removal	Reference
Fe ²⁺	4-CP	0.389 mM	0.389 – 19.44 mM	0.389 – 19.44 mM	95	Dionysiou (2005)
	2,4-CP	0.194 mM	0.97 mM	0.97 mM	94	
	2,4,6-CP	0.194 mM	0.97 mM	0.97 mM	95	
	2,3,4,5-CP	0.194 mM	0.97 mM	0.97 mM	79	
	Naphthalene(model PAHs)	N/A	N/A	Naphthalene : Oxidant : Fe(II)=1:10:1	76.86	
	2-CB (model PCBs)	26.5 μM	26.5 μM – 1.325 mM	26.5 μM – 1.325 mM	100	
Fe ²⁺	PCBs	0.396 mM	0.99 mM	3.96 mM	65	Rastogi et al. (2009)
Fe ²⁺ with citrate	PCBs	0.396 mM	0.99 mM with 0.99 mM Cit	3.96 mM	90	
Fe ²⁺	RhB	0.02 mM	0.20 mM	0.10 mM	60	Wang and Chu (2011)
		0.02 mM	0.20 mM	0.20 mM	100	
		0.02 mM	0.20 mM with 0.1 M NaCl	0.20 mM	90	
UV (254 nm)	2,4,5-T	0.1 mM	None	0.25 mM	80	Wang et al. (2012)
Fe ²⁺		0.1 mM	0.25 mM	0.25 mM	52	
Fe ²⁺ with UV(254 nm)		0.1 mM	0.25 mM	0.25 mM	100	

However, the Fe^{2+} was not the most effective transition metal to activate peroxymonosulfate. Anipsitakis et al., (2004) investigated the radical formation reaction by coupling of nine metals (Fe^{2+} , Fe^{3+} , Co^{2+} , Ru^{3+} , Ag^+ , Ce^{3+} , Mn^{2+} , Ni^{2+} , and V^{3+} for the activation of peroxymonosulfate compared with hydrogen peroxide and persulfate (Table 2.5). The results indicated that oxidation of chlorophenol were obtained by ferrous iron activated Fenton reagents (H_2O_2) (91% and 95%), KHSO_5 (75% and 21%), $\text{K}_2\text{S}_2\text{O}_8$ (35% and 15%) within 4 hours. But the Co^{2+} - KHSO_5 system showed very high reactivity as 98% of the chlorophenol was transformed within 1 min. Also the system of Ru^{3+} - KHSO_5 preformed the same transformation rate as cobalt. Co^{2+} and Ru^{3+} coupling with the other oxidants didn't shown acceptable degradation. The Ag^+ is a very efficient activator of decomposition of $\text{K}_2\text{S}_2\text{O}_8$ led to 85% transformation of chlorophenol within 4 hours, but it shown the far less reactivity while the coupling with H_2O_2 and KHSO_5 . The coupling of Ce^{3+} , V^{3+} , Mn^{2+} , and Ni^{2+} with KHSO_5 obtained over 10% oxidation of 2,4-DCP than the other oxidants in 4 hours.

Therefore Co^{2+} was the best transition metal activator for peroxymonosulfate activation. Table 2.5 provide a list of examples of cobalt activation of PMS. Anipsitakis et al., (2003) applied Co/PMS reagent to degrade 2,4-DCP in aqueous system. The results indicated that Co^{2+} at a low concentration (0.07mg/L) catalyzed the peroxymonosulfate would have complete degradation of 50mg/L of 2,4-DCP and 30% total organic carbon removal. And there is no pH adjustment due to activity of PMS in wide range of pH (2-8).

Other studies based on Co-PMS system were applied for degradation of different organic contaminants. Pagano et al., (2012) applied Co^{2+} -PMS oxidation system for removal of Brij 35, which is alcohol ethoxylate. The best removal of Brij 35 was found between 86 to 94% at pH

Table 2.5 Examples of cobalt activation for peroxymonosulfate

Activator	Target Compounds	Contaminant Conc.	Activator Conc.	Peroxymonosulfate Conc.	% Removal	Reference
Co ²⁺	2,4-DCP	0.307 mM	0.307 mM	0.613 mM	90	Anipsitakis et al. (2003)
Fe ²⁺		0.311 mM	1.244 mM	1.244 mM	75	Anipsitakis et al. (2004)
Fe ³⁺		0.311 mM	1.244 mM	1.244 mM	21	
Co ²⁺		0.311 mM	1.244 mM	1.244 mM	98	
Ag ⁺		0.311 mM	0.622 mM	1.244 mM	85	
Ru ²⁺		0.311 mM	2.533 mM	1.244 mM	97	
Ce ³⁺		0.311 mM	1.244 mM	1.244 mM	32	
V ³⁺		0.311 mM	1.244 mM	1.244 mM	27	
Mn ²⁺		0.311 mM	1.244 mM	1.244 mM	24	
Ni ²⁺		0.311 mM	1.244 mM	1.244 mM	16	
Co ²⁺	bisphenol A	0.05 mM	5.00 ppb	0.10 mM	100	Huang et al. (2009)
Co ²⁺	Brij 35	680-2410 mg/L	15 μM	5.9 mM	86-94	Pagano et al. (2012)
Co ²⁺	carbamazepine	50 μM	150 μM	150 μM	90	Matta et al. (2011)
Co(NO ₃) ₂	ATZ	0.1 mM	6.8 mM	0.1 mM	95	Chan et al. (2009)
CoSO ₄		0.1 mM	6.8 mM	0.1 mM	95	
CoCl ₂		0.1 mM	6.8 mM	0.1 mM	75	
Co(CH ₃ COO) ₂		0.1 mM	6.8 mM	0.1 mM	95	
Co-TiO ₂		0.1 mM	20 mg	0.1 mM	89	
Co-TiO ₂ with UV 419nm		0.1 mM	20 mg	0.1 mM	100	

Table 2.5 continued

TiO ₂ with UV <420nm	AO7	0.1 mM	1 g/L	2 mM	100	Chen et al. (2012)
Co/MgO	Methylene blue (MB)	40 mg/L	10 mg in 200 mL	0.5 mM	100	Zhang et al. (2010)
Co/ZnO		40 mg/L	10 mg in 200 mL	0.5 mM	90	
Co/P25		40 mg/L	10 mg in 200 mL	0.5 mM	50	
Co/ZrO ₂		40 mg/L	10 mg in 200 mL	0.5 mM	49	
Co/Al ₂ O ₃		40 mg/L	10 mg in 200 mL	0.5 mM	38	
Co/SBA-15		40 mg/L	10 mg in 200 mL	0.5 mM	25	
Co/MnO ₂	phenol	25 mg/L	0.1 g/L	0.5 g/L	100	Liang, et al. (2012)
Co/MCM41	caffeine	0.05 mM	200 mg/L	0.2 mM	98	Qi et al. (2013)
Co/SBA-15 at 400°C	phenol	50 mg/L	0.1 g/L	2.125 mM	>98	Hu et al. (2011)

2.3. Matta et al., (2011) investigated the degradation of carbamazepine in urban wastewater based on cobalt activated PMS which was compared with the Fenton' reagent. The results showed that sulfate radicals generated by Co-PMS system were more effective than hydroxyl radicals for the oxidation of carbamazepine. Also, Huang et al., (2009) investigated that Co^{2+} /PMS oxidation used in bisphenol A (BPA) degradation. They found it was more efficiency on TOC removal (40%) than 1% removal of TOC by UV/persulfate oxidation.

According to above studies, PMS coupled with Co^{2+} ions is the best combination for generation of sulfate radicals for degradation of organic contaminants. However, the second environmental pollution caused by the dissolved Co^{2+} ions in water, which would be restricted to apply in environment. Thus, the activation of PMS by heterogeneous cobalt sources has been considered recently. For example, Zhang et al. (2010) investigated various oxides (MgO , ZnO , Al_2O_3 , ZrO_2 , P25, SBA-15) as catalysts for cobalt activation of PMS for degradation of organic dyes. The results showed the Co/MgO system was the most effective to achieve complete degradation. Also, Liang, H.W. et al. (2012) investigated that cobalt- MnO_2 as formation of nanoparticles for phenol degradation, and the completely oxidation obtained in 20 min. Moreover, Qi et al., (2013) applied MCM41, which is a mesoporous silica with hexagonal order pore canal, coupled with cobalt to activate PMS and obtained 98% caffeine decay. Additionally, Hu et al., (2011) found calcination at 400°C for 5 hours could generate Co-O-Si species which could inhibit Co leaching. They studied on Co coupled with SBA-15, which is one of silica mesoporous molecule sieves, and the more than 98% removal of phenol was obtained.

In addition to supported materials, Chan and Wu (2009) applied cobalt-mediated activation of peroxymonosulfate for degradation of atrazine. The different cobalt counter-anions contain cobalt nitrate ($\text{Co}(\text{NO}_3)_2$), cobalt sulfate (CoSO_4), cobalt chloride (CoCl_2), and cobalt

acetate ($\text{Co}(\text{CH}_3\text{COO})_2$). The results indicated that CoCl_2 shown the inhibitory effect in the process because the scavenging of $\text{SO}_4^{\bullet-}$ and the formation of weaker radical species Cl^{\bullet} and $\text{Cl}_2^{\bullet-}$. And $\text{Co}(\text{NO}_3)_2$, CoSO_4 , and $\text{Co}(\text{CH}_3\text{COO})_2$ shown the significant efficiencies in degradation of ATZ. At $\text{pH} < 3$, PMS couldn't be activated by cobalt ion effectively and the process was retarded due to the insufficient generation of $\text{SO}_4^{\bullet-}$. At $\text{pH} > 10$, the process was held back a little bit due the formation of precipitate $\text{Co}(\text{OH})_2$. Moreover, recycling capability of CoO was nearly perfect as the spent CoO would be easily reused and no defective effect after 3 runs of recycling tests. In addition, the Co-TiO_2 catalyst synthesized in their work was found to be very effective in degrading ATZ as well as its intermediate in the presence of UV irradiation.

Also, Chen et al., (2012) applied photo-catalysis (visible light/ TiO_2) coupled with addition of the peroxymonosulfate to degrade the target compound Acid Orange 7 (AO7) in aqueous solutions. The results indicate that the order of degradation efficiencies is $\text{Vis/TiO}_2/\text{PMS} > \text{Vis/TiO}_2/\text{PS} > \text{Vis/TiO}_2/\text{H}_2\text{O}_2$, which primarily because PMS can react with the free electrons on the surface of TiO_2 to produce both $\text{SO}_4^{\bullet-}$ and HO^{\bullet} . Also they investigate that effect of humic acids on the degradation of AO7, which is positive effect.

2.4.2. Other novel activations

Besides transition metal activation, recently there were some novel activation methods were studied which shown in Table 2.6.

As mentioned in previous review, MnO_2 was a supported material which could couple with cobalt to generate sulfate radicals by activating peroxymonosulfate and limit the cobalt leaching. Saputra et al., (2012) found that $\alpha\text{-MnO}_2$ has ability in activation of PMS to generate

sulfate radicals for phenol degradation, which is due to the particular structure and morphology. The results showed 100% phenol degradation obtained in 90 min.

According to persulfate review, the zero-valent iron was considered as an activator for persulfate oxidation. Thus, it also can be applied for activated PMS. For example, Sun et al., (2012) studied on nanoscale ZVI activated PMS for degradation of phenol compared with heat, common ZVI, and nanoscale ZVI with heat. Their results performed that nano-Fe⁰ at 550 °C has highest efficiency in activation of PMS for degradation, because nano-Fe⁰ at 550 °C has a porous structure with high specific surface area and pore volume which can control the usage of iron and attract substrates.

Moreover, Lou et al., (2013) investigated that chloride induced PMS activation for dye degradation without any transition metal. Rhodamine B (RhB) was selected as organic dye pollutant. The results showed that RhB could be decomposed completely in terms of destruction of chromophore. The byproducts were generated and there was no complete degradation. After GC-MS analysis, RhB could be degraded to aromatic compounds which were biodegradable.

In addition to oxone, Hajipour et al., (2000) applied the benzyltriphenylphosphonium peroxymonosulfate (PhCH₂Ph₃P+HSO₅⁻)-(BTPPMS) (1.5 mol), as a mild and novel oxidizing reagent for oxidation of allylic and benzylic alcohols under the non-aqueous conditions at the room temperature. Even though this compound shown the good oxidation of alcohols (>80%), the sequential results indicated that the rate was at the most efficiency (>90%) with adding a catalytic amount of bismuth chloride (BiCl₃) (0.4mM) compared with in the presence of ZnCl₂, FeCl₃, and AlCl₃. In addition, they reported that BTPPMS is mild, inexpensive, and stable oxidizing reagent, which could be easily prepared and stored for months without losing its activity.

