

**Novel Simultaneous Reduction/Oxidation
Process for Destroying Organic Solvents**

By

Anita Rema Padmanabhan

A Thesis

Submitted to the Faculty

of the

WORCESTER POLYTECHNIC INSTITUTE

In partial fulfillment of the requirement for the

Degree of Master of Science

In

Environmental Engineering

By

April 2008

APPROVED:

Professor John Bergendahl, Major Advisor

Professor James C. O'Shaughnessy, Co-Advisor

Professor Tahar El-Korchi, Head of Department

Acknowledgements

I would like to thank Mr. Don Pelligrino for all his help with the lab equipment and chemical supplies. I would also like to thank Mr. Sachin Sharma for his time and assistance with the GC analysis.

I would like to thank the Civil and Environmental Engineering Department at Worcester Polytechnic Institute for the teaching assistantship which provided the funding to make this research possible.

Finally, I would like to thank Dr. John Bergendahl for all the support he provided during this research project. Dr. Bergendahl's insight and advice during this project was a valuable asset.

Abstract

Trichloroethylene (TCE) is one of the most common groundwater pollutants in the United States and is a suspected carcinogen. The United States Environmental Protection Agency (EPA) estimated that between 9% and 34% of the drinking water sources in the United States may contain TCE, and have set a maximum contaminant level of 5 $\mu\text{g/L}$ for drinking water. Traditional treatment technologies such as granular activated carbon and air stripping have only had marginal success at removing TCE from contaminated sites. Chemical oxidation processes have provided a promising alternative to traditional treatment methods.

The objective of this research was to examine the conditions under which zero valent iron (Fe^0) activates persulfate anions to produce sulfate free radicals, a powerful oxidant used for destroying organic contaminants in water. With batch experiments, it was found that persulfate activated by zero valent iron removed TCE more effectively than persulfate oxidation activated by ferrous iron. This laboratory study also investigated the influence of pH (from 2 to 10) on TCE removal. TCE was prepared in purified water and a fixed persulfate/TCE molar ratio was employed in all tests. The results indicated that this reaction occurred over a wide range of pH values. The production and destruction of daughter products cis 1,2 dichloroethylene and vinyl chloride were observed. The effect of persulfate dose on this reaction was also studied. Results showed that a molar ratio of 10/1/1 (persulfate/ZVI/TCE) yielded over 95 percent TCE destruction. Increasing the persulfate dose resulted in greater TCE destruction as well as destruction of the daughter products. Kinetic experiments at a molar ratio of 10/1/1 (persulfate/ZVI/TCE) show that approximately 90 percent of the TCE was destroyed in less than 15 minutes.

Table of Contents

Chapter 1: Introduction	1
Chapter 2: Background	2
2.1 Trichloroethylene	2
2.1.1 Health Aspects	3
2.2 Current Treatment Methods	4
2.3 Advanced Oxidation Processes	6
2.4 Persulfate Oxidation.....	9
2.4.1 Persulfate Oxidation Activated by Ferrous Iron	12
2.5 Zero Valent Iron.....	15
2.6 TCE Daughter Products	18
2.7 Hypotheses and Objectives	19
Chapter 3: Materials and Methods	20
3.1 Materials	20
3.2 Equipment.....	21
3.2.1 Gas Chromatographic Analysis	21
3.3 Methods.....	22
3.3.1 Preparation of Stock Solutions.....	22
3.3.2 ZVI Activated Persulfate Oxidation of TCE	23
3.3.3 Headspace Technique	24
3.3.4 Micro-Liquid-Liquid Extraction	25
Chapter 4: Results and Discussion.....	27
4.1 Preliminary Experiments	27

4.2 Varying pH Experiments	29
4.2 Varying Persulfate Dose Experiments	32
4.3 Proposed TCE Degradation Pathways	36
4.4 Reaction Kinetics	39
Chapter 5: Summary	46
Chapter 6: Conclusions and Future Work.....	48
Reference List	50
Appendix A: Standard Curves	53
Appendix B: Preliminary Experiments.....	56
Appendix C: pH Experiments.....	58
Appendix D: Persulfate Experiments.....	61

List of Figures

Figure 1: Chemical Structure of TCE.....	2
Figure 2: Chemical Structure of Trans-DCE, Cis-DCE and 1,1 DCE.....	19
Figure 3: Chemical Structure of Vinyl Chloride.....	19
Figure 4: Schematic of typical head space procedure.....	25
Figure 5: Schematic of MLLE procedure.....	26
Figure 6: Comparison of ferrous iron activated persulfate oxidation and ZVI activated persulfate oxidation. While both yield greater than 90% destruction of TCE, ZVI appears to have a higher destruction rate. All samples were at a pH of 4 and molar ratio of 10/1/1 (Persulfate/ZVI or Fe^{2+} /TCE). (Initial TCE = 375 mg/L, error bars represent the 95% confidence interval, n= 3 for all samples).....	28
Figure 7: Effects of pH on ZVI activated persulfate oxidation of TCE. Experiments were conducted in triplicate at a molar ratio of 10/1/1 (persulfate/ZVI/TCE). (Initial TCE concentration= 375 mg/L, error bars represent 95% confidence intervals, n= 3 for all pH values).....	30
Figure 8: Effects of persulfate dose on ZVI activated persulfate oxidation of TCE. All experiments were conducted at a pH of 7 and an initial TCE concentration of 375 mg/L. Increasing persulfate doses result in the formation and degradation of daughter products Cis 1,2 DCE and VC.....	34
Figure 9: Proposed TCE degradation pathways.....	39
Figure 10: The degradation of TCE by ZVI activated persulfate oxidation over 60 minutes. All experiments were conducted at a molar ratio of 10/1/1 (persulfate/ZVI/TCE), a pH of 7 and an initial TCE concentration of 375 mg/L.	41

Figure 11: The degradation of TCE by ZVI activated persulfate oxidation over 20 minutes. All experiments were conducted at a molar ratio of 50/1/1 (persulfate/ZVI/TCE), a pH of 2 and an initial TCE concentration of 375 mg/L. 41

Figure 12: Kinetics of TCE destruction. First order reaction rate constant (k) of TCE destruction as a function of time. All experiments were conducted at a molar ratio of 10/1/1 (persulfate/ZVI/TCE) and a pH of 7..... 45

Figure 13: Kinetics of TCE destruction. First order reaction rate constant (k) of TCE destruction as a function of time. All experiments were conducted at a molar ratio of 50/1/1 (persulfate/ZVI/TCE) and a pH of 2..... 45

List of Tables

Table 1: Chemical Properties of TCE.....	3
Table 2: Second-Order Rate Constants for the Reactivity of Common Contaminants with Hydroxyl Radical	7
Table 3: Properties of ZVI	20
Table 4: Retention Times & Method Detection Limits	22

Chapter 1: Introduction

Trichloroethylene (TCE) was introduced into the environment primarily through various industrial activities. According to the United States Environmental Protection Agency (EPA), from 1987 to 1993, over 291,000 lbs of TCE was released to water and land (Environmental Protection Agency).

The EPA estimates that between 9% and 34% of the public drinking water sources in the United States may contain TCE. It should be noted that this estimate does not include private wells, which may also be contaminated especially if the wells are located near TCE disposal/contamination sites where leaching may occur. Reported levels in water are typically between 10 and 100 parts per billion (ppb) (World Health Organization, 1985).

The EPA has set an enforceable standard for TCE called a Maximum Contaminant Level (MCL) (Environmental Protection Agency). The MCL for TCE is 5 ppb, and TCE must not be present in drinking water at concentrations higher than this.

Since TCE is one of the most frequently reported groundwater contaminants, there is a need to find innovative ways of removing this solvent from the water supply. This research focused on the effectiveness of zero valent iron (ZVI) activated persulfate oxidation for the destruction of TCE in an aqueous environment.

Chapter 2: Background

2.1 Trichloroethylene

TCE is an organic solvent that appears as a colorless liquid with a sweet odor and burning taste. The main use of TCE is as a degreaser to metal parts; however other uses include an ingredient in adhesives, paint removers, typewriter correction fluids, and spot removers (Agency for Toxic Substances and Disease Registry, 2007).

The presence of TCE in the environment is a direct result of improper disposal methods from industry as well as industrial leaks and spills. TCE is commonly found in surface waters, wells and groundwater supplies in the vicinity of industries that use TCE (Agency for Toxic Substances and Disease Registry, 2007).

The molecular formula for TCE is C_2HCl_3 and its chemical structure is illustrated in Figure 1. TCE has several trade names including but not limited to, Chlorylea, TRI-Plus M, Triad, Vitran, Perm-A-Chlor and Dow-Tri (Hazard Evaluation System and Information Service, 1997).

When TCE is in a soil medium, it will either evaporate or leach into ground water. Similarly, when TCE is introduced to surface water, it will quickly evaporate; therefore may not pose a major health hazard to aquatic life (Russell et al., 1992). In the gas phase, TCE is stable in air, but unstable in light or moisture. The general properties of TCE are included as Table 1.

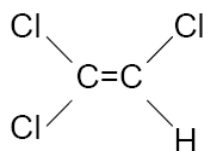


Figure 1: Chemical Structure of TCE

Table 1: Chemical Properties of TCE

Density (g/mL)	1.46
Solubility (mg/L @ 20°C)	1000
Henry's Law Constant (atm-m ³ /mol @ 20°C)	0.00892
Molecular Weight (g)	131.4
Boiling Point (°C)	86.7
Melting Point(°C)	-73
Vapor Pressure @ 20°C(mm Hg)	57.8

Adapted from (Russell et al., 1992)

Since pure TCE has a density greater than pure water, when TCE is released in the pure phase, it migrates down through an aquifer due to gravitational force and forms a pool of dense non-aqueous phase liquid (DNAPL) perched above impermeable strata. Subsequent to the formation of the DNAPL, TCE can further contaminate an aquifer by spreading via dissolution, advection and dispersion (Agency for Toxic Substances and Disease Registry, 2007).

Transformation and degradation processes of TCE in the environment are limited. TCE is conducive to aerobic and anaerobic biodegradation in soil at a slow rate, with a half-life estimated at six months to one year. TCE does not absorb ultraviolet light at wavelengths less than 290 nanometers; therefore it will not directly photolyze in the atmosphere or in water (Environmental Protection Agency).

2.1.1 Health Aspects

Since TCE is extremely volatile, exposure is mainly through inhalation, ingestion and dermal absorption (World Health Organization, 1985). TCE is not a proven carcinogen but a suspected one. Once TCE is introduced to the body, it is distributed and

accumulates in adipose tissue (World Health Organization, 1985). TCE exits the body unchanged in exhaled air and to a lesser degree in feces, sweat and saliva and may be rapidly metabolized in the liver (World Health Organization, 1985). The symptoms of exposure to TCE are central nervous system problems that may include headache, drowsiness, hyperhydrosis and tachycardia, in more severe cases, a coma may result (World Health Organization, 1985). Psychomotor impairment was noticed after inhalation exposure to 5,400 mg/m³ (1,000 ppm) for 2 hours in work place conditions (World Health Organization, 1985). TCE vapors can cause eye irritation. High oral doses, 200 mL to 300 mL, can be toxic to the liver and kidneys. The lethal dose for an adult is generally 7,000 mg/kg body weight (World Health Organization, 1985).

2.2 Current Treatment Methods

Current drinking water treatment plant operations such as coagulation, sedimentation, precipitation, softening, filtration and chlorination are ineffective at reducing the concentration of TCE to meet MCL standards set by the EPA.

Air stripping is an effective method for removing TCE from water. Air stripping involves the use of a stream of air and sufficient contact between the air and water phases for the TCE to transfer from the contaminated water to the air phase. However, large volumes of air are needed for the transfer. Additionally, this process simply shifts the contaminant to the air phase, which still maintains an environmental hazard if released into the atmosphere (Russell et al., 1992).

In another treatment method, TCE may be removed from water through adsorption onto granular activated carbon (GAC). However there are limitations with removal of organics from water with adsorbents because sorbents have limited capacities

for specific contaminants. When the sorption limit is reached in fixed bed adsorbers, the contaminant will be present in the effluent (breakthrough). Once breakthrough has happened, the GAC media must be regenerated or replaced. Hugh et al., (1992) stated that with a TCE concentration of 1 mg/L, a neutral pH and a temperature of 20°C, the capacity of TCE on GAC is about 28 mg/g. An additional disadvantage to GAC is that other organic compounds are also susceptible to adsorb to the GAC, thus lowering the efficiency of TCE adsorption (Hugh et al., 1992).

The combination of air stripping and carbon adsorption is another approach to remove TCE from water. The first step is to use air stripping to reduce concentrations of TCE to an intermediate concentration. Then the water is sent through GAC as a second treatment step to effectively reduce the TCE concentration to below the MCL (Hugh et al., 1992).

Biological treatment may also be used to treat TCE. Biological processes use bacteria to degrade TCE to CO₂, water and chloride ions. Anaerobic and aerobic degradation have been shown to work in laboratory experiments with the use of readily oxidizable substrates and nutrients. Certain microorganisms need a primary metabolite for the bacteria to produce the proper enzymes to consume TCE (Hugh et al., 1992). In laboratory experiments, microorganisms that oxidize methane have been shown to use co-metabolic oxidation to degrade TCE. Intermediate by products, such as dichloroethylene and vinyl chloride; have been seen in many experiments (Hugh et al., 1992).

Permeable reactive barriers are another mode of treatment for TCE. In this method, the contaminant passes through the barrier wall, which is typically composed of

iron and the media inside the wall reduce the TCE to harmless end products. The major disadvantage with this method is complete breakdown of the TCE will not occur until the entire contaminant plume has passed through the wall. This can take on the order of months to years. Another disadvantage is the cost for the installation of these walls is great and increases with depth (Tech Tree, 2002).