Table 2.6 Examples of novel activation for peroxymonosulfate

Activator	Target Compounds	Intensity/ Concentration of activator	Contaminant Concentration	Peroxymonosulfate Concentration	% Removal	Reference
α -MnO ₂	phenol	0.4 g/L	30 ppm	2.0 g/L	100	Saputra et al. (2012)
Cl ⁻	RhB	120 mM with pH =3	10 μ M	0.5 mM	96	Lou et al. (2013)
Heat at 550°C	phenol	0.5 g/L	20 ppm	2 g/L	100	Sun et al. (2012)
Fe ⁰		0.5 g/L	20 ppm	2 g/L	15.8	
HR-Fe ⁰ at 550°C		0.5 g/L	20 ppm	2 g/L	54.6	
Fe ⁰ at 550°C		0.5 g/L	20 ppm	2 g/L	86.9	
BTPPMS - ZnCl ₂ , FeCl ₃ , AlCl ₃	Allylic & Benzylic alcohols	0.5 mmol	1 mmol	1.5 mmol	78-98	Hajipour et al. (2000)
BTPPMS - BiCl ₃		0.4 mmol	1 mmol	1.5 mmol	90-98	
BTPPMS – BiCl ₃ under Microwave	trimethylsilyl and tetrahydropyranyl ethers; and ethylene acetals	MW 2450 MHz, 900 W with 0.4 mmol BiCl ₃	1 mmol	1 mmol	80-99	Hajipour et al. (2001)
BTPPMS	aromatic and aliphatic sulfides; and thiols	None	1 mmol	1.5 mmol	78-99	Hajipour et al. (2002)

And the reagent would dissolve in acetonitrile, chloroform and dichloromethane and slightly soluble in carbon tetrachloride, ether and hexane. In 2001, Hajipour et al. enhanced this method by applied microwave irradiation. The results shown trimethylsilyl and tetrahydropyranyl ethers (oxidative deprotection), and ethylene acetals (deprotection) could be transformed to the corresponding carbonyl compounds in high yields (80-99%) at relative low concentration of BTPPMS (1 mol). In 2002, Hajipour et al. applied BTPPMS for oxidation of aromatic and aliphatic sulfides, and thiols. These compounds could be transformed to their corresponding sulfoxides and disulfides in high yield (78-99%) under non-aqueous and aprotic condition without catalyst.

2.5. Summary

2.5.1. Understanding of persulfate and peroxymonosulfate oxidation

The methods of persulfate activation for soil and groundwater treatment own a lot of promise, because persulfate has high oxidizing power and stability. Based on above reviews, heat activation would be an ideal technology and maximally exploit its property for targeted activation applied in the subsurface, although it has big challenge for a large contaminated zone. Iron activation is also a very promising technology depends on variability of this method in terms of which types of iron and types of chelates, the field application of this processes is at an early stage and true potential need be evaluated. The combinations of persulfate with high pH or peroxide are economical for field application. Some novel activators such as UV, ultrasound, and microwave has been proved that could enhance the oxidation of persulfate in lab scales.

This review found that persulfate could be an effective method to destruct the commonly target organic compounds in soil and groundwater system but still need be developed. The

organic compounds contain BTEX, chlorinated solvents, MTBE, PAHs, and PCBs. BTEX, chloroethenes, and chlorobenzenes only need a short reaction time in aqueous system. The higher concentration of persulfate and longer reaction time would contribute to degrade the recalcitrant contaminants.

Peroxymonosulfate performed similar oxidizing ability as persulfate due to generation of sulfate radicals. Differently, most of studies focused on cobalt activation for peroxymonosulfate oxidation, which has been developed by using different type of cobalt and coupling with supported materials. Even though cobalt was proved that was the best activator for peroxymonosulfate oxidation, it will cause secondary environmental issue. Also, peroxymonosulfate was confirmed that was more effective than persulfate in short term reaction.

2.5.2. Unknown of persulfate and peroxymonosulfate oxidation

As mentioned previously, information is deficient on the existing field applications of persulfate and peroxymonosulfate. For example, the interactions of persulfate with the soil constituents and the consumption of persulfate due to activation are still poorly understood. Further study of persulfate application both in the lab and at the field scale, the different soil constituents were selected for required soil environment which contain more constraints than aqueous system.

Even though some novel technologies were pointed out in recent studies mentioned previously, all of those are immature and need be advanced. Based on the complicate propitiates, some methods like microwave, ultrasound, and various nonoparticles as supported materials are hardly achieved and controlled for the field application. And also the cost will be the huge issue for coming true in field. Future researches require a well understanding of the kinetic rate of

persulfate and peroxymonosulfate decomposition in terms of these novel technologies in order to design a successful oxidation system.

For the recommendation, the technologies of persulfate and peroxymonosulfate oxidation were flexible to use in field based on choosing an activation aid, contaminant type, environmental conditions, and costs and availability of equipment.

And also, the microorganisms is poor area when applied persulfate and peroxymonosulfate oxidation. Future researches are necessary to study the subsequent biological treatment of contaminated zone. The combination of persulfate or peroxymonosulfate oxidation with other remediation technologies, especially bioremediation, generates a significant potential when it comes to overcome the limitations of persulfate and peroxymonosulfate.

2.6. References

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CHAPTER 3

OXIDATION OF 2,4-D BY IRON-ACTIVATED PERSULFATE OR PEROXYMONOSULFATE

Abstract

This study investigates the oxidation of 2,4-dichlorophenoxyacetic acid (2,4-D), a common herbicide, by using sulfate free radicals oxidation processes. Several approaches can be used to activate persulfate anion ($S_2O_8^{2-}$) and peroxymonosulfate anion (HSO_5^-), to generate sulfate free radical ($SO_4^{\bullet-}$), a powerful oxidant. In this study, we investigate ferrous ion, (Fe^{2+}) as an activator. Experiments were conducted using different molar ratios of 2,4-D, oxidants, and Fe^{2+} . 2,4-D concentrations used in the experiments were fixed at 0.045 mM. 2,4-D was rapidly oxidized within minutes but plateaued to a asymptotic concentration. A possible reason for the slowdown in the oxidation was the rapid conversion of Fe^{2+} to Fe^{3+} which in turn slowed the activation process. Experiments with sequential addition of Fe^{2+} at different times resulted in further 2,4-D oxidation which indicates that Fe^{2+} was limiting in the activation process. The optimal molar ratio of persulfate: Fe^{2+} or peroxymonosulfate: Fe^{2+} for the oxidation of 2,4-D was found to be 1:1. Of the three kinetic models, first-order, bi-exponential first-order, and availability-adjusted first-order, used to model the experimental degradation data, the bi-exponential first-order model provided the best fit of the experimental data with R^2 values greater than 90%. The results of the experiments showed that a low cost material such as Fe^{2+} can be applied to activate persulfate or peroxymonosulfate for the removal of 2,4-D and other organic compounds in contaminated groundwater and drinking water.

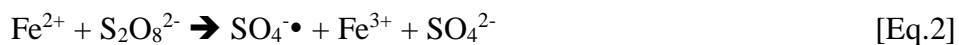
Key words: persulfate, peroxymonosulfate, 2,4-D, oxidation, activation

3.1. Introduction

Chemical oxidation has been used for the treatment and detoxification of hazardous industrial wastewater, contaminated groundwater and for the remediation of contaminated soils. Some of the more common oxidation chemicals used for removal of hazardous organic compounds included hydrogen peroxide, and ozone. With the need for more powerful oxidizing agents, advanced oxidation processes (AOPs) with the generation of hydroxyl radicals have been developed such as Fenton's reagent (hydrogen peroxide and Fe(II)), use of ultraviolet light with ozone and hydrogen peroxide. In recent years, researchers and engineers have explored other less common but more stable oxidant such as persulfate or peroxymonosulfate. Both these chemicals have been applied in analytical chemical analysis but have not been fully explored as an oxidizing agent for hazardous waste systems.

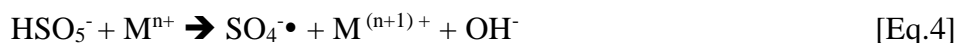
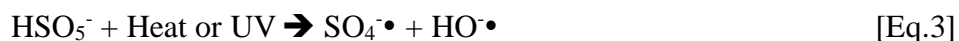
Persulfate ion ($S_2O_8^{2-}$) is a strong oxidizing agent but under certain conditions, it can generate a powerful oxidant, sulfate free radicals ($SO_4^{2\cdot-}$). Due to its sufficiently high stability at ambient temperature (25°C) and high water solubility, sodium persulfate is the most common persulfate salt used in bench-scale experiments and in the field. The main products of persulfate decomposition are sulfate ions and water which are relatively harmless (Liang et al., 2003; Huling et al., 2006). Persulfate has been applied in oxidizing reactions for industrial applications but the body of knowledge on persulfate oxidation for environmental pollutants is lacking in comparison to other oxidizing agents such ozone, and catalyzed hydrogen peroxide (Huling, 2006).

Persulfate's ability to generate free radicals is particularly important for chemical oxidation applications. Two common methods of activation are thermal activation and metal activation (such as Fe^{2+}). The reactions are shown as follows:



The redox potential for sulfate free radicals is 2.6 volts.

An alternative compound for the generation of sulfate free radicals is peroxymonosulfate ion (PMS) (HSO_5^-). The commercially available peroxymonosulfate is oxone with a chemical formula of $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$. Oxone is inexpensive, water soluble, and a stable oxidizing agent but is insoluble in common organic solvents. Due to its acidic properties, buffering is needed in aqueous solutions. The redox potential (E^0) of PMS is about 1.44 V and has been used as an alternative bleaching agent for chlorine in the paper and pulp industry as well as a disinfection agent in swimming pools and spas. Kennedy and Stock (1960) found that the oxone could oxidize various organic compounds based on the PMS itself and generation of free radicals in the natural conditions. Few organic compounds are completely degraded when oxone is used without external activation. Highly reactive sulfate radicals ($\text{SO}_4^{\bullet-}$) and hydroxyl radicals (HO^{\bullet}) can be generated through the hemolytic cleavage of the peroxide bond of HSO_5^- of oxone by photolysis or thermolysis or generation of $\text{SO}_4^{\bullet-}$ via an electron transfer by transition metal (M^{n+}) (e.g. Co^{2+} and Fe^{2+}). Eq. 3 and 4 show the stoichiometric chemical reactions.



Over the last ten years, researchers have focused on cobalt activation of PMS and have obtained satisfactory results (Anipsitakis et al., 2004). However, use of Co^{2+} as an activator produces a secondary environmental contamination. The search for an alternative metal without secondary polluting tendency would make the peroxymonosulfate an attractive oxidizing agent for disposal and treatment of hazardous wastewater and groundwater. Iron (II) or Fe^{2+} is a good

candidate – abundantly available, environmentally innocuous and is low cost. It can be easily delivered for the treatment of various contaminants in wastewater or even in the aquifer to treat contaminated groundwater. Activation of PMS by Fe^{2+} is given by the following reaction:



Persulfate and peroxymonosulfate have been shown to oxidize various organic compounds such as benzene, methyl-tert-butyl-ether (MTBE), trichloroethylene and PAHs (Liang et al. 2007a, Huang et al. 2002, Achugasium et al. 2011, and Park et al. 2010). The body of knowledge for the treatment of herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D) with sulfate radicals is lacking. 2,4-D is a weed killer found in residential, agricultural, and commercial herbicides and pesticides products for the control of broad leaf weeds. 2,4-D has been found in contaminated groundwater and in raw water sources of drinking water. Short term exposure of 2,4-D at levels above the maximum concentration level (0.07 mg/L) can potentially cause nervous system damage while for long term exposure can damage the kidneys and liver (Gervais, 2008).

The objectives of this study is to evaluate iron (II) activated persulfate and PMS for the oxidation of 2,4-D in aqueous system for different molar concentrations of persulfate or PMS and Fe^{2+} . The kinetics will be investigated along with modeling of the degradation kinetics. A comparison will be made to assess the oxidizing potential of persulfate and PMS.

3.2. Methods and Materials

3.2.1. Chemicals

The following chemicals were obtained for the chemical oxidation experiments: 2,4-dichlorophenoxyacetic acid (2,4-D) (CAS No. 94-75-7, purity > 95%), sodium persulfate (CAS

No. 7775-27-1, purity > 98%), potassium peroxymonosulfate (CAS No. 10361-76-9, purity > 98%), Ferrous sulfate heptahydrate (CAS No. 7782-63-0, 98% purity), methanol (CAS No. 67-56-1, purity > 99.9%), phosphoric acid (CAS No. 7664-38-2, HPLC Grade), and acetonitrile (CAS No. 75-05-8, HPLC Grade). The first three chemicals were purchased from Sigma-Aldrich, St. Louis, MO. The last four chemicals were purchased from COMPANY Fair Lawn, New Jersey.

3.2.2. Chemical oxidation experiments

A 0.045 mM (10 mg/L) solution of 2,4-D was prepared for the chemical oxidation experiments. Various peroxymonosulfate and persulfate stock solutions of concentrations (0.225 mM, 0.45 mM, and 0.9 mM) were prepared using nano-pure water. Similarly, various ferrous iron stock solutions of concentrations (0.225mM, 0.45mM, and 0.9 mM) were also prepared using nanopure water. The ferrous iron stock solutions were prepared fresh before each chemical oxidization experiment due to oxidation of ferrous iron. Batch experiments were conducted at ambient room temperature with an average water temperature of $23\pm 2^{\circ}\text{C}$. Experiments were conducted by transferring 49 mL of the prepared 2,4-D solution to a 100 mL Erlenmeyer flask. The solution was stirred with a magnetic stir bar and appropriate amounts of PMS or persulfate and ferrous solutions were then added to obtain the defined molar ratios of 2,4-D:PMS or persulfate: Fe^{2+} (Table 3.1). Volume of PMS or persulfate and ferrous solutions added were 0.45 mL, respectively. After addition of all the chemicals from their respective stock solutions, the initial volume of reaction solution was 49.9 mL. The pH of the batch experiment was not controlled and was measured throughout the experiment. For each experimental run, 1 mL samples were collected at various times to measure the change in 2,4-D concentration and to

study the kinetics of 2,4-D oxidation. Each experimental run was conducted over a 2 hour period. The 1 mL sample was immediately quenched with 0.5 mL of methanol, a known quenching agent for sulfate reaction (Anipsitakis et al., 2011).

Table 3.1 List of experimental matrix

Ratio of 2,4-D:oxidants:Fe ²⁺	2,4-D, mM	Oxidants (PMS and PS), mM	Fe ²⁺ , mM
1:0:5	0.045	0.225	0
1:5:5	0.045	0.225	0.225
1:10:5	0.045	0.225	0.45
1:20:5	0.045	0.225	0.9
1:0:10	0.045	0.45	0
1:5:10	0.045	0.45	0.225
1:10:10	0.045	0.45	0.45
1:20:10	0.045	0.45	0.9
1:0:20	0.045	0.9	0
1:5:20	0.045	0.9	0.225
1:10:20	0.045	0.9	0.45
1:20:20	0.045	0.9	0.9

3.2.3. Analytical methods

2,4-D in the samples was analyzed without any extraction by a High Performance Liquid Chromatograph (Model 1100 Series, Agilent Technologies, Santa Clara, CA) equipped with a Quart Pump and UV-diode array detector. The column used was a 150×4.6mm C18 column (Agilent Technologies, Santa Clara, CA). The mobile phase used was 60% (v/v) of 0.05% phosphoric acid and 40% (v/v) acetonitrile. The flow rate was 1.0 mL/min and the UV-vis detector wavelength was set at 225 nm. 2,4-D was detected at a retention time of 11 minutes. A standard 2,4-D curve was prepared using 2,4-D concentrations between 0.0005 mM and 0.045mM. Samples were analyzed with 24 hours after they were quenched.

3.3. Results and Discussions

3.3.1. Effects of 2,4-D:oxidants:Fe²⁺ ratios

Previous studies have shown that Fe²⁺ can be used as an activator to activate peroxymonosulfate and persulfate to produce sulfate radicals (Liang 2004a; Rastogi 2009). In Figure 3.1, for a 2,4-D concentration of 0.045 mM and a fixed PMS or persulfate concentration of 0.225 mM, 2,4-D concentration were found to decrease rapidly within the first or two minutes and then leveled off for different Fe²⁺ concentration added. With 0 mM of Fe²⁺, 2,4-D were found to be reduced by about 10 percent for both PMS and persulfate added. For 2,4-D:oxidant:Fe²⁺ ratios of 1:5:5, 1:5:10, and 1:5:20 (i.e., addition of 0.225 mM, 0.45 mM, and 0.9 mM of Fe²⁺, the best 2,4-D percent removal was observed (about 50%) with an addition 0.225 mM of Fe²⁺ or a ratio of oxidant:Fe²⁺ of 1:1. Adding higher concentration of Fe²⁺ to the solution did not show an increased in 2,4-D reduction but resulted in a slightly worst percent removal (about 30%). Results for PMS and persulfate were similar (see Figure 3.1). This set of experiments may imply that either the amount of oxidant added was insufficient to obtain a higher 2,4-D oxidation or that too much iron had been added which in turn may have quenched the sulfate free radicals formed.

Figures 3.2 and 3.3 provide the oxidation results for 2,4-D:oxidants ratios of 1:10 and 1:20 and various amounts of Fe(II). These two figures can be compared with Figure 3.1 which provide oxidation results for 2,4-D:oxidant ratio of 1:5. The first observation that can be drawn from Figures 3.1 to 3.3 was that the percent removal of 2,4-D increased with an increase in the concentration of the oxidant added to the fixed amount of 2,4-D. This is in line with the observation for Figure 3.1 in that the amount of oxidant added may be insufficient.

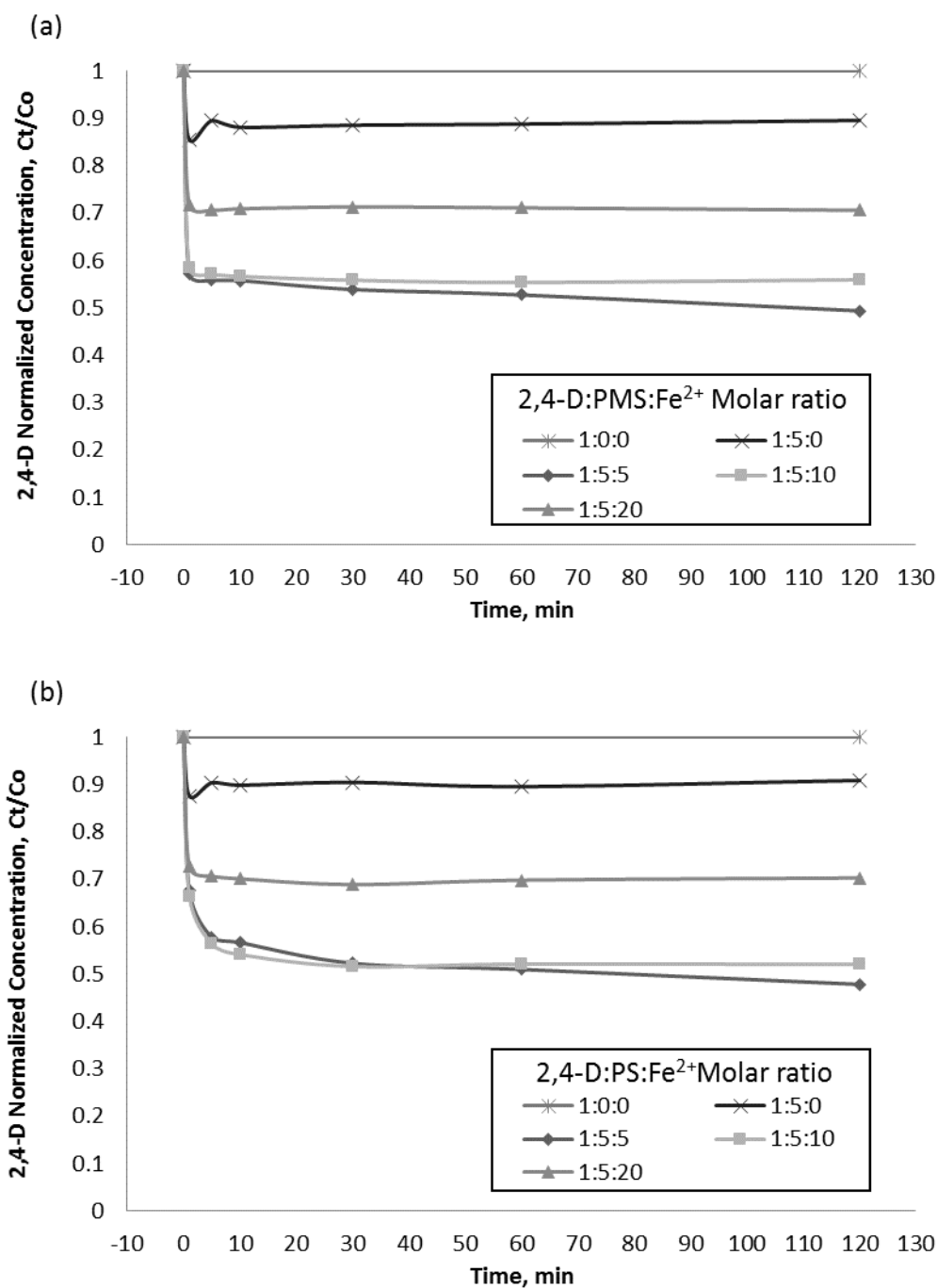


Figure 3.1 Effect of Fe²⁺ concentration on 2,4-D oxidation (a) PMS = 0.225 mM and (b) Persulfate = 0.225 mM. (2,4-D = 0.045 mM; Fe²⁺ = 0, 0.225 mM, 0.45 mM, 0.9 mM)

The second observation that can be made from the Figures 3.1 to 3.3 for both PMS and persulfate was that the highest 2,4-D percent removals were for oxidant:Fe²⁺ ratios of approximately 1:1. Approximately 75 and 80 percent removal of 2,4-D were obtained for PMS and persulfate, respectively and Fe²⁺ concentrations of 0.45 mM (i.e., a ratio of 1:1 for oxidant:Fe²⁺). When the oxidant:Fe²⁺ ratios were less or more than 1:1 ratio, the percent removals of 2,4-D were found to be less than the percent removals for an oxidant:Fe²⁺ ratio of 1:1. Figure 3.3 shows that when the oxidant:Fe²⁺ was increased to a ratio of 1:1, the 2,4-D percent removal improved. For experiments where the concentration of Fe²⁺ was twice the amount of the oxidant, the 2,4-D percent removal appeared to be less than that for experiments where the concentration of Fe²⁺ was half of the concentration of the oxidant. For example, in Figure 3.2, percent removal for oxidant:Fe²⁺ ratio of 1:2 (shown as 1:10:20 for 2,4-D:oxidant:Fe²⁺ ratio) was found to be less than the percent removal for a oxidant:Fe²⁺ ratio of 1:0.5 (shown as 1:10:5 for 2,4-D:oxidant:Fe²⁺ ratio). A probable reason may be that excess amount of Fe²⁺ may have a scavenging effect on the chemical oxidation reaction. Liang et al. (2004a, 2004b) in their experiments on the oxidation of trichloroethylene hypothesized that the sulfate radicals can be consumed by excess ferrous iron present. Based on the experimental results, it is probable that oxidant:Fe²⁺ of 1:1 may be an optimal ratio for 2,4-D oxidation. Similar conclusions were arrived by Wang and Chu (2011) in their study for the oxidation of RhB in aqueous solution using Fe²⁺ and PMS.

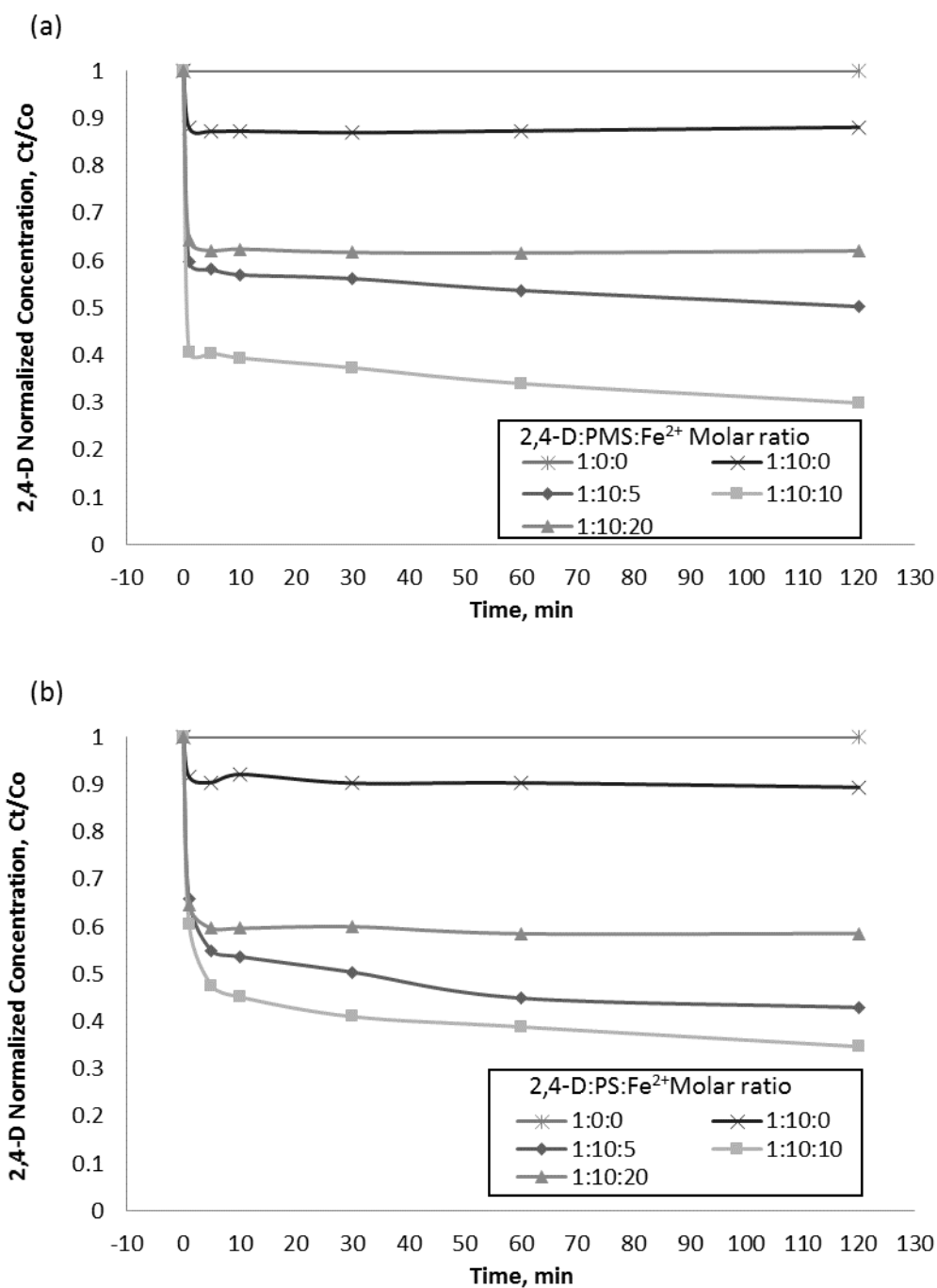


Figure 3.2 Effect of Fe²⁺ concentration on 2,4-D oxidation (a) PMS = 0.45 mM and (b) Persulfate = 0.45 mM. (2,4-D = 0.045 mM; Fe²⁺ = 0, 0.225, 0.45, 0.9 mM)