2.3 Advanced Oxidation Processes

Advanced oxidation involves the generation of hydroxyl radicals (OH^\bullet). Hydroxyl radicals are one of the strongest oxidants known in chemistry. Hydroxyl radicals are typically produced with hydrogen peroxide/ultraviolet light, Fenton's reagent (hydrogen peroxide/ferrous iron), hydrogen peroxide/ozone and others. The produced hydroxyl radicals react with dissolved constituents through a series of complex reactions, and can completely mineralize the organics under favorable conditions. Watts and Teel (2006) describe the rate of reaction of hydroxyl radical with an organic compound (C) by the second-order rate expression included as equation (1).

$$-\frac{dC}{dt} = k[C][\text{OH}^\bullet] \quad (1)$$

Table 2 shows the second-order rate constants for the reactivity of hydroxyl radicals with various toxic chemicals. As can be seen in Table 2, most of the aromatic compounds react effectively with hydroxyl radicals. Exceptions include compounds such as carbon tetrachloride (CTC), which is resistant to hydroxyl radicals (Watts and Teel, 2006). The general equation that describes the reaction between the hydroxyl radical and TCE is shown in equation (2). The end products of oxidation of TCE are carbon dioxide and chloride ions.

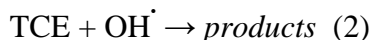


Table 2: Second-Order Rate Constants for the Reactivity of Common Contaminants with Hydroxyl Radical

Compound	k_{OH^\cdot} ($\text{M}^{-1}\text{s}^{-1}$)
Pentachlorophenol	4.0×10^9
Benzene	7.8×10^9
Toulene	3.0×10^9
Nitrobenzene	2.9×10^9
Carbon tetrachloride	$<2.0 \times 10^6$
Chloroform	5.0×10^6
Tetrachloroethylene (PCE)	2.8×10^9
Trichloroethylene (TCE)	4.0×10^9
Methyl tert-butyl ether (MTBE)	$(3.9 \pm 0.73) \times 10^9$

Adapted from (Watts and Teel, 2006)

Studies have been conducted on the effectiveness of Fenton's reagent for treating chlorinated organics such as TCE. These studies show that during classical Fenton's oxidation of TCE, 78% of the initial TCE was degraded and 2.5 moles of H_2O_2 were consumed per mole of TCE. Approximately 1.9 moles of chloride were released per mole of TCE, showing that not all of the chlorine was displaced from the TCE (Teel et al., 2001).

Bergendahl and Thies (2004) studied Fenton's oxidation of MTBE in the presence of zero valent iron. Their results showed the oxidation reactions were able to destroy over 99% of the MTBE within 10 min, and showed significant generation, and subsequent degradation of the oxidation by-product, acetone. Kinetic analysis found

second-order rate constants for MTBE degradation were $1.9 \times 10^8 \text{ M}^{-1} \text{ S}^{-1}$ at pH 7.0 and $4.4 \times 10^8 \text{ M}^{-1} \text{ S}^{-1}$ at pH 4.0 (Bergendahl and Thies, 2004).

A study performed by Chen et al. (2001) showed that Fenton's reagent was able to degrade aqueous phase TCE by 90 to 100% at a pH of 3. The experiments were also conducted in a sandy soil column and showed that Fenton's reagent with iron addition was able to oxidize TCE in the presence of soil (Chen et al., 2001/10/12).

Gates and Siegrist (1995) researched the chemical oxidation of TCE using hydrogen peroxide in fine grained soils. Gates and Siegrist found 98% removal of TCE with an initial concentration of 1.9 mg/kg soil and the H_2O_2 dose varied from 0.1 g/kg soil to 28.3 g/kg soil. The iron used for the experiment was simply the existing iron content in the soil. The removal efficiency was reported to be independent of initial TCE concentration and is more dependent on the soil chemistry (Gates and Siegrist, 1995). The hydrogen peroxide dose however did have an effect on the removal, higher doses yielded more destruction. Kinetic studies showed that the reaction is very fast reaches completion approximately 2 hours after addition of hydrogen peroxide (Gates and Siegrist, 1995).

Photo-Fenton oxidation involves a combination of UV light, ferric iron (Fe^{3+}), and H_2O_2 to produce hydroxyl radicals. Engwall et al. (1999) used photo-Fenton oxidation to remove pentachlorophenol (PCP) and creosote from water. The PCP was entirely dechlorinated in 10-20 minutes, and the total organic carbon decreased by 80% in 180 minutes (Engwall et al., 1999).

Although previous research shows the effectiveness of advanced oxidation via Fenton's reagent in destroying contaminants such as TCE, there are shortcomings to

treatment with Fenton's oxidation. One main disadvantage is that the pH has to be lowered to less than 4 to keep the iron in solution. There is a significant cost for acid addition, and subsequent base addition to raise the pH back up to neutral. Due to the non-selective nature of hydroxyl radicals, they can be "scavenged" or consumed by competing reactions before reacting with the target organic contaminants. Scavenging occurs when the hydroxyl radicals react with the non target species such as naturally-occurring nitrate and sulfate, and can result in a higher reactant dose. In addition, recent research has shown that hydroxyl radicals have a shorter lifetime in water than other oxidants such as persulfate (Jiasheng et al., 2008). According to Jiasheng et al. (2008), persulfate is a superior oxidant to Fenton's reagent because persulfate has the ability to sustain for weeks. By contrast, Fenton's can deplete hydrogen oxide and produce hydrogen gas within minutes to hours. This depletion causes an increase in gas pressure in the subsurface, which has been known to cause explosions as well as property damage (Jiasheng et al., 2008).

2.4 Persulfate Oxidation

Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) is a more recent addition to the list of possible oxidants for TCE oxidation. When persulfate salts dissociate in water, it forms the persulfate anion ($\text{S}_2\text{O}_8^{2-}$). The persulfate anion is a strong oxidant ($E^\circ = 2.01 \text{ V}$), but the use of it in treatment processes has kinetic limitations as it reacts much slower than other oxidants (e.g. hydroxyl radicals) (Liang et al., 2007). When the persulfate anion is chemically or thermally activated, it produces the sulfate free radical ($\text{SO}_4^{\cdot-}$), which is a stronger oxidant ($E^\circ = 2.6 \text{ V}$) than the persulfate anion (Liang et al., 2007). Once the

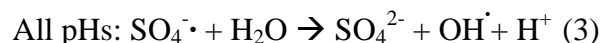
sulfate radical is formed it can destroy oxidizable contaminants including organic solvents such as TCE (Liang et al., 2007).

Huang et al. (2005) investigated the effectiveness of thermally activated persulfate oxidation for the degradability of 59 VOCs listed in the USEPA SW-846 Method 8260B. The results showed that persulfate is able to degrade many frequently detected VOCs in contaminated soil and groundwater, with the rate of degradation increasing with higher temperature and oxidant concentration (Huang et al., 2005). Huang et al., 2005 concluded that to completely degrade organic compounds it is important to have sufficient persulfate in the system. One of the VOC's studied was carbon tetrachloride (CTC). CTC is highly resistive to oxidation mechanisms, however some of the data in this work showed degradation of CTC (Huang et al., 2005). Therefore, Huang et al. concluded the degradation observed was through reductive mechanisms similar to that shown by Watts et al. (2005). Watts et al. (2005) showed that CTC could be reduced using modified Fenton's reactions by the superoxide radical anion. Huang et al. (2005) concluded the dechlorination of CTC with persulfate can be obtained, however was not able to identify the responsible reducing agent.

Liang et al. (2003) looked at thermally activated persulfate oxidation of TCE and 1,1,1-trichloroethane (TCA) in aqueous systems and soil slurries. The objective of the study was to compare TCE and TCA oxidation at a temperature range from 40 to 99°C. Results showed little or no TCE/TCA degradation at a temperature of 20°C however, there was good degradation at 40, 50 and 60°C. Kinetic analysis showed a first order rate reaction, with TCE/TCA degradation increasing with higher temperatures. The TCE/TCA was mostly destroyed within 6 hours (Liang et al., 2003).

Liang et al. (2007) investigated the effect of various levels of chloride and carbonate concentrations on thermally activated persulfate oxidation of TCE at 20°C. Chloride and carbonate concentrations can scavenge the sulfate free radicals, which would then make them unavailable to react with the TCE. Liang et al. (2007) found that with bicarbonate/carbonate concentrations within the range of 0–9.20 mM and at a pH of 7, the degradation of TCE was not affected. There was a reduction in TCE degradation at higher carbonate levels and at higher pH levels. At chloride levels below 0.2 M, TCE degradation is not affected; however at chloride levels above 0.2 M, TCE degradation is reduced when chloride ions increase (Liang et al., 2007).

When the sulfate radicals are in aqueous solution, radical interconversion reactions can occur, which produce hydroxyl radicals having an oxidation potential of 2.7 V (Liang et al., 2007). The interconversion reactions are described in equations (3) and (4).

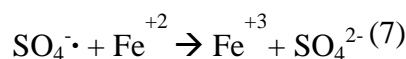
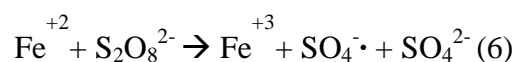
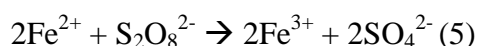


Depending on the pH conditions of the contaminated water, both sulfate radicals and hydroxyl radicals are responsible for the destruction of TCE, which was studied by Liang et al. (2007). Liang et al. found that the pH of the water will determine whether the sulfate radical or the hydroxyl radical will dominate over the other. There are three ways in which sulfate and hydroxyl radicals react with organic compounds: hydrogen abstraction, hydrogen addition, and electron transfer (Liang et al., 2007). According to Liang et al. (2007) sulfate radicals exhibit a higher standard reduction potential than hydroxyl radicals at neutral pH but both radicals exhibit similar reduction potentials

under acidic conditions. Sulfate radicals usually participate in electron transfer, while hydroxyl radicals participate in hydrogen abstraction or addition reactions (Liang et al., 2007). The sulfate free radical predominates in acidic to neutral conditions, while the hydroxyl radical predominates in basic conditions (Liang et al., 2007).

2.4.1 Persulfate Oxidation Activated by Ferrous Iron

The persulfate anion can decompose to form sulfate free radicals in the presence of transition metal activators at room temperature. An example of a widely studied transition metal activator is ferrous iron (Fe^{2+}). The stoichiometric relationship between, persulfate and ferrous iron is described in equations (5), (6) and (7) (Liang et al., 2004/6a). In addition to ferrous iron, metal ions of silver, copper, manganese, cerium and cobalt have also been studied.



The rate of reaction between persulfate and ferrous iron is reliant on the concentration of each reactant (Liang et al., 2004/6a). Based on the stoichiometry of equation (5), the reaction requires a $\text{Fe}^{+2}/\text{S}_2\text{O}_8^{2-}$ molar ratio of 2. The rate-determining step is equation (6), where there is reaction between $\text{S}_2\text{O}_8^{2-}$ and Fe^{+2} to form $\text{SO}_4^{\cdot-}$, which then rapidly reacts with a second Fe^{+2} as shown in equation (7) (Balabanova and Markevich, 1966). When the reactions have gone to completion, no sulfate radical is available for further destruction of the target organic contaminants (Liang et al., 2004/6a). If the concentration of Fe^{+2} were increased, the reactions in equations (6) and

(7) would happen faster. The conversion of Fe^{+2} to Fe^{+3} results in the production of $\text{SO}_4^{\cdot-}$, which destroys the target organic contaminant (Liang et al., 2004/6a).

One limitation to the use of ferrous iron as an activator of persulfate is that the sulfate radicals and excess ferrous iron react so rapidly, that the sulfate radicals could be destroyed, which would hinder the destruction of the organic solvent (Liang et al., 2004/6a). This happens because the TCE and excess ferrous iron are competing for the $\text{SO}_4^{\cdot-}$ (Liang et al., 2004/6a). To optimize this reaction, the reaction shown in Eq. (7) must be minimized by slowly providing small quantities of Fe^{+2} activator which prevents the fast conversion of Fe^{+2} to Fe^{+3} by $\text{SO}_4^{\cdot-}$ (Liang et al., 2004/6a). Experiments conducted by Liang et. al. 2004, using Fe^{+2} as an activator under various molar ratios of $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{+2}/\text{TCE}$ in an aqueous system showed that partial TCE degradation happened rapidly but then the reaction stopped (Liang et al., 2004/6a). It was found that by adding the Fe^{+2} in small increments, the degradation efficiency was enhanced. Liang et al. (2004/6a) hypothesized that the addition of sodium thiosulfate to the oxidation reaction may decrease the oxidizing conditions by converting Fe^{+3} to Fe^{+2} which could then activate the persulfate. This hypothesis proved to be true, as Liang's results showed that adding the thiosulfate in installments after the reaction stalled improved the destruction of the TCE (Liang et al., 2004/6a). This reaction was found to happen rather quickly in water, but was slower in the presence of soil (Liang et al., 2004/6a).

Another limitation to ferrous iron as an activator is that the iron must be kept in solution. Liang et al. (2004) completed another study on ferrous iron activated persulfate oxidation of TCE. This research focused on the ability of various chelating agents to hold Fe^{+2} in solution (dissolved) for activated persulfate oxidation of TCE in soil slurries.

The chelating agents tested included: ethylenediaminetetraacetic acid (EDTA), sodium triphosphate (STPP), citric acid and 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). The research found that citric acid is the most effective chelating agent (Liang et al., 2004/6b). The advantages to citric acid include that it is readily available, harmless to the environment, cost effective and is able to extract toxic metals from contaminated soils and slurries (Liang et al., 2004/6b). TCE degradation occurred in both soil slurries and aqueous systems. TCE degradation of approximately 34%, 73% and 41% during activated persulfate oxidation were observed in aqueous systems when EDTA-Fe^{+2} , STPP-Fe^{+2} , and HEDPA-Fe^{+2} were used respectively. Degradation was slightly lower in soil slurries with the same chelating agents and molar ratio, at 33%, 67% and 54% respectively. For the same conditions using citric acid as the chelating agent TCE degradation was approximately 90% in aqueous systems and approximately 80% in soil slurries. Almost 100% destruction of the TCE was found after 1 hr in aqueous and soil systems. Liang et al. (2004) thus concluded that using a citric acid chelated ferrous ion achieves superior results than that on an unchelated ion (Liang et al., 2004/6b).