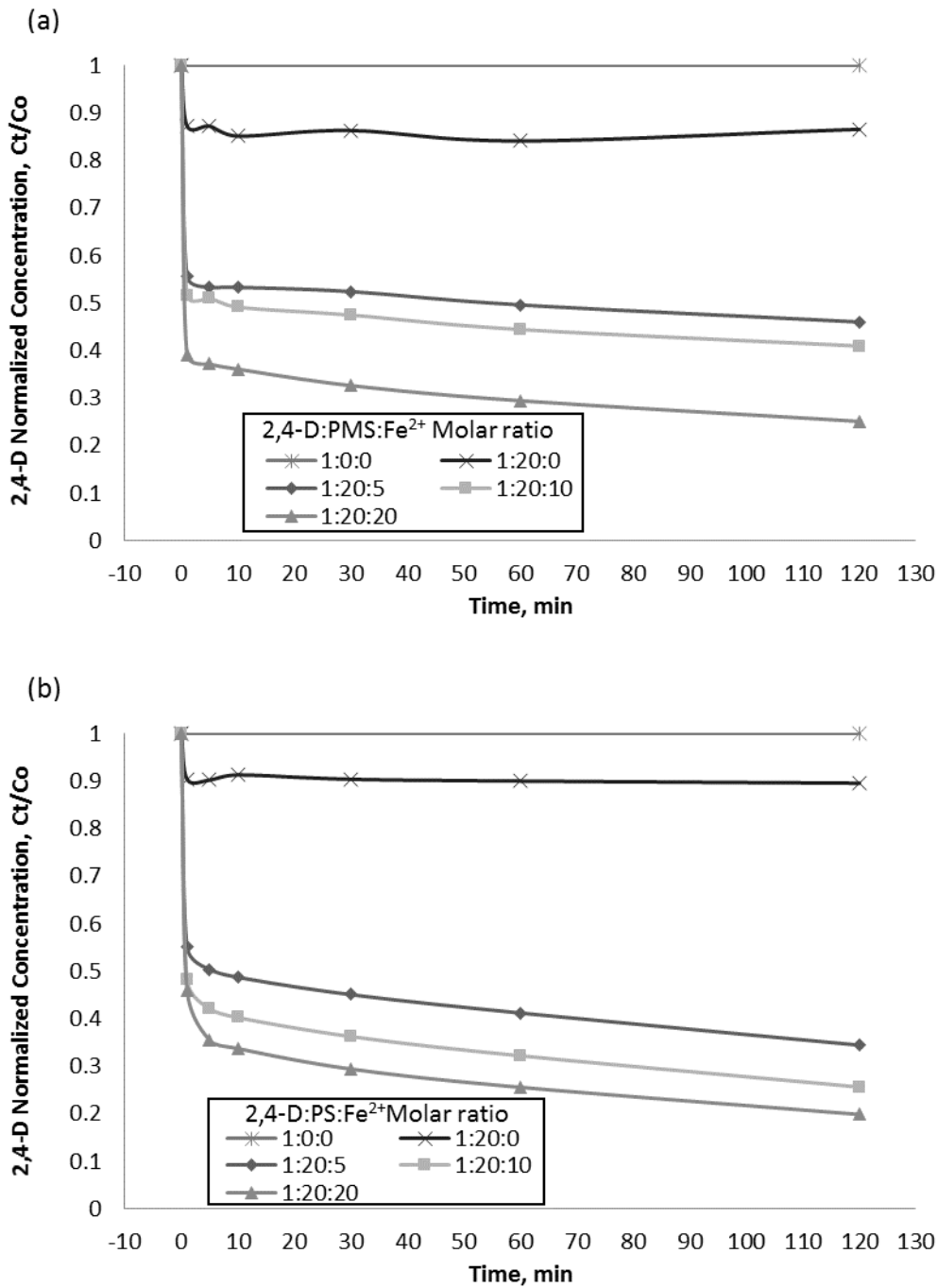


Figure 3.3 Effect of Fe^{2+} concentration on 2,4-D oxidation . (a) PMS = 0.9 mM and (b) Persulfate = 0.9 mM (2,4-D = 0.045 mM; Fe^{2+} = 0, 0.225, 0.45, 0.9 mM).

The percent removals of 2,4-D after 2 hours for the above experiments are summarized in Table 3.2 along with the initial and final pH of the aqueous solutions. In all experiments, persulfate gave slightly better results than PMS as shown by the percent removals for the same molar ratios. The highest percent removals were 75% and 80% for persulfate and PMS, respectively for a 2,4-D: oxidant: Fe^{2+} of 1:20:20. The initial pH of the solutions were between 3.2 and 3.6 with a slightly lower final pH of the solution after the oxidation reaction.

Table 3.2 2,4-D removal and initial and final pH after 2 hours.

2,4-D:PMS: Fe^{2+}				2,4-D:PS: Fe^{2+}			
Molar ratio	Removal	Start pH	Final pH	Molar ratio	Removal	Start pH	Final pH
1:05:00	10%	3.4	3.4	1:05:00	9%	3.6	3.6
1:05:05	51%	3.4	3.2	1:05:05	52%	3.5	3.3
1:05:10	44%	3.4	3.3	1:05:10	48%	3.5	3.3
1:05:20	29%	3.4	3.3	1:05:20	30%	3.5	3.4
1:10:00	12%	3.3	3.4	1:10:00	11%	3.5	3.5
1:10:05	50%	3.2	3.1	1:10:05	57%	3.2	3.2
1:10:10	70%	3.2	3.0	1:10:10	65%	3.2	3.0
1:10:20	38%	3.2	2.9	1:10:20	41%	3.2	2.9
1:20:00	13%	3.2	3.4	1:20:00	10%	3.3	3.3
1:20:05	54%	3.3	3.1	1:20:05	66%	3.4	3.1
1:20:10	51%	3.3	3.0	1:20:10	74%	3.4	3.1
1:20:20	75%	3.3	2.9	1:20:20	80%	3.4	3.0

3.3.2. Effects of sequential addition of Fe^{2+} on the degradation of 2,4-D

As indicated earlier, the sharp reduction of 2,4-D followed by a constant concentration may be due to insufficient amount of oxidant added or too much iron had been added which in turn may have quenched the sulfate free radicals formed. Figures 3.1 to 3.3 showed that higher concentrations of persulfate or PMS resulted in higher removal of 2,4-D. However, the

asymptotic behavior or plateauing was seen for all experiments even for the highest concentrations of persulfate and PMS used. A possible reason for the plateauing of the oxidation may be due to the destruction of persulfate or PMS in the presence of excess Fe^{2+} . Another possible reason may be the rapid conversion of Fe^{2+} to Fe^{3+} which results in the termination of the activation process due to a lack of Fe^{2+} (as per eq. 4 and 5).

An experiment with sequential addition of Fe^{2+} after the initial addition PMS was conducted. 0.45 mL of 0.45 mM of PMS was added to a 0.045 mM solution of 2,4-D followed by the addition of 0.45 mL of 0.225 mM of Fe^{2+} each at time 0 min and then at 30 min, 60 min, and 90 min. The final solution had a 2,4-D:PMS: Fe^{2+} ratio of 1:10:20.

Results of this experiment as shown in Figure 3.4 indicate that subsequent addition of Fe^{2+} resulted in further degradation of 2,4-D. The first addition of Fe^{2+} resulted in 44 percent removal of 2,4-D which was the same as in the experiment with a molar ratio of 2,4-D:PMS: Fe^{2+} of 1:10:5. The second addition of Fe^{2+} at 30 minutes resulted in an overall percent removal of 72 percent of removal after 60 mins. The third addition of Fe^{2+} at 60 minutes resulted in a further 8 percent removal of 2,4-D after 90 min. The final addition of Fe^{2+} resulted in negligible percent removal of 2,4-D. After the second addition of Fe^{2+} , the amount of Fe^{2+} added would be equal to the molar concentration of PMS. Theoretically from eqn. 5, one molar of Fe^{2+} would react with one molar of PMS. Therefore as seen in Figure 3.4, subsequent addition of Fe^{2+} after the second did not gain any 2,4-D removal which would indicate that the PMS may be completely consumed by Fe^{2+} . The percent removal for this experiment was close to 80% as compared to 40% when all the Fe^{2+} was added all at once – showing an increase in oxidation performance. The results implied that Fe^{2+} was converted to Fe^{3+} very rapidly before it can fully activate all the

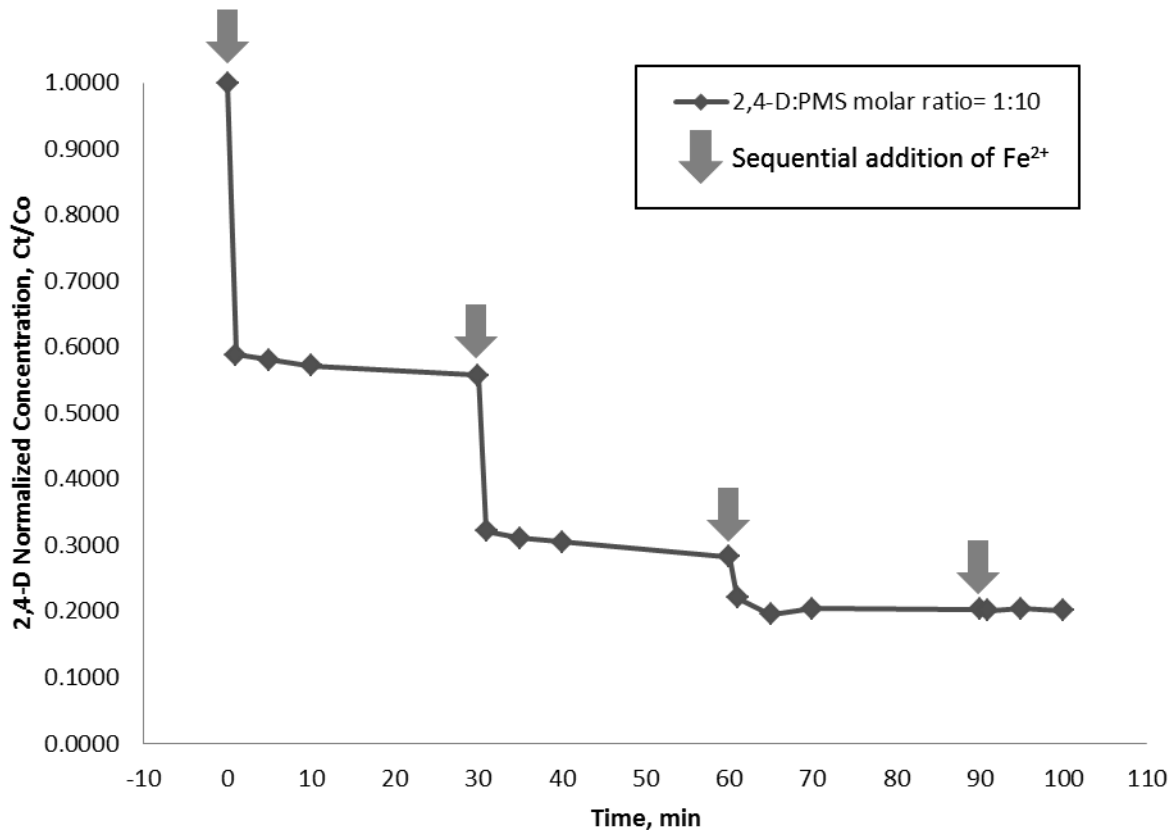


Figure 3.4 Sequential addition of Fe²⁺ solution at 0, 30, 60, and 90 min. (2,4-D = 0.045 mM; Fe²⁺ = 0.225 mM; PMS = 0.45 mM).

PMS present in solution. PMS remaining was then activated with the subsequent addition of Fe²⁺. In addition, the initial clear solution turned to a light yellow color during the reaction processes indicating that the Fe²⁺ was converted to Fe³⁺. Liang et al. (2004a) tried pulse addition and gradual addition of Fe²⁺ to activate persulfate for degradation of TCE and found that gradual addition of Fe²⁺ gave better TCE removals than pulse addition. Killian et al. (2007) found that sequential addition of Fe²⁺ to persulfate for the degradation of BTEX and PAHs in soil gave slightly better results. Therefore, sequential addition of Fe²⁺ seemed to be the appropriate approach to activate persulfate and PMS to obtain higher removal efficiency as compared to adding the Fe²⁺ all at once.