In 2008, Jiasheng et al. studied the oxidation of lindane with ferrous iron activated persulfate oxidation. Lindane is a proven carcinogen, and a prevalent organic in the environment. The study aimed to compare the oxidation of lindane via Fenton's reaction versus persulfate activated by ferrous iron. Jiasheng et al. (2008) found that persulfate activated by ferrous iron was rapid and successful in degrading the lindane and persulfate proves to be more sustainable in the environment than Fenton's reagent.

2.5 Zero Valent Iron

For this study, the role of ZVI (Fe^0) is to activate the persulfate by providing ferrous iron. Since our research has oxidation and reduction reactions occurring, it is crucial to look at previous research which has employed the use of ZVI and how it relates to this research. The majority of the research that has been done with ZVI is in regard to its capability as a reductant.

The use of Fe^0 as an alternative to traditional Fenton's reagent has been studied by Doong and Chang (1998). This study was done on the photo-assisted degradation of organophosphorous pesticides, where Fe^0 and Fe^{2+} were compared as catalysts in a UV/ H_2O_2 system. Doong and Chang (1998) found pesticide removal rates between 90 and 99 percent after 240 minutes when 1 g of Fe^0 or 50 ug of Fe^{2+} was added to a UV/ H_2O_2 system. All reactions were first order and showed minimal variation in rate constants when Fe^{2+} was used compared with Fe^0 (Doong and Chang, 1998).

Doong and Chang (1998) concluded that $\text{Fe}^{+3}/\text{H}_2\text{O}_2$ is the predominant reaction for the oxidation of organophosphorous pesticides. They theorized that when only Fe^{2+} was present it was oxidized to Fe^{+3} by H_2O_2 , which leads to $\text{Fe}^{+3}/\text{H}_2\text{O}_2$ becoming the predominant reaction. Conversely, when Fe^0 is present, it oxidizes to Fe^{2+} and then Fe^{+3} by dissolved oxygen (Doong and Chang, 1998).

Lavine et al. (2001) investigated the capabilities of Fe^0 as a reductant of nitroaromatics. Lavine et al. (2001) found that due to the dissolved oxygen, Fe^0 was not an acceptable reductant for nitrobenzene. It was theorized that competition by oxygen for Fe^0 reduces the efficiency of nitrobenzene reduction. In addition, when O_2 is present, hydroxide ions may form on the surface of the Fe^0 , which inhibits the interaction between

Fe^0 and the contaminant. This phenomenon generally occurs at higher pH values. Lavine et al. (2001) de-aerated the samples by bubbling nitrogen through them for 15 minutes, at which time it was observed that the reduction efficiency of the nitrobenzene was increased (Lavine et al., 2001). The research by Lavine et al. (2001) showed that there is a connection between pH and the reductive capabilities of Fe^0 .

Chen et al. (2001) conducted a study on the effects of pH on the dechlorination of TCE. The study showed that as the pH was increased, the rate constant for the reduction of TCE decreased. It was theorized that the reason for this is at a higher pH, the ferrous and hydroxide ions form ferrous hydroxide which can precipitate onto the surface of the ZVI and encumber the transport of TCE by blocking reaction sites (Chen et al., 2001).

Research has shown that ZVI has been successful at reducing organic and inorganic compounds and dechlorinating chlorinated compounds (Chen et al., 2001), (Lavine et al., 2001), (Krishna et al., 2001). ZVI reduces organic compounds by coming in contact with the organic compound and being stripped of two electrons. For metal ions, removal happens through reduction of ions to an insoluble state (Ponder et al., 2000). Ponder et al. (2000) showed that aqueous chromium and lead could be removed in the presence of ZVI without any other remediation procedures. Chen et al. (2001) studied the dechlorination of TCE in the presence of ZVI, and Lavine et al. (2001) researched the reduction of nitroaromatics in the presence of ZVI. Both Lavine and Chen found satisfactory removal. According to Krishna et al. (2001) removal of arsenic in an aqueous environment in the presence of ZVI was found when reduction preceded advanced oxidation.

Liu et al. (2006) studied the effects of ferrous ions on the reductive dechlorination of TCE by ZVI. The results showed that the acid-washing a metallic iron sample enhanced the efficiency of TCE degradation by ZVI. The acid washing changes the surface area and the formation of the oxides on the surface of the ZVI. When ferrous iron was added simultaneously with TCE to water, the extent of TCE degradation was reduced as the ferrous iron concentration increased. This occurred because of the formation of passive precipitates of ferrous hydroxide that coated the acid washed ZVI and inhibited electron transfer reactions. In samples where the ZVI was not acid washed, the electron transfer could take place despite the formation of the passive precipitates (Liu et al., 2006/8/25).

A study of the effectiveness of ZVI for destroying pure phase TCE (DNAPL) was conducted by Orth et al. (1998). The results showed that ZVI could be used to destroy DNAPL TCE if the ZVI could be directly injected into the DNAPL zone. The TCE was subjected to reductive dechlorination by the ZVI. The kinetic experiments showed that it took approximately 19.4 days for a TCE concentration of 5,880 mg/L to be reduced to 1,000 mg/L (Orth et al., 1998).

In 2006, Sharma found that ZVI activated persulfate oxidation of TCE using ozone saturated water in a soil slurry was effective in destroying TCE when the persulfate /TCE molar ratio was 10/1. Complete (100%) TCE destruction took place when the ZVI powder was added to the slurry test. All results showed that ZVI worked much better than ferrous iron in terms of TCE degradation efficiency (Sharma, 2006).

2.6 TCE Daughter Products

The potential daughter products of TCE reduction are the dichloroethylenes and vinyl chloride (VC) (Arnold and Roberts, 2000). The dichloroethylenes are: cis-1,2-DCE (cis-DCE), trans-1,2-DCE (trans-DCE), and 1,1-DCE. The DCE isomers are formed when the TCE is dechlorinated (Arnold and Roberts, 2000). In air, cis-DCE and trans-DCE can react with hydroxyl radicals (photochemically produced) with a half life of 8 days and 3.6 days respectively (EPA, 2001). Cis-DCE is the most commonly found DCE isomer and accounts for 95 percent of the DCE in reduction reactions (EPA, 2001). Trans-DCE has the same chemical formula and molecular weight as cis-DCE, however has a different physical makeup, as shown in Figure 2. 1-1 DCE has the same chemical formula and molecular weight as cis-DCE and trans-DCE, however 1,1-DCE has a different orientation, as shown in Figure 2. EPA has set the MCL's for cis and trans DCE at 0.07 mg/L and 0.1 mg/L respectively (United States Environmental Protection Agency, 2006).

Vinyl chloride is another daughter product of TCE reduction and forms when the DCE isomers are dechlorinated. VC has the molecular formula C_2H_3Cl and the structure shown Figure 3. VC is a known human carcinogen and the US EPA set a drinking water MCL of 2 $\mu\text{g/L}$ for VC (United States Environmental Protection Agency, 2006). Vinyl chloride is actually considered to be more harmful than TCE and therefore has a lower MCL than TCE. The vinyl chloride may be further dechlorinated to form ethene, which is the final daughter product of TCE reduction.

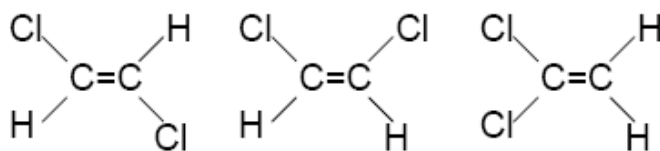


Figure 2: Chemical Structure of Trans-DCE, Cis-DCE and 1,1 DCE

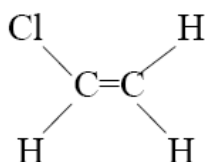


Figure 3: Chemical Structure of Vinyl Chloride

2.7 Hypotheses and Objectives

This study will look at the optimal conditions under which the destruction of TCE can occur, such as the pH and persulfate dose. The hypotheses of this work are:

- ZVI can be substituted for Fe^{2+} for activating persulfate for destruction of TCE.
- ZVI activated persulfate oxidation can be an effective tool for the destruction of TCE in contaminated waters.

To evaluate these hypotheses, we:

- Evaluated the optimal conditions under which ZVI activated persulfate oxidation of TCE can occur,
- Measured the destruction of TCE as well as the formation and degradation of cis 1,2 DCE and vinyl chloride (TCE daughter products),
- Studied the kinetics of TCE destruction.

Chapter 3: Materials and Methods

3.1 Materials

All glassware was washed with Alconox detergent. The glassware was rinsed four times in tap water and once in E-pure water. Stock solutions were kept in a 4 °C refrigerator until use. The TCE, sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), hexane and methanol were all A.C.S grade from Fisher Scientific. The TCE was an assay of 99.9%, the sodium persulfate was an assay of 98.0%, and the hexane and methanol were an assay of 99.9%. The ZVI used was a carbonyl iron micro powder supplied from ISP technologies. The properties of the ZVI are summarized in Table 3. The water was from an RO pure ST reverse osmosis system, followed by an E-pure system supplied by Barnstead/Thermolyne (Dubuque, Iowa). The cis-dichloroethylene (5,000 $\mu\text{g}/\text{mL}$), trans-dichloroethylene (5,000 $\mu\text{g}/\text{mL}$), 1,1-DCE (1,000 $\mu\text{g}/\text{mL}$) and Vinyl Chloride (100 $\mu\text{g}/\text{mL}$) standards, all diluted in methanol, were from Ultra Scientific (N.Kingstown, Rhode Island).

Table 3: Properties of ZVI

Color	Grey
Density (g/cm^3)	2-3
Sieve Analysis (200 Mesh, HSV-6)	0.3
Particle Size @ 10% (microns, HSV-6)	3
Particle Size @ 50% (microns, HSV-6)	3.5-5.5
Particle Size @ 90% (microns, HSV-6)	10
% Iron	97 minimum
% Carbon	<1
% Oxygen	<1
% Nitrogen	<1
Molecular Weight	55.85
Boiling Point ($^{\circ}\text{F}$)	4982
Melting Point ($^{\circ}\text{F}$)	2795
Solubility	Insoluble in water

3.2 Equipment

3.2.1 Gas Chromatographic Analysis

The gas chromatograph (GC) used for this research was an Agilent 6890 Series GC with an Agilent 7683 Series Injector auto-sampler. The software supplied with the GC was Hewlett Packard ChemStation software. Ultra high purity nitrogen gas from ABCO welding supplies (Waterford,CT) was used as the carrier gas. The injector was equipped with a 10 μ L syringe. The sample was injected into a split-less inlet with an initial temperature of 50°C and pressure of 8.06 psi. A 250°C ECD detector was used. The column was a Restek Rtx-5SILMS with a nominal length of 30.0 m, nominal diameter of 320 μ m and a nominal film thickness of 0.5 μ m. The column was housed in the oven with an initial temperature of 28°C. After 7 minutes the temperature in the oven raised 10°C/minute until a temperature of 200°C was reached. The output from the ECD detector is translated by the software into a peak area using the following constraints: initial slope sensitivity of 120, initial peak width of 0.8, and initial area and height rejects of 0.5. The sampling depth was set to 12 mm and the injection volume was 1 μ L.

The retention times for TCE, cis-DCE, trans-DCE, 1,1-DCE and VC were found by running a known standard of each compound separately through the GC. The retention times are summarized in Table 4. Standard curves were created for each of the five chemicals, which can be seen in Appendix A. The points used to create the standard curves were from pre-determined contaminant concentrations and the corresponding output peak areas from the GC. A linear regression was performed on the plotted data to find the best fit line. A good fit was found if the variation (r^2 value) was close to 1.

Hypothesis testing was used to determine if there was a statistical difference between the lowest concentrations of a compound compared with the sample blank. The lowest concentration with a statistical difference from the sample blank was deemed as the method detection limit. Any peak areas that were below the method detection limit were considered as non-detect. The method detection limit for the five compounds is included in Table 4.

Table 4: Retention Times & Method Detection Limits

Contaminant	Retention Time	Method Detection Limits
TCE	6.9 minutes	10 mg/L
1,1 Dichloroethylene	2.7 minutes	1 mg/L
1,2 Cis-Dichloroethylene	4.1 minutes	5 mg/L
1,2 Trans-Dichloroethylene	3.2 minutes	5 mg/L
Vinyl Chloride	2.2 minutes	10 mg/L

3.3 Methods

3.3.1 Preparation of Stock Solutions

Stock solutions of TCE and persulfate were pre mixed to meet the various required molar ratios for experiments. TCE stock solutions were prepared in 250 mL brown glass bottles. First, the bottles were filled with E-pure water, and then the appropriate amount of TCE was pipetted directly into the 250 mL bottle from a stock of pure TCE. The stock solution was immediately capped, and foil wrapped before being placed on a stir plate. The solution was allowed to mix overnight in the dark at room temperature to ensure

complete dissolution of TCE. All TCE stock solutions were prepared at a TCE concentration of 750 mg/L.

Persulfate stock solutions were prepared specific to the molar ratio required for the experiments. Persulfate stock solutions were also prepared in 250 mL brown glass bottles. First the bottles were filled with E-pure water and then the appropriate quantity of persulfate powder was measured and directly funneled into the stock solution. The amount of persulfate added was determined by the necessary persulfate/TCE molar ratio desired as well as the volume of the stock solution vessel. The bottle was then capped and placed on a stir plate for approximately 5 hours or until all the persulfate was dissolved in the water.

3.3.2 ZVI Activated Persulfate Oxidation of TCE

The reaction vessels used in the experiments were 40 mL soda lime amber glass vials. Each 40 mL vial was filled up with the appropriate amount of water, persulfate, ZVI and TCE to make up the desired molar ratio of the sample. First, the E-pure water was added, followed by the appropriate amount of sodium persulfate which was pipetted in the 40 mL vial directly from a pre prepared stock solution. Next, the appropriate amount of ZVI powder was measured on a digital mass balance and then added to the vials. The pH was then adjusted as necessary using 10 percent sulfuric acid or sodium hydroxide to a pH of 2,3,4,5,6,7,8,9 and 10, each within ± 0.1 pH units. The pH was measured with an Orion model 420A pH meter equipped with an Orion pH probe. The meter was calibrated each day with buffer solutions of pH 4.00, pH 7.00 and pH 10.00 (Fisher Scientific, Fair Lawn, NJ). After the pH adjustment, the TCE was pipetted into the 40 mL vial directly from a prepared stock solution. The sample volume was also 40

mL so that there was no headspace in the vials. The vials were capped with Teflon lined screw caps immediately upon the addition of the TCE to minimize the loss due to volatilization. The 40 mL vials were then foil wrapped to prevent UV degradation and placed securely on an orbit shaker at 100 rpm and allowed to react for approximately 24 hours. After the 24 hour time period, the 40 mL vials were centrifuged for 10 minutes at 1000 rpm on an Eppendorf Centrifuge 5804. The vials were centrifuged due to the tiny ZVI particles which could clog the GC syringe. Following the centrifuging of the vials, the head space or micro liquid liquid extraction techniques were used to analyze the samples.

3.3.3 Headspace Technique

The headspace sampling method was used in initial experiments to compare the potential of ZVI activated persulfate oxidation with the work of Sharma (2006). For this sampling method, 440 mg of sodium chloride was added to the sample vial in order to help volatilize compounds in solution. Then 1 mL of sample was added to the vial, and the remaining area is the headspace. After tightly capping the vial it was hand agitated for one minute and then placed on the shaker table allowing time for volatilization of the chemicals from the liquid. Then the vials were put on the auto sampler for GC analysis. The sample taken by the GC was taken from the headspace as seen in Figure 4.

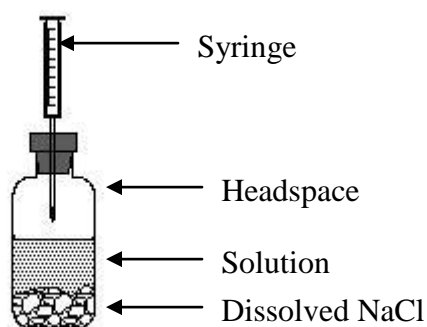


Figure 4: Schematic of typical head space procedure

Adapted from: (Szelewski and Quimby, 2000)

3.3.4 Micro-Liquid-Liquid Extraction

Liquid Liquid extraction (LLE) is a commonly used extraction method that separates two different compounds based on their solubilities (Klee, 2000). Micro Liquid Liquid Extraction (MLLE) is a type of LLE that can be used with the auto sampler on the GC (Klee, 2000). The first step in the process is to select an appropriate solvent for extraction, in this research hexane was the chosen solvent. Next, 0.5 mL of solvent is added to 1mL of sample in the standard 2 mL GC vials. The vial is then put on a vortex shaker and then the two layers are allowed to separate subsequent to GC analysis (Klee, 2000).

For each sample analyzed in this research, 0.5 mL of hexane was added to 1mL of aqueous sample. The vials were tightly capped and then allowed to mix on a vortex shaker for approximately 15 minutes. Once they had been mixed, they were allowed to separate for approximately 45 minutes. The vials are then analyzed on the GC with a 10 μ L syringe at an injection depth of 12 mm and injection volume of 1 μ L. The injection

depth was determined by observation, which witnessed the syringe drawing liquid and not headspace. A schematic of the MLLE procedure is shown in Figure 5.

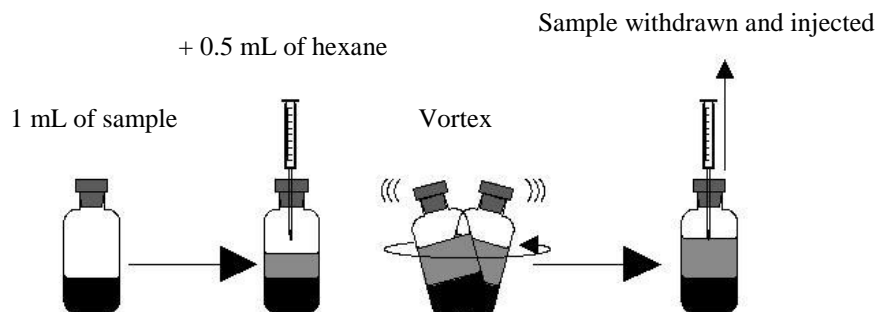


Figure 5: Schematic of MLLE procedure

Adapted from: (Klee, 2000)

Chapter 4: Results and Discussion

4.1 Preliminary Experiments

The first objective of this research was to determine if the ZVI activated persulfate oxidation of TCE was a viable method. A study conducted by Sharma (2006), showed that persulfate oxidation of TCE activated by ferrous iron and ZVI with ozone in a soil medium was successful, with ZVI showing greater degradation potential than ferrous iron. Therefore, a set of control experiments designed to see the effectiveness of ZVI activated persulfate oxidation was performed. The experiment had four controls which were TCE and water, TCE and ZVI, TCE and ferrous iron, and TCE and persulfate. The other two samples were ZVI activated persulfate and ferrous iron activated persulfate. Six 40 mL reaction vessels were prepared by adding the necessary combinations of water, persulfate, ZVI or ferrous iron, and TCE, pH adjustment was done prior to adding the TCE and all samples were adjusted to a pH of 4. For comparison purposes the molar ratio of persulfate/TCE/ZVI and persulfate/TCE/ferrous iron was kept consistent at 10/1/1, since Sharma (2006) experienced maximum destruction of TCE at this molar ratio. Upon addition of the TCE, the vials were tightly capped and foil wrapped and then placed on an orbit shaker at 100 rpm for 24 hours. After 24 hours, the samples were analyzed using the headspace method which is outlined in Chapter 3. Sharma (2006), successfully used the headspace method, therefore it was used to see if similar results were reproducible in an aqueous medium without ozone. It should be noted that Sharma (2006) used a chelating agent (citric acid) with the ferrous iron. This work did not use a chelating agent in the experiments. Each experiment was conducted in triplicate. The results are plotted as Figure 6.

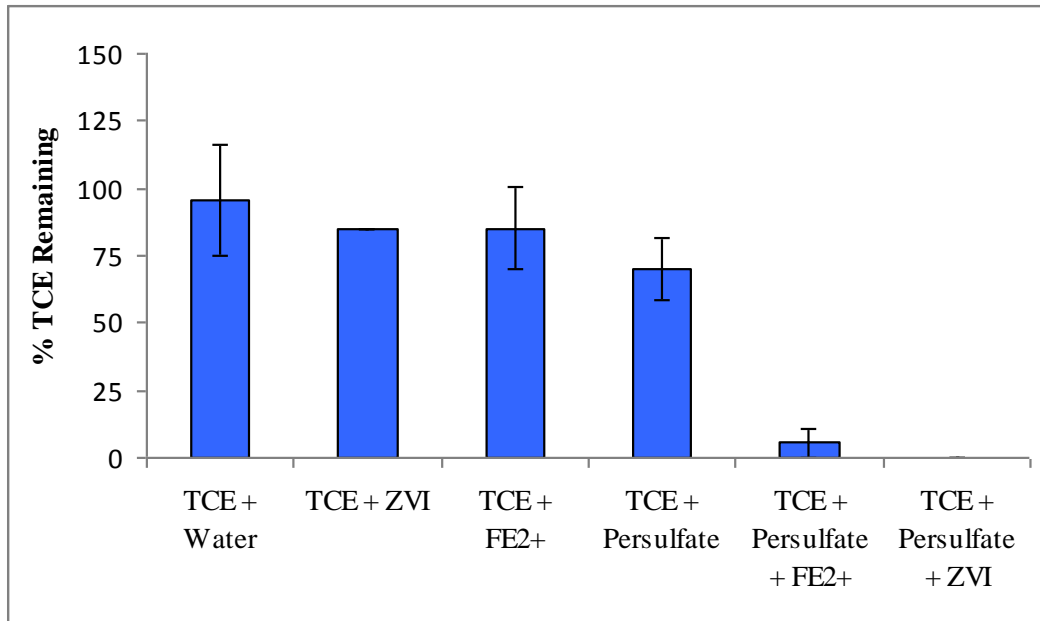


Figure 6: Comparison of ferrous iron activated persulfate oxidation and ZVI activated persulfate oxidation. While both yield greater than 90% destruction of TCE, ZVI appears to have a higher destruction rate. All samples were at a pH of 4 and molar ratio of 10/1/1 (Persulfate/ZVI or Fe²⁺/TCE). (Initial TCE = 375 mg/L, error bars represent the 95% confidence interval, n= 3 for all samples).

The results showed that the control experiments were successful and therefore the results of the ferrous iron and ZVI activated persulfate oxidation experiments are valid. As can be seen in Figure 7, the samples that had TCE with only ZVI or ferrous iron experienced very little reduction in TCE concentration. We know that ZVI has reductive properties and therefore over a long period of time, would most likely be able to reduce the TCE. When TCE was mixed with only persulfate, there was still no substantial loss of the TCE. This agrees with the results experienced by Huang et al. (2005), when trying to destroy CTC with only persulfate. Huang et al. (2005) also experienced little or no destruction of the CTC with only persulfate, however did observe loss of CTC, most likely through reduction, when the persulfate was thermally activated since CTC is

resistant to oxidation. When comparing the ZVI activated results to the ferrous iron activated results, it is evident that both iron catalysts were effective at activating the persulfate and able to destroy the TCE greater than 90 percent, however less remaining TCE concentration was observed with the ZVI. Since both iron catalysts are effective, other factors such as feasibility must be considered. For instance, ZVI may be added to the samples in powder form and does not need to be kept in solution. When ferrous iron is used it must be kept in solution so that the reaction does not stall, which is why a chelating agent is typically added. Therefore one advantage of ZVI is that there is no chelating agent required. The next set of experiments was designed to investigate the role of pH in ZVI activated persulfate reactions.

4.2 Varying pH Experiments

Previous research has shown that pH plays a prominent role in iron catalyzed and iron mediated reactions. Prior studies of ferrous iron activated persulfate oxidations of TCE showed that the reaction favored acidic conditions (Liang et al., 2004). It was unknown whether ZVI would also follow a similar trend to ferrous iron and favor acidic conditions. Therefore, a set of experiments designed to investigate the effects of pH on TCE destruction with ZVI activated persulfate was performed. A pH range from 2 to 10 was studied for full effect. Nine 40 mL vials were prepared with 375 mg/L TCE, with a persulfate/ZVI/TCE molar ratio of 10/1/1. Each reaction vial was then adjusted to a specified pH (2-10) as outlined in Chapter 3. All vials were allowed to react on the orbit shaker for 24 hours. After 24 hours, each vial was centrifuged for 10 minutes and then samples were extracted using the MLLE procedure and analyzed on the GC as described

in Chapter 3. Each experiment was run in triplicate, and the results were averaged. The results are shown in Figure 7.

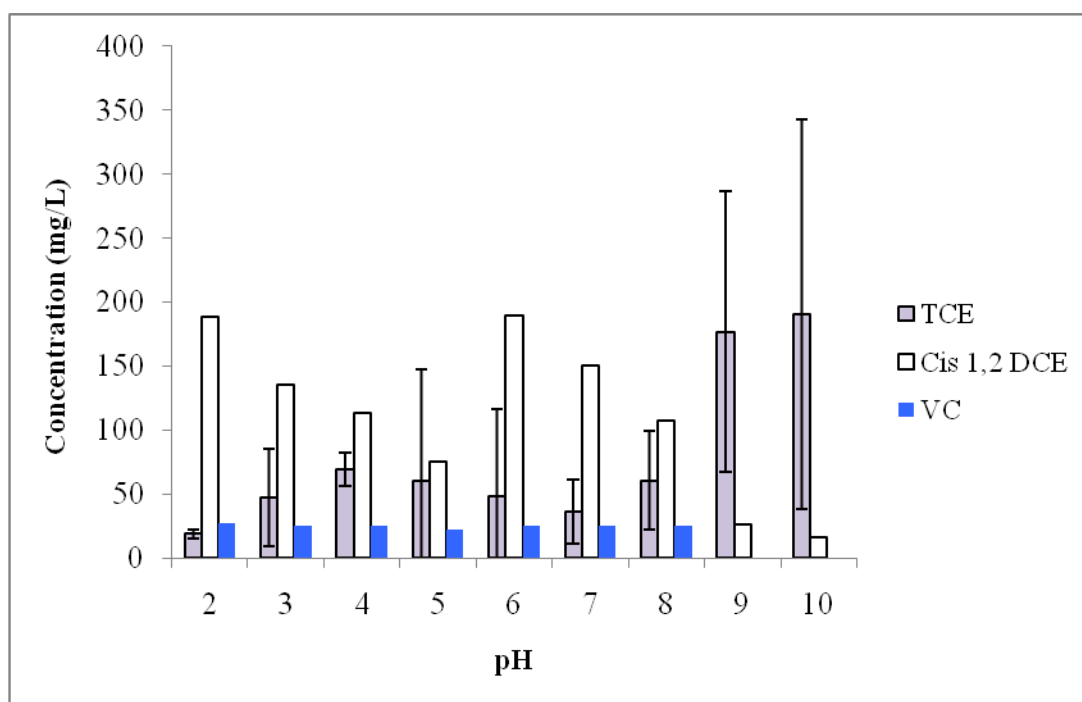


Figure 7: Effects of pH on ZVI activated persulfate oxidation of TCE. Experiments were conducted in triplicate at a molar ratio of 10/1/1 (persulfate/ZVI/TCE). (Initial TCE concentration= 375 mg/L, error bars represent 95% confidence intervals, n= 3 for all pH values).

The results showed that TCE destruction was seen for all samples after 24 hours. Greater than 80% destruction of TCE was seen at a pH range of 2 to 8. The highest destruction of TCE within that range occurred at a pH of 2 and 7, with 95 and 91% TCE being destroyed respectively. The presence of cis DCE and VC in the samples after 24 hours confirms that the decrease in TCE concentration is partially due to reduction reactions and not experimental error. The least amount of TCE destruction was seen at a pH of 9 and 10, which also coincided with the least amount of cis DCE and VC concentrations.