3.3.4. Oxidation kinetics

The kinetics of the experiments were modeled using three models: (a) first order model, (b) bi-exponential first-order model and (c) availability-adjusted first-order model.

The first-order model can be expressed as:

$$dC / dt = -k \cdot C \text{ or } C(t) = C_0 \exp(-k \cdot t) \quad (\text{eq. 6})$$

where C_0 is the initial concentration, t is the reaction time, and k is the rate constant. This simple model assumes that the change in chemical concentration over time $[dC/dt]$ is related to its concentration with a constant at the certain time.

The second model used was the bi-exponential first-order model. This model assumes two completely separate pools of 2,4-D with independent decay rates of k_1 and k_2 . The equation is expressed as:

$$C(t) = C_1(t) + C_2(t) = C_{01} \exp(-k_1 \cdot t) + C_{02} \exp(-k_2 \cdot t) \quad (\text{eq. 7})$$

where C_{01} and C_{02} represent the concentrations initially distributed between the two pools. In the context of this study, this model assumes that the two pools of 2,4-D has different levels of degradability (Krogh et al., 2009). The pool with the lower level of degradability may be viewed as the lesser activation activity of the ferric ion (from the oxidation of ferrous ion) in the activation of the peroxymonosulfate and persulfate (Anipsitakis et al., 2004a and Rastogi et al., 2009).

The third model used is the availability-adjusted first-order model. This model has been applied for the degradation of pesticides and organic contaminants in soils (Wang et al., 2006b, Wang and Yates, 2008; Krogh et al., 2009). The equation can expressed as:

$$dC / dt = -k'' C \exp(-at) \text{ or } C(t) = C_0 \exp(-(k''(1-\exp(-at))/a)) \quad (\text{eq. 8})$$

where $C(t)$ is the concentration of the 2,4-D (mg/L) at time t (min); C_0 is the initial concentration of 2,4-D (mg/L); k'' is the availability adjusted rate constant and α is a first order coefficient describing change in the available fraction. k'' can be viewed as equal to $k\lambda_0$ where k is the first-order rate constant and λ_0 is the proportion of the compound available in the solution at time 0. α is a positive constant and is identified as the availability coefficient.

Table 3.3 showed the first order reaction rate constants for different molar concentration. R^2 values for all experimental runs were less than 30% for PMS and less than 52% for persulfate. This indicates that the reaction is not a simple oxidation reaction kinetic and cannot be modeled using a first-order model. Liang et al. (2003, 2008c) found that under certain conditions, they were able to fit the oxidations of the TCE using first-order reaction.

Table 3.3 Effect of different molar ratios (2,4-D:PMS:Fe²⁺) and first order reaction rate constant for 2,4-D degradation.

2,4-D:PMS:Fe ²⁺ Molar ratio	first order reaction rate constant for 2,4- D degradation $\times 10^{-3}$, k,(min ⁻¹)	R ²	2,4-D:PS:Fe ²⁺ Molar ratio	first order reaction rate constant for 2,4- D degradation $\times 10^{-3}$, k,(min ⁻¹)	R ²
1:5:0	0.2	0.02	1:5:0	0.2	0.03
1:5:5	3	0.26	1:5:5	4	0.40
1:5:10	2	0.14	1:5:10	3	0.25
1:5:20	1	0.12	1:5:20	1	0.13
1:10:0	0.3	0.08	1:10:0	0.4	0.25
1:10:5	3	0.29	1:10:5	4	0.46
1:10:10	5	0.33	1:10:10	5	0.45
1:10:20	1	0.13	1:10:20	2	0.17
1:20:0	0.5	0.13	1:20:0	0.4	0.18
1:20:5	3	0.29	1:20:5	5	0.50
1:20:10	4	0.32	1:20:10	7	0.51
1:20:20	6	0.38	1:20:20	9	0.53

Table 3.4 Bi-exponential first-order model and availability-adjusted first-order model for PMS oxidation

Molar ratio of 2,4-D:PMS:Fe ²⁺	Bi-exponential first-order (BFO) model					Availability-adjusted first-order (AAFO) model		
	C ₀₁	k ₁	C ₀₂	k ₂	R ²	k''	a	R ²
1:5:0	6.87±0.08	0.0002±0.0002	0.91±0.152	9.91±1.00	0.91	2.42±0.11	17.35±0.00	0.93
1:5:5	4.43±0.02	0.0011±0.0002	3.47±0.030	3.62±0.31	1.00	1.40±0.41	2.23±0.68	0.98
1:5:10	4.47±0.03	0.0002±0.0001	3.43±0.059	3.19±0.41	1.00	1.57±0.17	2.72±0.30	1.00
1:5:20	5.61±0.02	0.00002±0.00005	2.30±0.033	3.67±0.56	1.00	1.17±0.13	3.41±0.37	1.00
1:10:0	6.77±0.01	0.0001±0.00001	1.01±0.023	2.61±0.30	1.00	0.46±0.10	3.06±0.67	1.00
1:10:5	4.58±0.02	0.0012±0.0001	3.31±0.036	3.20±0.26	1.00	1.19±0.36	1.99±0.62	0.98
1:10:10	3.21±0.03	0.0026±0.0002	4.70±0.046	6.01±3.98	1.00	2.22±0.89	2.19±0.91	0.98
1:10:20	4.903±0.02	0.00003±0.00006	3.00±0.034	2.79±0.18	1.00	1.21±0.06	2.53±0.13	1.00
1:20:0	6.69±0.07	0.00001±0.00018	1.10±0.134	2.33±1.22	0.96	0.39±0.14	2.33±0.84	0.97
1:20:5	4.26±0.02	0.0013±0.0001	3.63±0.035	3.27±0.25	1.00	1.36±0.40	2.02±0.62	0.98
1:20:10	3.99±0.05	0.0019±0.0002	3.91±0.081	3.77±0.89	1.00	1.54±0.55	2.02±0.75	0.97
1:20:20	2.94±0.05	0.0035±0.0003	4.97±0.079	3.39±0.46	1.00	1.98±0.67	1.74±0.62	0.98

Table 3.5 Bi-exponential first-order model and availability-adjusted first-order model for persulfate oxidation.

Molar ratio of 2,4-D:PS:Fe ²⁺	Bi-exponential first-order (BFO) model					Availability-adjusted first-order (AAFO) model		
	C ₀₁	k ₁	C ₀₂	k ₂	R ²	k''	a	R ²
1:5:0	6.99±0.07	0.0001±0.0002	0.80±0.12	19.93±1.00	0.95	1.40±0.10	11.33±0.00	0.95
1:5:5	4.49±0.08	0.0016±0.0003	3.40±0.15	1.38±0.16	1.00	0.59±0.14	0.93±0.23	0.97
1:5:10	4.30±0.09	0.0005±0.0004	3.60±0.17	1.33±0.17	1.00	0.65±0.07	1.03±0.12	0.99
1:5:20	5.52±0.04	0.00001±0.00011	2.38±0.073	2.41±0.33	1.00	0.81±0.08	2.25±0.24	1.00
1:10:0	7.10±0.04	0.0002±0.00001	0.69±0.07	3.03±2.17	0.98	0.26±0.10	2.26±0.87	0.96
1:10:5	4.29±0.10	0.0023±0.0004	3.60±0.18	1.37±0.19	1.00	0.61±0.17	0.86±0.25	0.95
1:10:10	3.67±0.09	0.0026±0.0005	4.24±0.16	1.32±0.13	1.00	0.71±0.16	0.80±0.20	0.97
1:10:20	4.72±0.02	0.0002±0.0001	3.180±0.05	2.11±0.11	1.00	0.94±0.06	1.19±0.28	1.00
1:20:0	7.05±0.02	0.0001±0.0001	0.73±0.05	6.22±0.00	0.99	0.57±0.89	4.86±7.64	0.99
1:20:5	3.98±0.04	0.0033±0.0002	3.91±0.06	2.35±0.16	1.00	1.05±0.38	1.28±0.49	0.94
1:20:10	3.33±0.04	0.0043±0.0003	4.57±0.07	2.24±0.15	1.00	1.25±0.41	1.19±0.42	0.95
1:20:20	2.80±0.05	0.0051±0.0004	5.10±0.09	1.80±0.100	1.00	1.19±0.32	0.96±0.28	0.96

Modelling results for Model 2 and Model 3 are presented in Table 3.4 and Table 3.5. The tables provide the R^2 values along with the best fitted model parameters using Microsoft Excel-Solver and JMP-nonlinear modeling software. The Solver uses a Generalized Reduced Gradient (GRG2) nonlinear optimization code and returns the best-fit parameters by minimizing the sum of square of the residuals between measured and fitted values. All optimized model parameters were obtained using the Solver for consistency. The initial C_0 was the measured initial concentration. From Tables 3.4 and 3.5, the model with the best fit of the experimental data was Model 2, bi-exponential first-order model, with R^2 equal to 0.99. The modeling results for bi-exponential first-order model implied that Fe^{2+} -based persulfate and peroxymonosulfate oxidation was a bi-modal reaction where Fe^{2+} was rapidly exhausted in initial part of reaction with persulfate or peroxymonosulfate remaining in solution (Figure 3.4). It is probable that the Fe^{3+} from the oxidation of Fe^{2+} may contribute towards the slow degradation found in the second phase of the reaction.

3.3.5. Effect of chloride on degradation of 2,4-D

The presence inorganic ions, such as chloride and bicarbonate in most waters (groundwater, drinking water or industrial wastewaters) may have an effect on the oxidation reactions of Fe^{2+} -activated persulfate and PMS reactions. Sulfate free radicals formed may be scavenged by inorganic ions (Park 2010).

Figure 3.5 provides the results of a study with and without chloride present in the water. The chloride experiment has a concentration of 7.04 mM (250 mg/L) which is close to the normal maximum level in groundwater. In the case of persulfate, the effect of chloride on the

degradation of 2,4-D was insignificant. However, for PMS, degradation of 2,4-D was found to be lower (about 15%) in the presence of chloride.

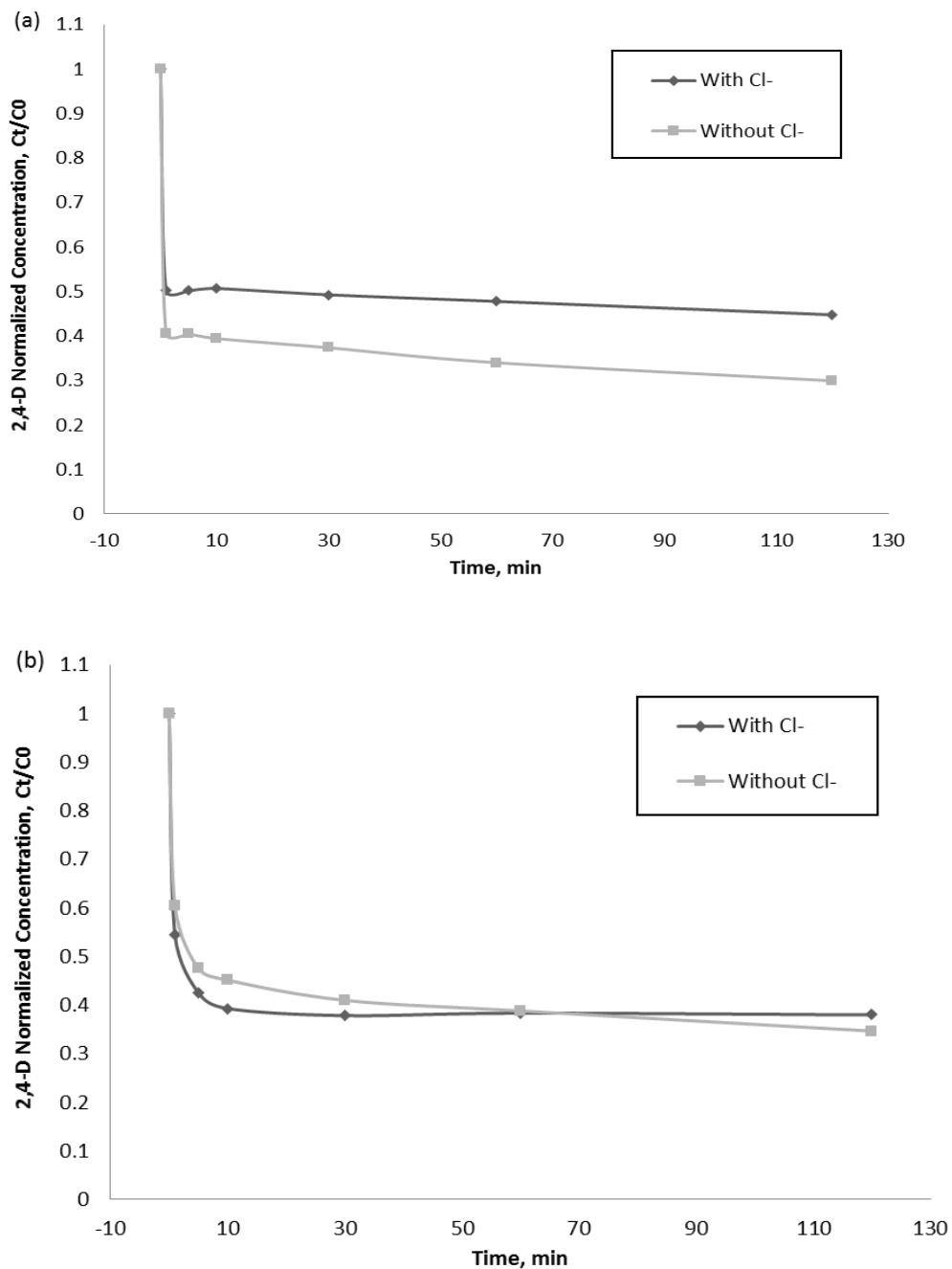


Figure 3.5. Effect of the chloride ion on the degradation of 2,4-D(a) PMS = 0.45 mM and (b) Persulfate = 0.45 mM. (Concentrations: 2,4-D = 0.045 mM; Fe^{2+} = 0.45 mM; Cl^- = 7.04 mM;