The results from these experiments show that this reaction can occur over a wide range of pH values. It is important to understand how the findings from these experiments compare with other studies done on iron catalyzed oxidation. We know that with Fenton reactions one of the shortcomings is that the pH must be kept low in order to keep the iron in solution. Huston and Pignatello (1999) showed that $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ advanced oxidation of pesticides was optimized at a pH of 2.8. The same pH was also optimal for a dark photo assisted Fenton's reaction of chlorophenoxyl herbicides studied by Pignatello (1992). Engwall et al. (1992) found maximum degradation of creosote and pentachlorophenol using a photo Fenton oxidation at 2.75. Bergendahl and Thies (2004) showed that maximum degradation of MTBE with Fenton's reagent in the presence of ZVI occurred at a pH of 4.

In ferrous iron activated persulfate oxidations, the iron must be held in solution for the reaction to proceed. The pH of the sample can have a significant effect on keeping the iron in solution similar to Fenton's reagent. Both ferrous iron activated persulfate oxidations of TCE conducted by Liang et al. (2004) showed that the successful destruction of TCE was achieved at the acidic pH range of 2-3. Jiasheng et al. (2008) showed that the ferrous iron activated persulfate oxidation of lindane was successful at a pH range of 3.5 to 9, with the reaction being optimized at a pH of 1.5 and 11.

Liang et al. (2006) achieved maximum TCE degradation using thermally activated persulfate oxidation at a pH of 7; with degradation rates increasing as the system pH was decreased.

All of the studies just mentioned are with the use of Fe^{3+} or Fe^{2+} or thermal activation. The research that employs the use of ZVI is typically in regard to its ability as

a reductant. Chen et al. (2001) showed that reductive dechlorination of TCE with ZVI was optimized at a pH of 4.9. Lavine et al. (2001) found that the reduction of nitroaromatics with ZVI was most successful at a pH of 6-7. Orth et al. (1998), who studied the dechlorination of DNAPL TCE by ZVI found that the TCE was successfully reduced at a pH range of 6.5 to 7.8. The successful reduction of TCE at a pH of approximately 7 as shown by Lavine et al. (2001), and Orth et al. (1998) are in agreement with our results.

In our study, greater than 80 percent TCE destruction was seen at a pH range from 2-8, with over 90 percent destruction occurring at a pH of 2 and 7. This research has the flexibility to be applied in a variety of pH conditions. One reason for this flexibility is that there is no concern of keeping the iron in solution, which effects Fenton's reactions as well as ferrous iron activated persulfate oxidation. Both Fenton's and ferrous iron activated persulfate are more effective in acidic solutions (i.e. pH of 4 or less). The effectiveness of ZVI as an activator of persulfate over a wide range of pH is a major advantage since the need for pH adjustment is unlikely. All the experiments going forward were adjusted to a pH of 7, since it is a fair representation of typical groundwater conditions.

4.2 Varying Persulfate Dose Experiments

Experiments were conducted to determine the most effective persulfate dose for this reaction. In order to study this, varying molar ratios of persulfate/ZVI/TCE were studied at a constant pH, with the only variable altered being the persulfate dose. Initially, six different reaction vessels were prepared with the following molar ratios of persulfate/ZVI/TCE: 1/1/1, 5/1/1, 10/1/1, 20/1/1, 30/1/1, and 40/1/1. First the vessels

were filled with Epure water, then the appropriate amount of persulfate was pipetted into the reaction vessels directly from different pre-prepared stock solutions. Each stock solution was prepared so that the amount of persulfate would satisfy the necessary molar ratios in the vials. Then the appropriate amount of ZVI powder was measured on a mass balance and added to the stock solution. Then the pH was adjusted to 7 for all samples using NaOH and/or HCL as needed. Finally, the TCE was added to the vials with an initial concentration of 375 mg/L. Once the TCE was added, the vials were capped, foil wrapped and placed on the orbit shaker for 24 hours as outlined in Chapter 3. After 24 hours, all the vials were centrifuged for 10 minutes at 1000 rpm and then analyzed using the MLLE technique described in Chapter 3. The results of this experiment are shown in Figure 8.

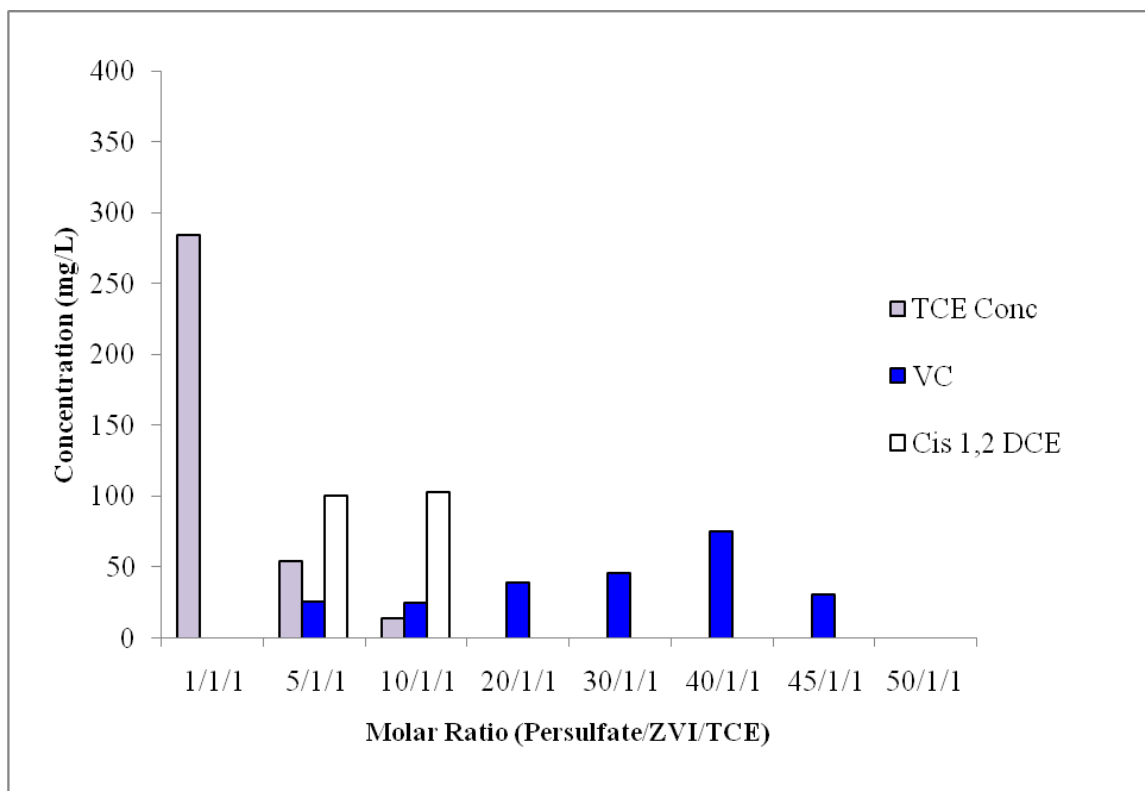


Figure 8: Effects of persulfate dose on ZVI activated persulfate oxidation of TCE. All experiments were conducted at a pH of 7 and an initial TCE concentration of 375 mg/L. Increasing persulfate doses result in the formation and degradation of daughter products Cis 1,2 DCE and VC.

The results showed that there was some TCE destruction with all the persulfate doses after 24 hours. The lowest molar ratio of 1/1/1 (persulfate/ZVI/TCE) only yielded a TCE destruction of 24 percent and no associated daughter products. When the persulfate dose was increased to 5/1/1, the TCE concentration was reduced by 86 percent with a resulting cis DCE and VC concentration of 100 mg/L and 26 mg/L respectively. At a persulfate/ZVI/TCE molar ratio of 10/1/1, the TCE concentration was reduced by 96 percent, with no significant change in daughter product concentrations from a molar ratio of 5/1/1. Finally, when the molar ratio was increased to 20/1/1 and higher, the TCE destruction was greater than 97 percent and below the method detection limit of the TCE which was 10 mg/L. Cis DCE also disappeared at persulfate doses of 20/1/1 and higher,

but VC concentrations were steadily increasing, with a maximum concentration of 75 mg/L at a molar ratio of 40/1/1.

Up to the molar ratio of 40/1/1, an increase in persulfate yielded a decrease in TCE and an increase in cis DCE and VC. Once the persulfate dosage was increased enough, the cis DCE disappeared as well. However, the VC concentrations were continually increasing. Ultimately, the complete destruction of TCE, should yield a loss of all the by products including VC. Therefore, one more experiment was conducted to demonstrate that the destruction of VC could be attained with an increased persulfate dose. For this experiment, the molar ratio of persulfate/ZVI/TCE was increased to 45/1/1 and 50/1/1. The results from this additional experiment are also plotted on Figure 8. As expected, at a molar ratio of 45/1/1, the TCE is still destroyed by greater than 97 percent and the VC concentration was approximately 30 mg/L, which is 60 percent less VC than a persulfate dose of 40/1/1. At a molar ratio of 50/1/1, the VC concentration was below the method detection limit of 10 mg/L. This is a significant reduction in VC concentration from the previous persulfate doses of 40/1/1 and 45/1/1. This demonstrates that increasing the dose of persulfate results in higher TCE destruction as well the eventual destruction in daughter products as well.

When determining the optimal persulfate dose, one important factor to consider is cost. It is important to pick the dose that provides sufficient TCE degradation with the least amount of persulfate possible. As can be seen in Figure 8, at molar ratios of 1/1/1 and 5/1/1, TCE degradation was below 90 percent, which indicates that the degradation was halted due to lack of sufficient persulfate. As persulfate concentration increased, so did the destruction of TCE. At a molar ratio of 10/1/1, the TCE destruction is at 96

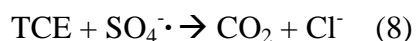
percent, with relatively low daughter product concentrations. At molar ratios of 20/1/1 and higher, the TCE concentration is below the method detection limit. Therefore with an initial TCE concentration of 375 mg/L, a minimum persulfate dose of 10/1/1 is required. Since a molar ratio of 10/1/1 is able to yield 96 percent TCE destruction, this would be the optimal dose as it utilizes the least amount of persulfate, which is considered more economical. It should be noted that the persulfate dose required is largely based on the initial TCE concentration. In this study the initial concentration of TCE is 375 mg/L, which is high. In a site with considerably less TCE contamination, the persulfate dose required would also be less than recommended in this study.

Sharma (2006), who studied persulfate oxidation of TCE activated by ferrous iron in a soil medium, also found that 10/1/1 (persulfate/ferrous iron/TCE) was the optimal molar ratio, with the same initial TCE concentration as this work, yielding greater than 90 percent reduction in TCE. Liang et al. (2004) used a chelated ferrous iron activated persulfate oxidation of TCE in soil and experimented with varying persulfate doses ranging from a molar ratio (persulfate/TCE) of 5/1 to 30/1. Liang et al. (2004) also showed that a minimum molar ratio of persulfate/TCE of 10/1 is required. Liang et al. (2004) also showed 96 percent destruction at this persulfate dose. The results from this work are in agreement with both of the above mentioned studies.

4.3 Proposed TCE Degradation Pathways

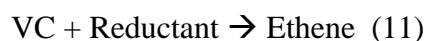
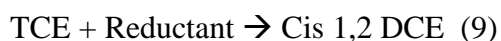
In this research, TCE is being destroyed by two mechanisms, oxidation and reduction. The zero valent iron loses two electrons to provide ferrous iron. When ferrous iron activates persulfate, it produces the sulfate radical, as described by equations (5)-(7) in Chapter 2. The general equation to describe the complete mineralization of TCE

through persulfate oxidation is included as equation (8). When TCE is oxidized by the sulfate free radical, the final end products of oxidation are carbon dioxide and chloride ions. For the purpose of this research the only oxidant we consider is the sulfate free radical since it is the predominant radical species at a neutral pH. As discussed previously, at basic pH values (8 or higher), the hydroxyl radical predominates the oxidation reaction.



This research shows that the TCE is not only being oxidized but also reduced through reductive dechlorination. As TCE goes through reductive dechlorination, it degrades into the daughter products mentioned previously: DCE isomers, vinyl chloride and then finally ethene. This research showed the presence of daughter products, specifically cis DCE and VC, which validated that significant reduction was also occurring. It is theorized that the reason the other DCE isomers did not appear in our experiments is that if they in fact existed it was in trace amounts and therefore undetectable. As mentioned previously, 95% of the DCE that results from TCE reduction is in the form of cis DCE. It has been mentioned that the capability of ZVI as a reductant has been widely studied and proven to be able to reduce TCE through dechlorination. However, the time in which the reaction takes place is on the magnitude of months such as in the study performed by Orth et al., (1998). The reduction reaction taking place in this study is very rapid and therefore the reductant is attributed to the persulfate rather than the ZVI. A study conducted by Huang et al., (2005) supports this theory. Huang et al., (2005) also found that persulfate may have reductive capabilities in a thermally activated persulfate study. In the study, Huang et al., (2005) observed a loss of CTC,

which is a compound known to be resistant to oxidation. In order to further investigate the reason for the decrease in CTC, Huang et al., (2005) conducted an experiment where it was attempted to destroy the CTC with persulfate alone. However, no CTC destruction was observed. Thus, it was concluded that under certain conditions the dechlorination of CTC with persulfate is possible. The general equation to describe the reduction of TCE to ethene is included as equations (9), (10) and (11).



It should be noted that a portion of the DCE isomers and VC can be directly oxidized to carbon dioxide and chloride ions, while the rest of it is reduced further. The ethene cannot be further reduced but can be oxidized to carbon dioxide and chloride ions. Figure 9 summarizes the proposed degradation pathways of the TCE in this research, illustrating the simultaneous oxidation and reduction reactions that are destroying the TCE.