Chloride ion (Cl^-) may have reacted with the sulfate free radicals as shown by the reaction below (Huie 1991):



The above reaction shows that Cl^- acts as a scavenger of sulfate free radicals (Liang et al., 2006). Huie (1991) stated that chloride radicals can react with chloride ions and chlorine will be formed when excess chloride ions are present. Liang et. (2006) found that the oxidation of TCE at chloride concentration ranging from 0 to 0.2 mM showed no significant effect, which is due to the $\text{SO}_4^{\cdot-}$ generated at relatively slow rate at a low activation temperature (i.e., 20°C). In this study, the use of molar ratio of 2,4-D:oxidants: Fe^{2+} of 1:10:10 showed about 5% more removal of 2,4-D by PMS oxidation than persulfate oxidation, which indicate that more sulfate radicals were generated in PMS oxidation. From the Figure 3.5, the sharper decline for PMS oxidation than persulfate oxidation may imply that faster generation of sulfate radicals in PMS oxidation than persulfate oxidation.

3.4. Conclusions

In this study, generation of sulfate radicals with the use of Fe^{2+} and iron activated persulfate and peroxymonosulfate was investigated. Ferrous iron was found to activate persulfate and peroxymonosulfate for oxidation of 2,4-D in an aqueous solution. The study shows that a PMS/ Fe^{2+} or persulfate: Fe^{2+} molar concentration ratio of 1:1 of oxidants: Fe^{2+} was the optimal ratio for the oxidation of 2,4-D. Both PMS and persulfate gave similar results in the oxidation of 2,4-D with persulfate having a slightly better percent removal of 2,4-D. Addition of Fe^{2+} at the start of the oxidation process gave a lower percent removal of 2,4-D as compared to sequential addition of Fe^{2+} . Fe^{2+} was assumed to be oxidized rapidly to

Fe^{3+} in comparison to the sulfate free radical generation from persulfate or peroxymonosulfate. Chloride ion was found to affect the oxidation of PMS more than persulfate oxidation. The bi-exponential first order model was found to fit well the two phase experimental data of the Fe^{2+} activated persulfate and PMS oxidation reactions.

3.5. Reference

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CHAPTER 4

CONCLUSIONS

Aqueous phase experiments using ferrous ion activator were designed to investigate the influence of ferrous ion content and persulfate content on degrading 2,4-D. With no direct measurements of Fe^{2+} and SO_4^{2-} available, conclusions are drawn on theoretical considerations and observed organic contaminant destruction.

This study demonstrates the importance of maintaining appropriate Fe^{2+} levels to activate the production of sulfate free radicals for the destruction of target organic compounds (e.g., 2,4-D). Organic contaminant destruction efficiency can be improved by either sequentially adding controlled amounts of Fe^{2+} .

Also, the common first order kinetic is not available for persulfate and PMS oxidation. There are two novel kinetic models, named bi-exponential first-order model and availability-adjusted first-order model, were investigated in this study, which could be used in future research to estimate the decomposition of oxidants.

APPENDIX A

CONCENTRATION OF 2,4-D AND PH WITH DIFFERENT MOLAR RATIO OF 2,4-

D:OXIDANTS:FE²⁺

2,4-D:PMS:Fe ²⁺	2,4-D Conc., mg/L	C _t /C ₀	Reaction Time, min	pH
1:5:0	7.78	1.00	0	4.3
	6.65	0.85	1	3.4
	6.96	0.89	5	N/A
	6.86	0.88	10	N/A
	6.89	0.89	30	N/A
	6.91	0.89	60	N/A
	6.97	0.90	120	3.4
1:5:5	7.89	1.00	0	4.3
	4.52	0.57	1	3.4
	4.41	0.56	5	N/A
	4.40	0.56	10	N/A
	4.25	0.54	30	N/A
	4.16	0.53	60	N/A
	3.90	0.49	120	3.2
1:5:10	7.90	1.00	0	4.3
	4.61	0.58	1	3.4
	4.51	0.57	5	N/A
	4.48	0.57	10	N/A
	4.41	0.56	30	N/A
	4.38	0.55	60	N/A
	4.42	0.56	120	3.3
1:5:20	7.90	1.00	0	4.3
	5.67	0.72	1	3.4
	5.58	0.71	5	N/A
	5.60	0.71	10	N/A
	5.63	0.71	30	N/A
	5.62	0.71	60	N/A
	5.58	0.71	120	3.3
2,4-D:PMS:Fe ²⁺	2,4-D Conc., mg/L	C _t /C ₀	Reaction Time, min	pH
1:10:0	7.78	1.00	0	4.3
	6.85	0.88	1	3.3
	6.79	0.87	5	N/A
	6.79	0.87	10	N/A
	6.77	0.87	30	N/A

	6.80	0.87	60	N/A
	6.86	0.88	120	3.4
1:10:5	7.89	1.00	0	4.3
	4.71	0.60	1	3.2
	4.58	0.58	5	N/A
	4.50	0.57	10	N/A
	4.43	0.56	30	N/A
	4.24	0.54	60	N/A
	3.97	0.50	120	3.1
	1:10:10	7.90	1.00	0
3.21		0.41	1	3.2
3.20		0.40	5	N/A
3.12		0.39	10	N/A
2.95		0.37	30	N/A
2.69		0.34	60	N/A
2.37		0.30	120	3
1:10:20		7.90	1.00	0
	5.09	0.64	1	3.2
	4.91	0.62	5	N/A
	4.93	0.62	10	N/A
	4.87	0.62	30	N/A
	4.87	0.62	60	N/A
	4.90	0.62	120	2.9
2,4-D:PMS:Fe ²⁺	2,4-D Conc., mg/L	C _t /C ₀	Reaction Time, min	pH
1:20:0	7.78	1.00	0	4.3
	6.79	0.87	1	3.2
	6.79	0.87	5	N/A
	6.62	0.85	10	N/A
	6.72	0.86	30	N/A
	6.54	0.84	60	N/A
	6.74	0.87	120	3.4
	1:20:5	7.89	1.00	0
4.40		0.56	1	3.3
4.21		0.53	5	N/A
4.21		0.53	10	N/A
4.14		0.52	30	N/A
3.92		0.50	60	N/A
3.63		0.46	120	3.1
1:20:10		7.90	1.00	0
	4.08	0.52	1	3.3

	4.04	0.51	5	N/A
	3.88	0.49	10	N/A
	3.75	0.47	30	N/A
	3.51	0.44	60	N/A
	3.24	0.41	120	3
1:20:20	7.90	1.00	0	4.3
	3.09	0.39	1	3.3
	2.94	0.37	5	N/A
	2.85	0.36	10	N/A
	2.58	0.33	30	N/A
	2.33	0.29	60	N/A
	1.99	0.25	120	2.9

2,4-D:PS:Fe ²⁺	2,4-D Conc., mg/L	C _t /C ₀	Reaction Time, min	pH
1:5:0	7.78	1.00	0	4.3
	6.82	0.88	1	3.6
	7.03	0.90	5	N/A
	6.99	0.90	10	N/A
	7.04	0.90	30	N/A
	6.97	0.90	60	N/A
	7.07	0.91	120	3.6
1:5:5	7.89	1.00	0	4.3
	5.33	0.68	1	3.5
	4.56	0.58	5	N/A
	4.47	0.57	10	N/A
	4.12	0.52	30	N/A
	4.02	0.51	60	N/A
	3.77	0.48	120	3.3
1:5:10	7.90	1.00	0	4.3
	5.25	0.66	1	3.5
	4.45	0.56	5	N/A
	4.28	0.54	10	N/A
	4.08	0.52	30	N/A
	4.12	0.52	60	N/A
	4.11	0.52	120	3.3
1:5:20	7.90	1.00	0	4.3
	5.74	0.73	1	3.5
	5.58	0.71	5	N/A
	5.54	0.70	10	N/A
	5.44	0.69	30	N/A

	5.51	0.70	60	N/A
	5.55	0.70	120	3.3

2,4-D:PS:Fe ²⁺	2,4-D Conc., mg/L	C _t /C ₀	Reaction Time, min	pH
1:10:0	7.78	1.00	0	4.3
	7.13	0.92	1	3.5
	7.04	0.90	5	N/A
	7.17	0.92	10	N/A
	7.02	0.90	30	N/A
	7.03	0.90	60	N/A
	6.96	0.89	120	3.5
1:10:5	7.89	1.00	0	4.3
	5.19	0.66	1	3.2
	4.33	0.55	5	N/A
	4.24	0.54	10	N/A
	3.98	0.50	30	N/A
	3.54	0.45	60	N/A
	3.39	0.43	120	3.2
1:10:10	7.90	1.00	0	4.3
	4.78	0.61	1	3.2
	3.76	0.48	5	N/A
	3.57	0.45	10	N/A
	3.24	0.41	30	N/A
	3.07	0.39	60	N/A
	2.74	0.35	120	3
1:10:20	7.90	1.00	0	4.3
	5.11	0.65	1	3.2
	4.71	0.60	5	N/A
	4.71	0.60	10	N/A
	4.74	0.60	30	N/A
	4.62	0.58	60	N/A
	4.63	0.59	120	2.9

2,4-D:PS:Fe ²⁺	2,4-D Conc., mg/L	C _t /C ₀	Reaction Time, min	pH
1:20:0	7.78	1.00	0	4.3
	7.03	0.90	1	3.3
	7.02	0.90	5	N/A
	7.10	0.91	10	N/A
	7.03	0.90	30	N/A
	7.00	0.90	60	N/A
	6.97	0.90	120	3.3

1:20:5	7.89	1.00	0	4.3
	4.34	0.55	1	3.4
	3.98	0.50	5	N/A
	3.84	0.49	10	N/A
	3.56	0.45	30	N/A
	3.25	0.41	60	N/A
	2.72	0.34	120	3.1
1:20:10	7.90	1.00	0	4.3
	3.80	0.48	1	3.4
	3.33	0.42	5	N/A
	3.18	0.40	10	N/A
	2.86	0.36	30	N/A
	2.55	0.32	60	N/A
	2.03	0.26	120	3.1
1:20:20	7.90	1.00	0	4.3
	3.63	0.46	1	3.4
	2.80	0.35	5	N/A
	2.67	0.34	10	N/A
	2.33	0.29	30	N/A
	2.02	0.26	60	N/A
	1.57	0.20	120	3

APPENDIX B

CONCENTRATION OF 2,4-D WITH SEQUENTIAL ADDITION OF Fe^{2+}

2,4-D:PMS: Fe^{2+}	2,4-D Conc., mg/L	C_t/C_0	Reaction Time, min
1:10:5	7.91	1.00	0
	4.65	0.59	1
	4.60	0.58	5
	4.53	0.57	10
	4.41	0.56	30
1:10:10	2.55	0.32	31
	2.46	0.31	35
	2.41	0.30	40
	2.23	0.28	60
1:10:15	1.74	0.22	61
	1.54	0.19	65
	1.61	0.20	70
	1.61	0.20	90
1:10:20	1.59	0.20	91
	1.61	0.20	95
	1.59	0.20	100

APPENDIX C

OXIDATION KINETICS - BFO MODEL

2,4-D:PMS:Fe ²⁺	Ct, mg/L	Time, min	Estimate Ct	χ^2						
1:5:5	7.89	0	7.89	9.52E-11		C1	4.427		SST	11.48
	4.52	1	4.52	3.44E-09		k1	0.001		SSE	0.00
	4.41	5	4.40	1.72E-05		C2	3.465		SSR	11.48
	4.40	10	4.38	3.87E-04		k2	3.616			
	4.25	30	4.29	1.25E-03					R squared	1.00
	4.16	60	4.15	7.04E-05		$\Sigma\chi^2$	0.002			
	3.90	120	3.89	9.89E-06					StDev	0.02
1:10:5	7.89	0	7.89	4.76E-12		C1	4.581		SST	10.78
	4.71	1	4.71	5.63E-12		k1	0.001		SSE	0.00
	4.58	5	4.55	8.70E-04		C2	3.310		SSR	10.78
	4.50	10	4.53	9.45E-04		k2	3.199			
	4.43	30	4.42	2.06E-04					R squared	1.00
	4.24	60	4.26	5.22E-04		$\Sigma\chi^2$	0.003			
	3.97	120	3.96	9.59E-05					StDev	0.02
1:20:5	7.89	0	7.89	8.23E-12		C1	4.262		SST	12.80
	4.40	1	4.40	2.71E-11		k1	0.001		SSE	0.00
	4.21	5	4.23	5.14E-04		C2	3.629		SSR	12.79
	4.21	10	4.21	2.18E-06		k2	3.266			
	4.14	30	4.10	1.62E-03					R squared	1.00
	3.92	60	3.93	3.59E-04		$\Sigma\chi^2$	0.002			
	3.63	120	3.63	1.43E-					StDev	0.02

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2,4-D:PMS:Fe ²⁺	Ct, mg/L	Time, min	Estimate Ct	χ^2					
1:5:10	7.90	0	7.90	1.28E-11	C1	4.470		SST	10.16
	4.61	1	4.61	3.03E-11	k1	0.000		SSE	0.01
	4.51	5	4.47	2.00E-03	C2	3.434		SSR	10.15
	4.48	10	4.46	1.51E-04	k2	3.187			
	4.41	30	4.45	1.41E-03				R squared	1.00
	4.38	60	4.43	2.76E-03	$\Sigma\chi^2$	0.007			
	4.42	120	4.39	1.10E-03				StDev	0.03
1:10:10	7.90	0	7.90	1.37E-08	C1	3.205		SST	21.83
	3.21	1	3.21	5.30E-08	k1	0.003		SSE	0.00
	3.20	5	3.16	1.11E-03	C2	4.698		SSR	21.83
	3.12	10	3.12	2.68E-05	k2	5.968			
	2.95	30	2.96	7.60E-05				R squared	1.00
	2.69	60	2.74	2.24E-03	$\Sigma\chi^2$	0.004			
	2.37	120	2.34	8.56E-04				StDev	0.02
1:20:10	7.90	0	7.90	1.58E-11	C1	3.992		SST	15.32
	4.08	1	4.08	1.13E-11	k1	0.002		SSE	0.01
	4.04	5	3.96	6.41E-03	C2	3.911		SSR	15.30
	3.88	10	3.92	1.25E-03	k2	3.765			
	3.75	30	3.78	6.02E-04				R squared	1.00
	3.51	60	3.57	3.60E-03	$\Sigma\chi^2$	0.013			
	3.24	120	3.20	1.62E-03				StDev	0.04

2,4-D:PMS:Fe ²⁺	Ct, mg/L	Time, min	Estimate Ct	χ^2						
1:5:20	7.90	0	7.90	1.37E-06		C1	5.610		SST	4.50
	5.67	1	5.67	9.56E-08		k1	0.000		SSE	0.00
	5.58	5	5.61	9.76E-04		C2	2.295		SSR	4.50
	5.60	10	5.61	4.28E-05		k2	3.706			
	5.63	30	5.61	8.04E-04					R squared	1.00
	5.62	60	5.60	2.81E-04		$\Sigma\chi^2$	0.002			
	5.58	120	5.59	2.08E-04					StDev	0.02
1:10:20	7.90	0	7.90	1.25E-11		C1	4.903		SST	7.62
	5.09	1	5.09	7.83E-14		k1	0.000		SSE	0.00
	4.91	5	4.90	2.23E-05		C2	3.001		SSR	7.62
	4.93	10	4.90	8.65E-04		k2	2.792			
	4.87	30	4.90	5.61E-04					R squared	1.00
	4.87	60	4.89	7.53E-04		$\Sigma\chi^2$	0.002			
	4.90	120	4.89	2.90E-04					StDev	0.02
1:20:20	7.90	0	7.90	6.17E-12		C1	2.935		SST	24.70
	3.09	1	3.09	2.19E-13		k1	0.003		SSE	0.01
	2.94	5	2.88	2.74E-03		C2	4.969		SSR	24.69
	2.85	10	2.83	3.23E-04		k2	3.388			
	2.58	30	2.65	4.07E-03					R squared	1.00
	2.33	60	2.38	2.95E-03		$\Sigma\chi^2$	0.013			
	1.99	120	1.94	2.48E-03					StDev	0.04

2,4-D:PMS:Fe ²⁺	Ct, mg/L	Time, min	Estimate Ct	χ^2					
1:5:0	7.78	0	7.78	6.85E-08	C1	6.873		SST	0.78
	6.65	1	6.87	4.87E-02	k1	0.000		SSE	0.07
	6.96	5	6.87	8.30E-03	C2	0.910		SSR	0.71
	6.86	10	6.87	2.81E-04	k2	9.915			
	6.89	30	6.87	2.31E-04				R squared	0.91
	6.91	60	6.87	1.24E-03	$\Sigma\chi^2$	0.068			
	6.97	120	6.87	9.05E-03				StDev	0.10
1:10:0	7.78	0	7.78	2.98E-11	C1	6.801		SST	0.82
	6.85	1	6.85	1.73E-10	k1	0.000		SSE	0.00
	6.79	5	6.80	1.44E-04	C2	0.983		SSR	0.82
	6.79	10	6.80	6.38E-05	k2	3.021			
	6.77	30	6.80	1.02E-03				R squared	0.99
	6.80	60	6.80	1.59E-05	$\Sigma\chi^2$	0.004			
	6.86	120	6.80	3.13E-03				StDev	0.02
1:20:0	7.78	0	7.78	1.68E-08	C1	6.686		SST	1.05
	6.79	1	6.79	1.69E-08	k1	0.000		SSE	0.04
	6.79	5	6.69	1.06E-02	C2	1.098		SSR	1.02
	6.62	10	6.69	3.64E-03	k2	2.329			
	6.72	30	6.68	1.10E-03				R squared	0.96
	6.54	60	6.68	1.85E-02	$\Sigma\chi^2$	0.038			
	6.74	120	6.68	3.67E-03				StDev	0.07

2,4-D:PS:Fe ²⁺	Ct, mg/L	Time, min	Estimate Ct	χ^2						
1:5:5	7.89	0	7.89	3.58E-12		C1	4.762		SST	12.09
	5.33	1	4.75	3.40E-01		k1	0.002		SSE	0.54
	4.56	5	4.71	2.30E-02		C2	3.129		SSR	11.55
	4.47	10	4.65	3.39E-02		k2	19.835			
	4.12	30	4.44	9.82E-02					R squared	0.96
	4.02	60	4.13	1.30E-02		$\Sigma\chi^2$	0.542			
	3.77	120	3.59	3.39E-02					StDev	0.28
1:10:5	7.89	0	7.89	9.39E-10		C1	4.592		SST	14.35
	5.19	1	4.58	3.80E-01		k1	0.003		SSE	0.63
	4.33	5	4.52	3.57E-02		C2	3.299		SSR	13.72
	4.24	10	4.45	4.57E-02		k2	19.816			
	3.98	30	4.18	4.01E-02					R squared	0.96
	3.54	60	3.80	6.41E-02		$\Sigma\chi^2$	0.627			
	3.39	120	3.14	6.17E-02					StDev	0.30
1:20:5	7.89	0	7.89	5.30E-14		C1	4.107		SST	17.33
	4.34	1	4.09	6.34E-02		k1	0.004		SSE	0.10
	3.98	5	4.03	3.11E-03		C2	3.785		SSR	17.23
	3.84	10	3.96	1.30E-02		k2	19.783			
	3.56	30	3.68	1.44E-02					R squared	0.99
	3.25	60	3.29	1.46E-03		$\Sigma\chi^2$	0.102			
	2.72	120	2.64	6.43E-03					StDev	0.12

2,4-D:PS:Fe ²⁺	Ct, mg/L	Time, min	Estimate Ct	χ^2					
1:5:10	7.90	0	7.90	1.44E-09	C1	4.597		SST	11.65
	5.25	1	4.59	4.35E-01	k1	0.001		SSE	0.69
	4.45	5	4.57	1.34E-02	C2	3.306		SSR	10.96
	4.28	10	4.54	6.82E-02	k2	19.827			
	4.08	30	4.42	1.17E-01				R squared	0.94
	4.12	60	4.25	1.69E-02	$\Sigma\chi^2$	0.687			
	4.11	120	3.92	3.64E-02				StDev	0.31
1:10:10	7.90	0	7.90	4.10E-09	C1	4.044		SST	18.96
	4.78	1	4.03	5.70E-01	k1	0.004		SSE	0.90
	3.76	5	3.96	4.17E-02	C2	3.859		SSR	18.06
	3.57	10	3.89	1.01E-01	k2	19.774			
	3.24	30	3.59	1.20E-01				R squared	0.95
	3.07	60	3.18	1.25E-02	$\Sigma\chi^2$	0.902			
	2.74	120	2.50	5.74E-02				StDev	0.36
1:20:10	7.90	0	7.90	1.72E-09	C1	3.499		SST	22.91
	3.80	1	3.48	1.04E-01	k1	0.005		SSE	0.17
	3.33	5	3.41	7.10E-03	C2	4.404		SSR	22.75
	3.18	10	3.33	2.18E-02	k2	19.732			
	2.86	30	3.01	2.11E-02				R squared	0.99
	2.55	60	2.59	1.96E-03	$\Sigma\chi^2$	0.168			
	2.03	120	1.92	1.20E-02				StDev	0.15

2,4-D:PS:Fe ²⁺	Ct, mg/L	Time, min	Estimate Ct	χ^2					
1:5:20	7.90	0	7.90	2.89E-11	C1	5.587		SST	4.75
	5.74	1	5.59	2.28E-02	k1	0.000		SSE	0.04
	5.58	5	5.58	3.61E-06	C2	2.316		SSR	4.71
	5.54	10	5.58	1.80E-03	k2	19.890			
	5.44	30	5.57	1.55E-02				R squared	0.99
	5.51	60	5.55	1.01E-03	$\Sigma\chi^2$	0.044			
	5.55	120	5.50	2.44E-03				StDev	0.08
1:10:20	7.90	0	7.90	1.40E-08	C1	4.839		SST	8.67
	5.11	1	4.84	7.28E-02	k1	0.000		SSE	0.11
	4.71	5	4.83	1.36E-02	C2	3.065		SSR	8.56
	4.71	10	4.82	1.10E-02	k2	19.854			
	4.74	30	4.77	9.36E-04				R squared	0.99
	4.62	60	4.70	6.08E-03	$\Sigma\chi^2$	0.108			
	4.63	120	4.57	3.61E-03				StDev	0.12
1:20:20	7.90	0	7.90	1.95E-09	C1	3.104		SST	27.52
	3.63	1	3.08	2.97E-01	k1	0.007		SSE	0.47
	2.80	5	3.00	4.03E-02	C2	4.799		SSR	27.05
	2.67	10	2.90	5.63E-02	k2	19.692			
	2.33	30	2.54	4.48E-02				R squared	0.98
	2.02	60	2.07	2.68E-03	$\Sigma\chi^2$	0.475			
	1.57	120	1.39	3.43E-02				StDev	0.26

2,4-D:PS:Fe ²⁺	Ct, mg/L	Time, min	Estimate Ct	χ^2					
1:5:0	7.78	0	7.78	2.08E-11	C1	6.986		SST	0.59
	6.82	1	6.99	2.86E-02	k1	0.000		SSE	0.04
	7.03	5	6.99	2.17E-03	C2	0.798		SSR	0.55
	6.99	10	6.99	4.44E-05	k2	19.928			
	7.04	30	6.99	2.56E-03				R squared	0.93
	6.97	60	6.99	3.00E-04	$\Sigma\chi^2$	0.041			
	7.07	120	6.99	6.82E-03				StDev	0.08
1:10:0	7.78	0	7.78	4.69E-12	C1	7.096		SST	0.48
	7.13	1	7.13	5.88E-11	k1	0.000		SSE	0.01
	7.04	5	7.09	2.91E-03	C2	0.687		SSR	0.47
	7.17	10	7.08	7.04E-03	k2	3.031			
	7.02	30	7.06	1.30E-03				R squared	0.98
	7.03	60	7.02	1.31E-05	$\Sigma\chi^2$	0.011			
	6.96	120	6.95	6.19E-06				StDev	0.04
1:20:0	7.78	0	7.78	2.54E-06	C1	7.054		SST	0.50
	7.03	1	7.05	5.10E-04	k1	0.000		SSE	0.00
	7.02	5	7.05	9.16E-04	C2	0.728		SSR	0.50
	7.10	10	7.05	3.28E-03	k2	6.224			
	7.03	30	7.03	1.40E-07				R squared	0.99
	7.00	60	7.01	4.79E-05	$\Sigma\chi^2$	0.005			
	6.97	120	6.97	5.47E-08				StDev	0.03