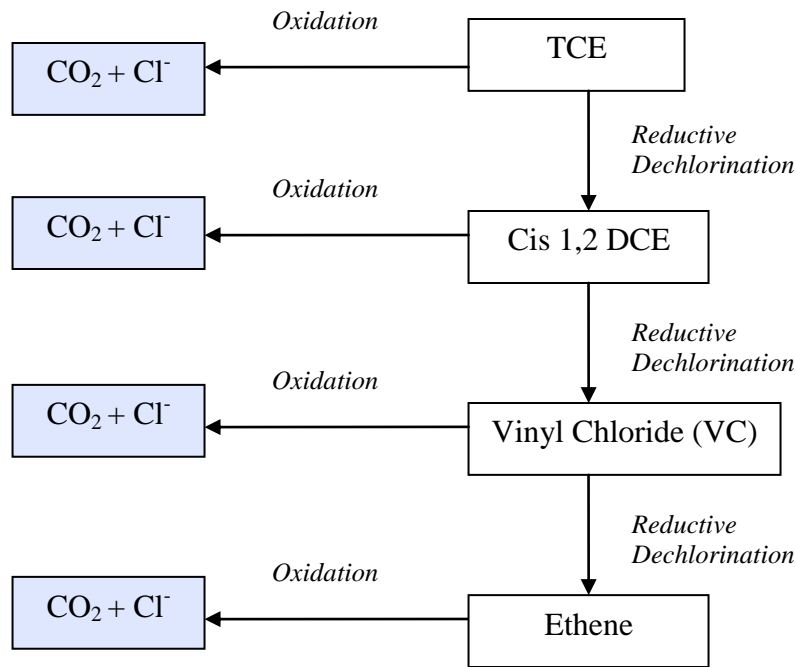


Figure 9: Proposed TCE degradation pathways

4.4 Reaction Kinetics

In order to apply this research in the field of engineering, it is important to determine a rate constant for TCE destruction. Rate constants provide information that will aid in the design of a treatment plant to destroy TCE.

The next experiments conducted were to determine the rate of TCE destruction. First, 13.3 mL of water was added to a 40 mL vial. Then, persulfate was pipetted directly from a pre-prepared stock solution at a dose of 10/1/1 (persulfate/ZVI/TCE). Next the ZVI powder was measured and added to the 40 mL vial. The pH was then adjusted to 7, using NaOH or HCl as appropriate. Next, the TCE was added directly from the pre-prepared stock solution. Then the vials were capped, foiled and placed on the orbit shaker. Once the appropriate amount of time had passed for the reaction to take place,

the sample would be taken off the orbit shaker and the reaction would be quenched by the addition of methanol. The amount of methanol added was calculated on the assumption that five times the concentration of TCE would be required. The first set of experiments had reaction times of 5,10,15,20,40 and 60 minutes. At a time of 60 minutes, the TCE was below the method detection limit, and therefore it was not necessary to run additional samples with longer reaction times. However, because of the rapid loss of TCE between 10 minutes and 15 minutes, additional experiments were added at 10.5, 11,12,13, and 14 minutes to gain a better understanding of the reaction. The results of this experiment are shown in Figure 10.

Additionally, another experiment was conducted to confirm the hypothesis that a higher persulfate dose would yield a faster TCE destruction rate. In this experiment all the same laboratory protocol was followed as with the aforementioned kinetic experiment. However, for this experiment the molar ratio of persulfate/ZVI/TCE was increased to 50/1/1 (five times the previous molar ratio), and the pH was adjusted to 2 instead of 7, since our pH experiments that 2 was the other optimal pH. The reaction times for the samples were 0, 5, 10, 12, 15 and 20 minutes. Since the destruction seemed to be taking place between, 0 and 5 minutes, additional samples were run at 2, 3 and 4 minutes. The results are plotted in Figure 11.

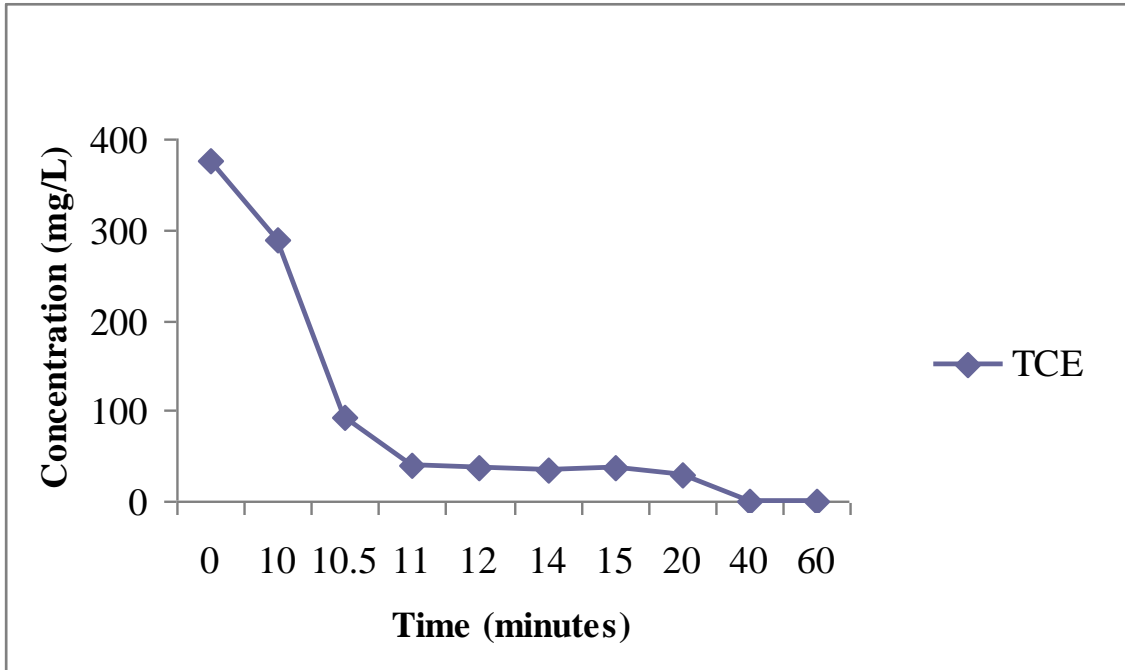


Figure 10: The degradation of TCE by ZVI activated persulfate oxidation over 60 minutes. All experiments were conducted at a molar ratio of 10/1/1 (persulfate/ZVI/TCE), a pH of 7 and an initial TCE concentration of 375 mg/L.

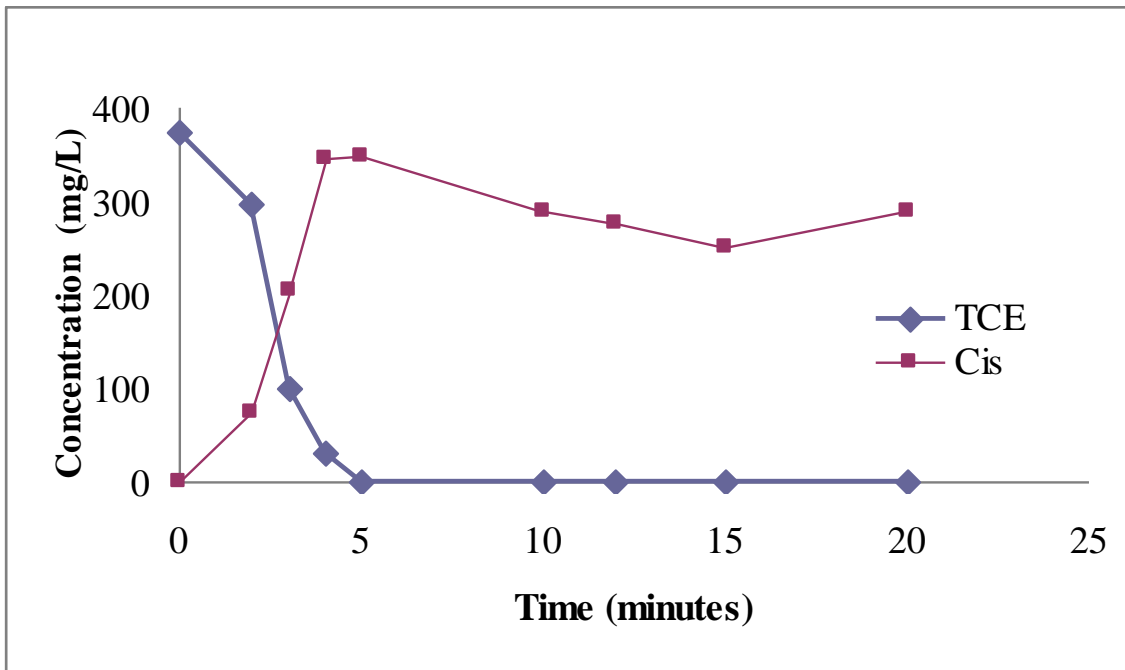


Figure 11: The degradation of TCE by ZVI activated persulfate oxidation over 20 minutes. All experiments were conducted at a molar ratio of 50/1/1 (persulfate/ZVI/TCE), a pH of 2 and an initial TCE concentration of 375 mg/L.

The results in Figure 10 show that the TCE is approximately 90 percent destroyed in 11 minutes. The reaction is rapid between 10 and 11 minutes, with the majority of the TCE degradation taking place in that time frame. Once the TCE reached the 90 percent destruction point, at 11 minutes, the reaction became very slow. Between the time interval of 12 and 20 minutes, there was no change in TCE concentration. At the time interval from 20 to 40 minutes, the TCE decreased again until the concentration was below the method detection limit at 40 minutes.

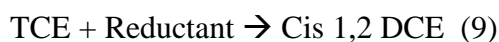
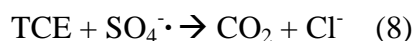
The results in Figure 11 show that the TCE is approximately 90 percent destroyed in 4 minutes. This reaction time is 7 minutes faster than that of the data shown in Figure 10. This can be attributed to the fact that the persulfate dose in Figure 11 is five times greater than the persulfate dose in Figure 10.

Liang et al., (2003) experienced a similar phenomenon in a thermally activated persulfate oxidation of TCE and TCA. Liang et al., (2003) showed that the contaminants were mostly degraded in 6 hours in an aqueous medium, however when the persulfate/contaminant molar ratio was increased the degradation occurred more rapidly.

These results also show that the reaction happened very fast between 0 and 4 minutes, and then the reaction slowed down with the TCE concentration being below the method detection limit at 5 minutes. The presence of the byproduct cis DCE was also detected. The concentration of the cis DCE appeared as the TCE destruction increased. The maximum cis DCE concentrations appeared at the 4 to 5 minute time interval, when the TCE was 90 percent or greater destroyed. Since the reaction was only monitored for 20 minutes, it can be assumed that at some time prior to 24 hours the cis DCE will

completely disappear, as none was detected in the equilibrium results shown in Figure 8 for the same molar ratio.

As mentioned in section 4.3, we hypothesize that the TCE is destroyed through simultaneous oxidation and reduction reactions. Equations (8)-(11) describe the general reactions occurring in detail. The kinetics of TCE removal was determined by assuming the following reactions:



Equations (8)-(11) in section 4.3 to show the formation and degradation of cis DCE and VC ending in ethene for the reduction reactions and the formation of end products carbon dioxide and chloride ions for oxidation reactions.

The rate of destruction of the TCE was calculated from the data collected in Figures 10 and 11 using the following equation:

$$\frac{dC_{TCE}}{dt} = \{-k_1 [\text{reductant}] + -k_2 [\text{SO}_4^{\cdot-}]\} \cdot C_{TCE} \quad (13)$$

By assuming the oxidant and reductant concentrations are steady state, equation (13) can be simplified to a pseudo-first order reaction.

$$\frac{dC_{TCE}}{dt} = -k'_{TCE} C_{TCE} \quad (14)$$

A value for k' was calculated through linear regression of the natural logarithm of the concentration versus time. The results are plotted in Figures 12 and 13. Since the destruction of the TCE occurred very quickly as shown in Figures 10 and 11, only the points until the reaction leveled off were used in the regression line. It was calculated that k'_{TCE} is -0.1464 min^{-1} and -0.6119 min^{-1} for a pH of 7 and molar ratio of 10/1/1 and a

pH of 2 and molar ratio of 50/1/1 respectively. As would be expected, the rate constant for the higher molar ratio of persulfate is greater than the rate constant for the lower persulfate dose. Other research that has looked at persulfate oxidation or TCE dechlorination have also used pseudo first order models for their kinetic analysis. It is important to note how their reaction constants compare with the constants of this study.

A study done by Jiasheng et al., (2008) investigated the oxidation of lindane with ferrous iron activated persulfate oxidation. In their study, they modeled the destruction of lindane as a first order reaction. The first order rate constant, k , was calculated to be 0.1462 h^{-1} .

Similarly, Liang et al., (2007) who studied the influence of pH on thermally activated persulfate oxidation of TCE found that a first order reaction best described the degradation of the TCE. The value of the first order reaction constant, k was found to be 0.0198 h^{-1} .

Hara et al., (2005) conducted a study on the kinetics of TCE dechlorination with iron powder. The iron powder was a metallic iron powder with impurities and was 20 percent ZVI. The objective of the study was to investigate the reaction pathways of TCE dechlorination and determine rate constants. All the reaction pathways were modeled based on a pseudo-first order rate model. The rate constants found for TCE as well as cis DCE and VC are 8.5×10^{-3} , 9.2×10^{-4} , and $4.9 \times 10^{-4} \text{ h}^{-1} \text{ m}^{-2}$ respectively (Hara et al., 2005).

Compared to the kinetic evaluations of the previously mentioned studies, the reaction rate in this work is higher. Which means that the destruction of TCE or other organic solvents should be destroyed quicker via ZVI activated persulfate oxidation than

other methods, including ferrous iron activated persulfate oxidation. Increasing the persulfate dose results in faster destruction rates.