APPENDIX D

OXIDATION KINETICS - AAFO MODEL

2,4-D:PMS:Fe ²⁺	Ct/C0	Time, min	Estimate Ct/C0	χ^2					
1:05:05	1.00	0	1.00	0.00E+00	k	1.396		SST	0.18
	0.57	1	0.57	8.56E-10	a	2.233		SSE	0.00
	0.56	5	0.54	5.47E-04	$\Sigma\chi^2$	0.003		SSR	0.18
	0.56	10	0.54	5.01E-04					
	0.54	30	0.54	1.33E-05				R squared	0.98
	0.53	60	0.54	6.39E-05					
	0.49	120	0.54	1.71E-03				StDev	0.02
1:10:05	1.00	0	1.00	0.00E+00	k	1.190		SST	0.17
	0.60	1	0.60	2.55E-09	a	1.991		SSE	0.00
	0.58	5	0.55	9.29E-04	$\Sigma\chi^2$	0.004		SSR	0.17
	0.57	10	0.55	3.75E-04					
	0.56	30	0.55	1.27E-04				R squared	0.98
	0.54	60	0.55	1.84E-04					
	0.50	120	0.55	2.25E-03				StDev	0.02
1:20:05	1.00	0	1.00	0.00E+00	k	1.364		SST	0.21
	0.56	1	0.56	1.22E-09	a	2.023		SSE	0.00
	0.53	5	0.51	5.86E-04	$\Sigma\chi^2$	0.004		SSR	0.20
	0.53	10	0.51	5.62E-04					
	0.52	30	0.51	2.13E-04				R squared	0.98
	0.50	60	0.51	1.76E-04					
	0.46	120	0.51	2.42E-03				StDev	0.02

2,4-D:PMS:Fe ²⁺	Ct/C0	Time, min	Estimate Ct/C0	χ^2					
1:5:10	1.00	0	1.00	0.00E+00	k	1.567		SST	0.16
	0.58	1	0.58	7.67E-11	a	2.716		SSE	0.00
	0.57	5	0.56	8.48E-05	$\Sigma\chi^2$	0.000		SSR	0.16
	0.57	10	0.56	2.17E-05					
	0.56	30	0.56	1.18E-05				R squared	1.00
	0.55	60	0.56	6.37E-05					
	0.56	120	0.56	5.86E-06				StDev	0.01
1:10:10	1.00	0	1.00	0.00E+00	k	2.222		SST	0.35
	0.41	1	0.41	1.69E-09	a	2.189		SSE	0.01

	0.40	5	0.36	1.77E-03	$\Sigma\chi^2$	0.007		SSR	0.34
	0.39	10	0.36	1.02E-03					
	0.37	30	0.36	1.26E-04				R squared	0.98
	0.34	60	0.36	4.90E-04					
	0.30	120	0.36	3.98E-03				StDev	0.03
1:20:10	1.00	0	1.00	0.00E+00	k	1.542		SST	0.25
	0.52	1	0.52	5.45E-09	a	2.021		SSE	0.01
	0.51	5	0.47	1.98E-03	$\Sigma\chi^2$	0.006		SSR	0.24
	0.49	10	0.47	6.40E-04					
	0.47	30	0.47	7.42E-05				R squared	0.97
	0.44	60	0.47	4.72E-04					
	0.41	120	0.47	3.20E-03				StDev	0.03

2,4-D:PMS:Fe ²⁺	Ct/C0	Time, min	Estimate Ct/C0	χ^2					
1:5:20	1.00	0	1.00	0.00E+00	k	1.173		SST	0.07
	0.72	1	0.72	5.88E-10	a	3.409		SSE	0.00
	0.71	5	0.71	9.20E-06	$\Sigma\chi^2$	0.000		SSR	0.07
	0.71	10	0.71	2.00E-14					
	0.71	30	0.71	1.64E-05				R squared	1.00
	0.71	60	0.71	4.09E-06					
	0.71	120	0.71	9.20E-06				StDev	0.00
1:10:20	1.00	0	1.00	0.00E+00	k	1.211		SST	0.12
	0.64	1	0.64	1.80E-10	a	2.530		SSE	0.00
	0.62	5	0.62	1.74E-06	$\Sigma\chi^2$	0.000		SSR	0.12
	0.62	10	0.62	1.89E-05					
	0.62	30	0.62	7.43E-06				R squared	1.00
	0.62	60	0.62	1.40E-05					
	0.62	120	0.62	6.62E-07				StDev	0.00
1:20:20	1.00	0	1.00	0.00E+00	k	1.982		SST	0.40
	0.39	1	0.39	4.13E-08	a	1.744		SSE	0.01
	0.37	5	0.32	2.56E-03	$\Sigma\chi^2$	0.010		SSR	0.39
	0.36	10	0.32	1.60E-03					
	0.33	30	0.32	3.15E-05				R squared	0.98
	0.29	60	0.32	6.88E-04					
	0.25	120	0.32	4.86E-03				StDev	0.04

2,4-	Ct/C0	Time,	Estimate	χ^2					
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D:PMS:Fe ²⁺		min	Ct/C0						
1:5:0	1.00	0	1.00	0.00E+00	k	2.016		SST	0.02
	0.84	1	0.87	7.78E-04	a	14.432		SSE	0.00
	0.88	5	0.87	1.33E-04	$\Sigma\chi^2$	0.001		SSR	0.01
	0.87	10	0.87	4.44E-06					
	0.87	30	0.87	3.76E-06				R squared	0.93
	0.87	60	0.87	1.99E-05					
	0.88	120	0.87	1.45E-04				StDev	0.01
1:10:0	1.00	0	1.00	0.00E+00	k	0.460		SST	0.02
	0.87	1	0.87	3.74E-12	a	3.064		SSE	0.00
	0.86	5	0.86	2.31E-06	$\Sigma\chi^2$	0.000		SSR	0.02
	0.86	10	0.86	1.03E-06					
	0.86	30	0.86	1.64E-05				R squared	1.00
	0.86	60	0.86	2.60E-07					
	0.87	120	0.86	5.00E-05				StDev	0.00
1:20:0	1.00	0	1.00	0.00E+00	k	0.390		SST	0.02
	0.86	1	0.86	1.14E-10	a	2.326		SSE	0.00
	0.86	5	0.85	1.81E-04	$\Sigma\chi^2$	0.001		SSR	0.02
	0.84	10	0.85	5.29E-05					
	0.85	30	0.85	1.89E-05				R squared	0.97
	0.83	60	0.85	3.02E-04					
	0.85	120	0.85	4.73E-05				StDev	0.01

2,4-D:PS:Fe ²⁺	Ct/C0	Time, min	Estimate Ct/C0	χ^2					
1:5:5	1.00	0	1.00	0.00E+00	k	0.592		SST	0.19
	0.68	1	0.68	1.86E-05	a	0.930		SSE	0.01
	0.58	5	0.53	2.00E-03	$\Sigma\chi^2$	0.006		SSR	0.19
	0.57	10	0.53	1.35E-03					
	0.52	30	0.53	4.55E-05				R squared	0.97
	0.51	60	0.53	3.96E-04					
	0.48	120	0.53	2.63E-03				StDev	0.03
1:10:5	1.00	0	1.00	0.00E+00	k	0.608		SST	0.23
	0.66	1	0.66	4.30E-05	a	0.855		SSE	0.01
	0.55	5	0.50	2.75E-03	$\Sigma\chi^2$	0.011		SSR	0.22
	0.54	10	0.49	2.04E-03					
	0.50	30	0.49	1.51E-04				R squared	0.95

	0.45	60	0.49	1.80E-03					
	0.43	120	0.49	3.86E-03				StDev	0.04
1:20:5	1.00	0	1.00	0.00E+00	k	1.054		SST	0.28
	0.55	1	0.55	2.33E-06	a	1.281		SSE	0.02
	0.50	5	0.44	4.10E-03	$\Sigma\chi^2$	0.016		SSR	0.26
	0.49	10	0.44	2.29E-03					
	0.45	30	0.44	1.31E-04				R squared	0.94
	0.41	60	0.44	7.31E-04					
	0.34	120	0.44	9.00E-03				StDev	0.05

2,4-D:PS:Fe ²⁺	Ct/C0	Time, min	Estimate Ct/C0	χ^2					
1:5:10	1.00	0	1.00	0.00E+00	k	0.650		SST	0.19
	0.66	1	0.67	3.84E-06	a	1.028		SSE	0.00
	0.56	5	0.53	8.88E-04	$\Sigma\chi^2$	0.001		SSR	0.19
	0.54	10	0.53	9.05E-05					
	0.52	30	0.53	2.48E-04				R squared	0.99
	0.52	60	0.53	1.14E-04					
	0.52	120	0.53	1.26E-04				StDev	0.01
1:10:10	1.00	0	1.00	0.00E+00	k	0.710		SST	0.30
	0.61	1	0.61	6.64E-05	a	0.801		SSE	0.01
	0.48	5	0.42	3.28E-03	$\Sigma\chi^2$	0.010		SSR	0.29
	0.45	10	0.41	1.57E-03					
	0.41	30	0.41	2.93E-06				R squared	0.97
	0.39	60	0.41	5.50E-04					
	0.35	120	0.41	4.21E-03				StDev	0.04
1:20:10	1.00	0	1.00	0.00E+00	k	1.245		SST	0.37
	0.48	1	0.48	4.45E-06	a	1.193		SSE	0.02
	0.42	5	0.35	4.61E-03	$\Sigma\chi^2$	0.017		SSR	0.35
	0.40	10	0.35	2.51E-03					
	0.36	30	0.35	1.04E-04				R squared	0.95
	0.32	60	0.35	9.15E-04					
	0.26	120	0.35	9.21E-03				StDev	0.05

2,4-D:PS:Fe ²⁺	Ct/C0	Time, min	Estimate Ct/C0	χ^2					
1:5:20	1.00	0	1.00	0.00E+00	k	0.806		SST	0.08
	0.73	1	0.73	4.23E-11	a	2.253		SSE	0.00
	0.71	5	0.70	5.01E-05	$\Sigma\chi^2$	0.000		SSR	0.08

	0.70	10	0.70	2.30E-06					
	0.69	30	0.70	1.13E-04				R squared	1.00
	0.70	60	0.70	2.30E-06					
	0.70	120	0.70	1.25E-05				StDev	0.01
1:10:20	1.00	0	1.00	0.00E+00	k	0.941		SST	0.14
	0.65	1	0.65	5.94E-10	a	1.797		SSE	0.00
	0.60	5	0.59	1.30E-05	$\Sigma\chi^2$	0.000		SSR	0.14
	0.60	10	0.59	1.33E-05					
	0.60	30	0.59	5.17E-05				R squared	1.00
	0.58	60	0.59	5.58E-05					
	0.59	120	0.59	4.85E-05				StDev	0.01
1:20:20	1.00	0	1.00	0.00E+00	k	1.194		SST	0.44
	0.46	1	0.46	2.02E-05	a	0.955		SSE	0.02
	0.35	5	0.29	4.20E-03	$\Sigma\chi^2$	0.016		SSR	0.43
	0.34	10	0.29	2.56E-03					
	0.29	30	0.29	5.85E-05				R squared	0.96
	0.26	60	0.29	9.47E-04					
	0.20	120	0.29	7.73E-03				StDev	0.05

2,4-D:PS:Fe ²⁺	Ct/C0	Time, min	Estimate Ct/C0	χ^2					
1:5:0	1.00	0	1.00	0.00E+00	k	1.398		SST	0.01
	0.86	1	0.88	4.58E-04	a	11.326		SSE	0.00
	0.89	5	0.88	3.48E-05	$\Sigma\chi^2$	0.001		SSR	0.01
	0.88	10	0.88	7.10E-07					
	0.89	30	0.88	4.10E-05				R squared	0.95
	0.88	60	0.88	4.80E-06					
	0.89	120	0.88	1.09E-04				StDev	0.01
1:10:0	1.00	0	1.00	0.00E+00	k	0.260		SST	0.01
	0.90	1	0.90	1.17E-11	a	2.256		SSE	0.00
	0.89	5	0.89	6.51E-07	$\Sigma\chi^2$	0.000		SSR	0.01
	0.91	10	0.89	2.52E-04					
	0.89	30	0.89	5.39E-06				R squared	0.96
	0.89	60	0.89	3.30E-06					
	0.88	120	0.89	1.19E-04				StDev	0.01
1:20:0	1.00	0	1.00	0.00E+00	k	0.573		SST	0.01
	0.89	1	0.89	9.14E-13	a	4.868		SSE	0.00
	0.89	5	0.89	5.06E-07	$\Sigma\chi^2$	0.000		SSR	0.01

0.90	10	0.89	9.81E-05						
0.89	30	0.89	6.49E-07					R squared	0.99
0.89	60	0.89	7.47E-06						
0.88	120	0.89	5.31E-05					StDev	0.00

APPENDIX E

CONCENTRATION OF 2,4-D WITH ADDITION OF CHLORIDE ION

2,4-D:PMS:Fe ²⁺	Cl ⁻ Conc., mg/L	2,4-D Conc., mg/L	C _t /C ₀	Reaction Time, min
1:10:10	250	7.98	1.00	0
		4.01	0.50	1
		4.00	0.50	5
		4.04	0.51	10
		3.93	0.49	30
		3.81	0.48	60
		3.57	0.45	120
1:10:10	250	7.98	1.00	0
		4.35	0.54	1
		3.40	0.43	5
		3.14	0.39	10
		3.02	0.38	30
		3.06	0.38	60
		3.03	0.38	120