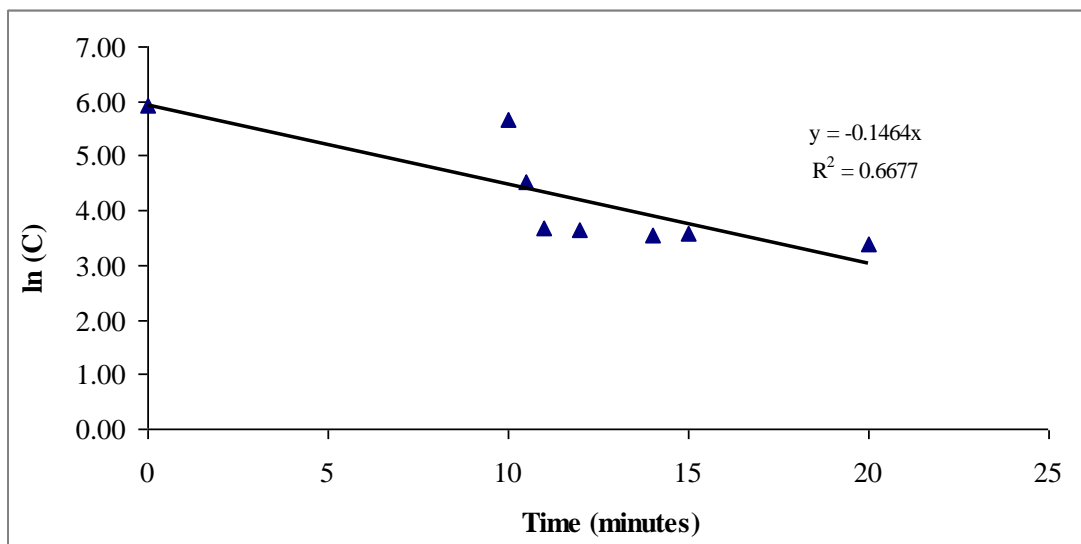


Figure 12: Kinetics of TCE destruction. First order reaction rate constant (k) of TCE destruction as a function of time. All experiments were conducted at a molar ratio of 10/1/1 (persulfate/ZVI/TCE) and a pH of 7.

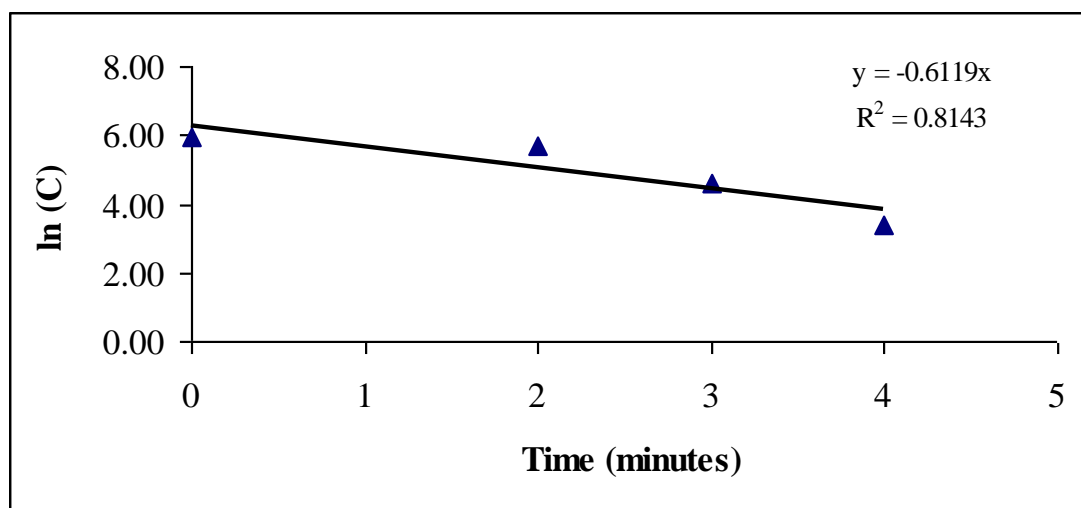


Figure 13: Kinetics of TCE destruction. First order reaction rate constant (k) of TCE destruction as a function of time. All experiments were conducted at a molar ratio of 50/1/1 (persulfate/ZVI/TCE) and a pH of 2.

Chapter 5: Summary

TCE is an organic solvent that has become prevalent in drinking water supplies across the United States. Since TCE is a suspected carcinogen and prolonged exposure can result in a variety of health problems, the EPA has set an MCL of 5 µg/L for drinking water. In an effort to meet this standard, and minimize human exposure, a host of remediation technologies have been used. Chemical oxidation is one of the promising technologies that have been explored as an alternative to more traditional methods such as GAC and air stripping.

The hypotheses of this research were (1) that ZVI can be substituted for Fe^{2+} in a persulfate oxidation by providing ferrous iron (by dissolution), thereby activating the persulfate under a wider range of conditions, and (2) ZVI activated persulfate oxidation can be an effective tool for the destruction of TCE in contaminated waters. To test these hypotheses, we studied the optimum conditions under which this reaction would occur, monitored the destruction of TCE as well as the formation and degradation of the daughter products cis DCE and VC and studied the kinetics of TCE destruction in a simultaneous oxidation/reduction reaction.

According to our results, ZVI activated persulfate oxidation effectively degraded over 80 percent TCE at a pH range of 2-8, with greater than 90 percent destruction occurring at a pH of 2 and 7 at a persulfate/ZVI/TCE molar ratio of 10/1/1. The disappearance of the TCE yielded the production of daughter products cis DCE and VC.

The appearance of these daughter products confirmed that in addition to oxidation, reduction was also taking place. Persulfate dosing experiments showed that with an initial TCE concentration of 375 mg/L, and a pH of 7, a molar ratio of at least 10/1/1 (persulfate/ZVI/TCE) is required. Increasing the persulfate dose results in greater destruction of TCE and associated daughter products. At a molar ratio of 50/1/1 (persulfate/ZVI/TCE) there is complete destruction of TCE, as well as cis DCE and VC.

When the destruction of TCE was measured over time, it was found that approximately 90 percent TCE destruction was seen in 11 minutes. The molar ratio and pH for this experiment was 10/1/1 (persulfate/ZVI/TCE) and 7 respectively. The rate of TCE destruction was -0.1464 min^{-1} . Another kinetic experiment was performed at a molar ratio of 50/1/1 and a pH of 2. It was found that approximately 90 percent TCE destruction was seen in 4 minutes. The rate of TCE destruction was -0.6119 min^{-1} , which is four times as fast as the lower molar ratio of persulfate. Therefore, increasing the persulfate dose, results in faster degradation rates.

Chapter 6: Conclusions and Future Work

Based on the hypotheses for this research, the following conclusions can be made:

- It is feasible to substitute ZVI for Fe^{2+} in a persulfate oxidation by providing ferrous iron (by dissolution).
- The use of ZVI allows the persulfate oxidation to take place under a wide range of conditions. Specifically, this reaction successfully takes place at a pH range of 2-8; therefore there is no need for pH adjustment.
- A minimum persulfate dose of 10/1/1 (persulfate/ZVI/TCE) is required to achieve over 95 percent TCE destruction. Increasing the persulfate dose results in greater destruction of daughter products as well as faster reaction rates.
- The destruction of TCE is taking place via two mechanisms: oxidation and reduction. The presence of daughter products cis DCE and VC confirm that reduction has occurred. Based on the fast nature of the TCE destruction seen in this work and previous research in this area, it is theorized that the responsible reductant is attributed to the persulfate.
- The use of ZVI activated persulfate oxidation has proven to be an effective tool to remediate waters contaminated with TCE. The flexibility of the reaction saves cost and time in comparison with other iron catalyzed oxidations.

Future work should be conducted in the following areas:

- Investigate the effects of varying zero valent iron concentrations.
- Investigate the application of this method in-situ.
- Investigate the possibility of destroying other organic solvents with this method, such as chloroform, toluene or chloromethanes.
- Investigate the effects of ZVI activated persulfate oxidation on a compound such as CTC, which is resistant to oxidation, to study the extent of reduction taking place.
- Further study should be completed to identify the exact reducing agent in this reaction and confirm that it is attributed to the persulfate.
- Finally, future work should look at various reactor configurations and treatment plants that can utilize this technique to remediate TCE.

Reference List

- Agency for Toxic Substances and Disease Registry. (2007). "ToxFAQs™ for Trichloroethylene (TCE)." <http://www.atsdr.cdc.gov/tfacts19.html> (3/12, 2008).
- Arnold, W. A., and Roberts, A. L. (2000). "Pathways and Kinetics of Chlorinated Ethylene and Chlorinated Acetylene Reaction with Fe(0) Particles." *Environ. Sci. Technol.*, 34(9), 1794-1805.
- Balabanova, S.A., Markevich, A.M., 1966. Kinetics of the reaction of ammonium peroxydisulfate with ferrous iron. *Zh. Fiz. Khim.* 40 (4), 775–780.
- Bergendahl J .A. and Thies T.P, Fenton's oxidation of MTBE with zero-valent iron. 2004. *Water Research*, 38(2) 327-334.
- Chen, G., Hoag, G. E., Chedda, P., Nadim, F., Woody, B. A., and Dobbs, G. M. (2001/10/12). "The mechanism and applicability of in situ oxidation of trichloroethylene with Fenton's reagent." *Journal of Hazardous Materials*, 87(1-3), 171-186.
- Chen, Jiann-Long; Al-Abed, Souhail R.; Ryan, James A.; Li, Zhenbin; Effects of pH on Dechlorination of Trichloroethylene by Zero Valent Iron, *Journal of Hazardous Materials*, B83, pp.243-254, 2001
- Doong R, Chang W. 1998. Photoassisted iron compound catalytic degradation of organophosphorous pesticides with hydrogen peroxide. *Chemosphere* 37(13): 2563–72.
- Environmental Protection Agency (EPA). 2001. Sources, Emission and Exposure for Trichloroethylene (TCE) and Related Chemicals. EPA/600/R-00/099. March, 2001. National Center for Environmental Assessment-Washington Office.
- Environmental Protection Agency. "Consumer Factsheet on: Trichloroethylene." http://www.epa.gov/safewater/contaminants/dw_contamfs/trichlor.html (February/6, 2007).
- Francis, A.J., Dodge, C.J., 1998. Remediation of soils and wastes contaminated with uranium and toxic metals. *Environ. Sci. Technol.* 32 (24), 3993–3998.
- Gates, D. D., and Siegrist, R. L. (1995). "In-Situ Chemical Oxidation of Trichloroethylene Using Hydrogen Peroxide." *J. Envir. Engrg.*, 121(9), 639-644.
- Hara, J., Ito, H., Suto, K., Inoue, C., and Chida, T. (2005). "Kinetics of trichloroethene dechlorination with iron powder." *Water Research*, 39(6), 1165-1173.
- Hazard Evaluation System and Information Service. (1997). "Trichloroethylene." <http://www.dhs.ca.gov/ohb/HESIS/tce.htm> (3/12, 2008).

Huang, K., Zhao, Z., Hoag, G. E., Dahmani, A., and Block, P. A. (2005). "Degradation of volatile organic compounds with thermally activated persulfate oxidation." *Chemosphere*, 61(4), 551-560.

Hugh, R., H., Matthews, J., E., and Sewell, G., W. (1992). "EPA Groundwater Issue: TCE Removal from Contaminated Soil and Ground Water." *EPA*, S-92(540),.

Jiasheng Cao, Wei-Xian Zhang, Derick G. Brown, Dalbir Sethi. *Environmental Engineering Science*. March 1, 2008, 25(2): 221-228. doi:10.1089/ees.2006.0244.

Klee, M. S. (2000). *Micro Liquid-Liquid Extraction with the Agilent 7683 Automatic Liquid Sampler*. Agilent Technologies, Inc., USA.

Krishna, M.V.; Chandrasekaran, K.; Karunasagar, D.; Arunachalam, J.; A Combined treatment Approach Using Fentons Reagent and Zero Valent Iron for the Removal of Arsenic from Drinking Water, *Journal of Hazardous Materials*, Vol. 84, No. 2-3, pp.229-240, 2001.

Lavine, Barry K.; Auslander, Glenn; Ritter, Jason; Polarographic Studies of Zero Valent Iron as a Reductant for Remediation of Nitroaromatics in the Environment, *Microchemical Journal*, Vol. 70, pp.69-83, 2001

Liang, C.J., Bruell, C.J., Marley, M.C., Sperry, K.L., 2003. Thermally activated persulfate oxidation of trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) in aqueous systems and soil slurries. *Soil Sedim.Contam.* 12, 207–228.

Liang, C., Bruell, C. J., Marley, M. C., and Sperry, K. L. (2004/6a). "Persulfate oxidation for in situ remediation of TCE. I. Activated by ferrous ion with and without a persulfate-thiosulfate redox couple." *Chemosphere*, 55(9), 1213-1223.

Liang, C., Bruell, C. J., Marley, M. C., and Sperry, K. L. (2004/6b). "Persulfate oxidation for in situ remediation of TCE. II. Activated by chelated ferrous ion." *Chemosphere*, 55(9), 1225-1233.

Liang, C., Wang, Z., and Bruell, C. J. (2007). "Influence of pH on persulfate oxidation of TCE at ambient temperatures." *Chemosphere*, In Press, Corrected Proof(66), 106.

Liang, C., Wang, Z., and Mohanty, N. (2006). "Influences of carbonate and chloride ions on persulfate oxidation of trichloroethylene at 20 °C." *Science of the Total Environment*, 370(2-3), 271-277.

Liu, C., Tseng, D., and Wang, C. (2006/8/25). "Effects of ferrous ions on the reductive dechlorination of trichloroethylene by zero-valent iron." *Journal of Hazardous Materials*, 136(3), 706-713.

Orth, R., Dauda, T., and McKenzie, D. E. (1998). "Reductive Dechlorination of DNAPL Trichloroethylene by Zero-Valent Iron." *Pract. Periodical of Haz., Toxic, and Radioactive Waste Mgmt.*, 2(3), 123-128.

Pignatello, J.J., Baehr, K., 1994. Ferric complexes as catalysts for “Fenton” degradation of 2,4-D and metolachlor in soil. *J. Environ. Qual.* 23, 365–370.

Pignatello, J.J., Day, M., 1996. Mineralization of methyl parathion insecticide in soil by hydrogen peroxide activated with iron (III)–NTA or –HEIDA complexes. *Hazard. Waste Hazard. Mater.* 13 (2), 237–244.

Ponder, Sherman M.; Darab, John G.; Mallour, Thomas E.; Remediation of Cr (IV) and Pb (II) Aqueous Solutions Using Supported Nanoscale Zero Valent Iron, *Environmental Science and Technology*, Vol. 34, No. 12, pp. 2564-2569, 2000

Russell, H. H., Matthews, J. E., and Sewell, G. W. (1992). "TCE Removal from Contaminated Soil and Ground Water." *EPA Ground Water Issue*, .

Sharma, Sachin (2006). “Slurry Test Evaluation for In-Situ Remediation of TCE Contaminated Aquifer”. Worcester Polytechnic Institute. Master of Science Thesis.

Szelewski, M. J., and Quimby, B. D. (2000). *Ambient Headspace GC and GC-MSD Analysis of Non-Polar Volatiles in Water*. Agilent Technologies, Inc., USA.

Tech Tree. (2002). "Permeable Barrier Wall."
<http://www.cpeo.org/techtree/ttdescript/permbarr.htm> (4/3, 2008).

Teel, A. L., Warberg, C. R., Atkinson, D. A., and Watts, R. J. ~2001. “Comparison of mineral and soluble iron Fenton’s catalysts for the treatment of trichloroethylene.” *Water Res.*, 35~4!, 977–984.

United States Environmental Protection Agency. (2006). "Consumer Factsheet on 1,2 Dichloroethylene." <http://www.epa.gov/SAFEWATER/dwh/c-voc/12-dich2.html> (3/12, 2008).

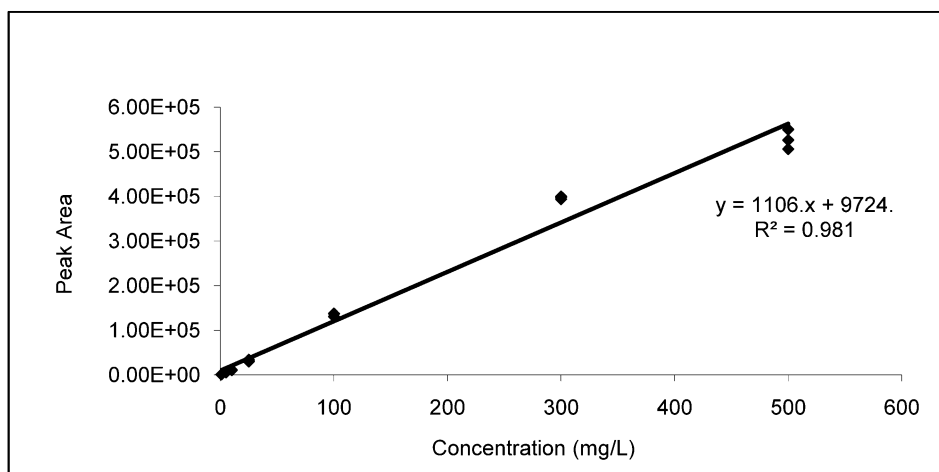
United States Environmental Protection Agency. (2006). "Consumer Factsheet on Vinyl Chloride." <http://www.epa.gov/ogwdw/dwh/c-voc/vinylchl.html> (4/15, 2008).

Watts, R. J., Howsawkeng, J., and Teel, A. L. (2005). "Destruction of a Carbon Tetrachloride Dense Nonaqueous Phase Liquid by Modified Fenton's Reagent." *J. Envir. Engrg.*, 131(7), 1114-1119.

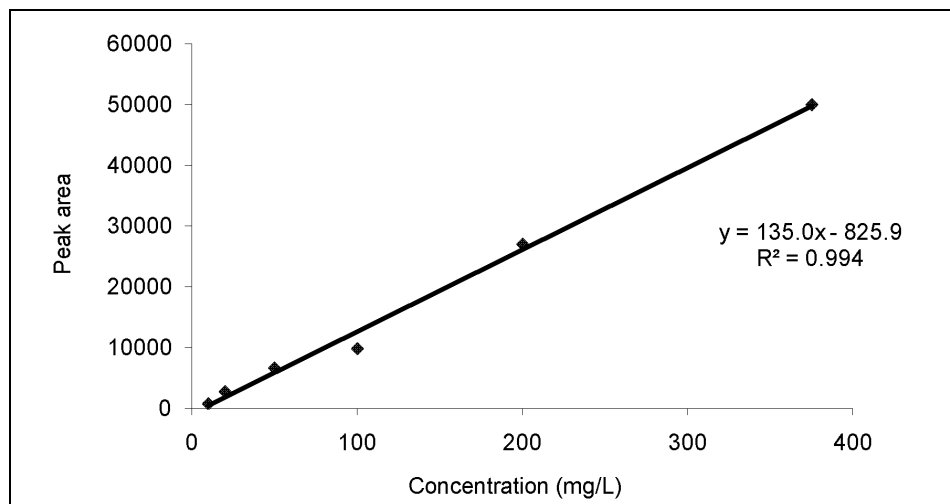
Watts, R. J., and Teel, A. L. (2006). "Treatment of Contaminated Soils and Groundwater Using ISCO." *Pract. Periodical of Haz., Toxic, and Radioactive Waste Mgmt.*, 10(1), 2-9.

World health Organization. Environmental Health Criteria 50: Trichloroethylene. Geneva, 1985.

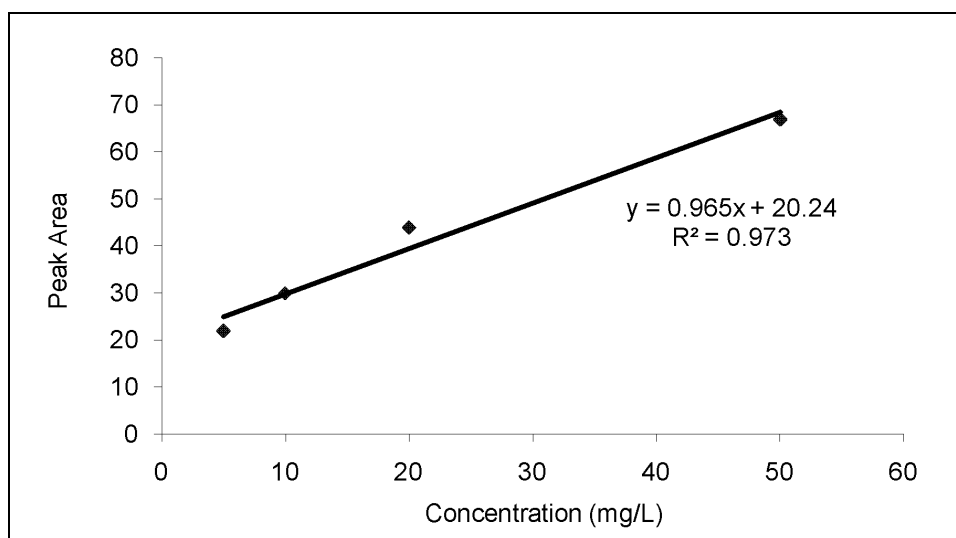
Appendix A: Standard Curves



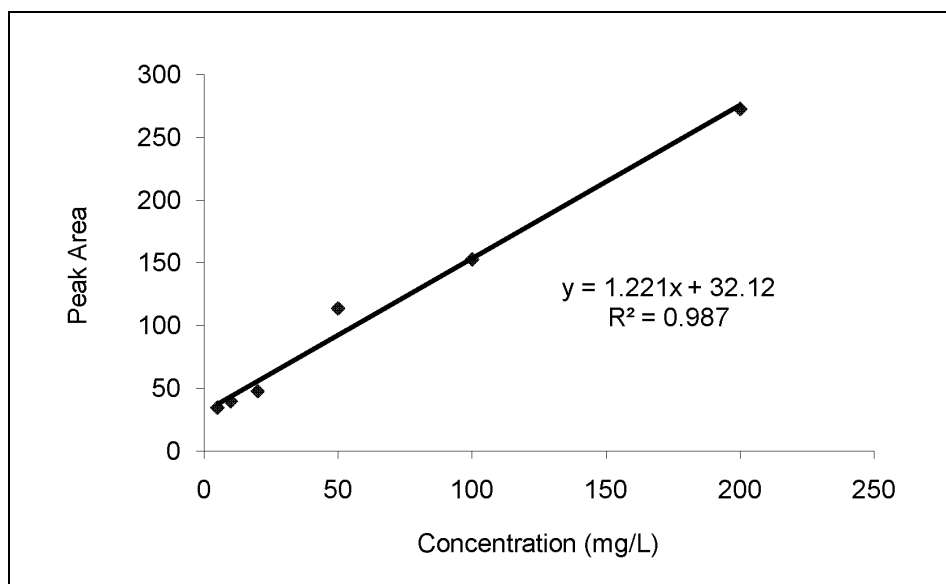
TCE Standard Curve for Head Space Method



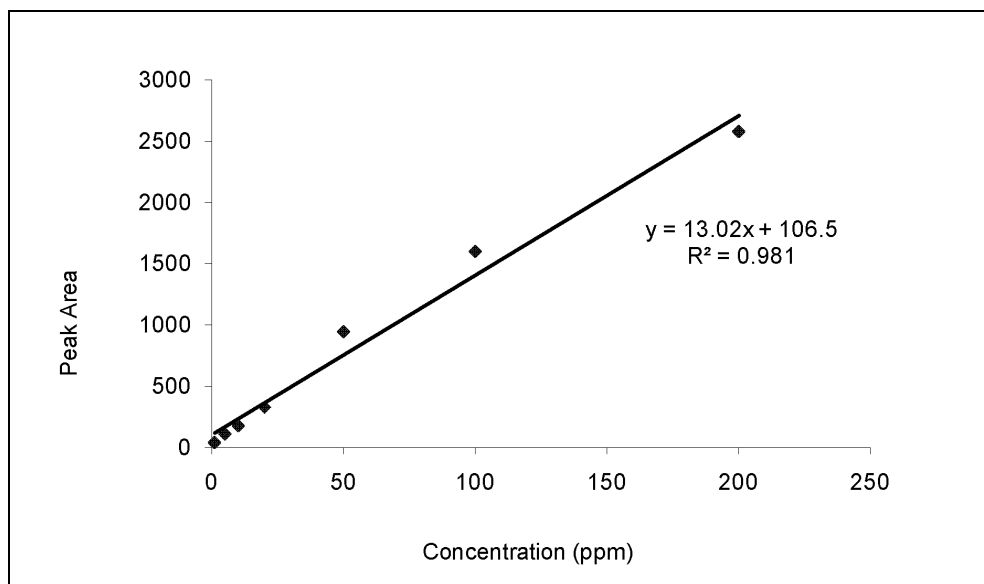
TCE Standard Curve for Micro Liquid Liquid Extraction



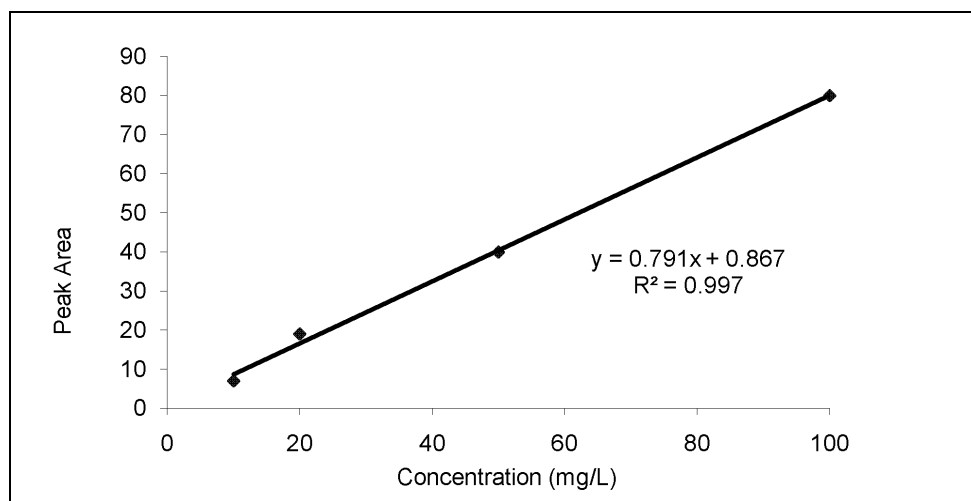
Cis 1,2 DCE Standard Curve for Micro Liquid Liquid Extraction



Trans 1,2 DCE Standard Curve for Micro Liquid Liquid Extraction



1,1 DCE Standard Curve for Micro Liquid Liquid Extraction



Vinyl Chloride Standard Curve for Micro Liquid Liquid Extraction

Appendix B: Preliminary Experiments

TCE + Water	
initial (mg/l)TCE	375
initial total volume(ml)	40
intial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
intial total molesof TCE	0.000114191
final (mg/l))	358
final total volume(ml)	40
final total <i>ug</i> of TCE	14320
MW of TCE <i>ug</i>	131359000
final total molesof TCE	0.000109014
%TCE REMAINING	95.5

TCE + ZVI	
initial (mg/l)TCE	375
initial total volume(ml)	40
intial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
intial total molesof TCE	0.000114191
final (mg/l))	320
final total volume(ml)	40
final total <i>ug</i> of TCE	12800
MW of TCE <i>ug</i>	131359000
final total molesof TCE	9.74429E-05
%TCE REMAINING	85.3

TCE + Fe ²⁺	
initial (mg/l)TCE	375
initial total volume(ml)	40
intial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
intial total molesof TCE	0.000114191
final (mg/l))	319.9
final total volume(ml)	40
final total <i>ug</i> of TCE	12796
MW of TCE <i>ug</i>	131359000
final total molesof TCE	9.74124E-05
%TCE REMAINING	85.3

TCE + Persulfate	
initial (mg/l)TCE	375
initial total volume(ml)	40
intial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
intial total molesof TCE	0.000114191
final (mg/l))	250
final total volume(ml)	40
final total <i>ug</i> of TCE	10000
MW of TCE <i>ug</i>	131359000
final total molesof TCE	7.61273E-05
%TCE REMAINING	66.7

TCE + Persulfate + Fe ²⁺	
initial (mg/l))TCE	375
initial total volume(ml)	40
intial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
intial total molesof TCE	0.000114191
final (mg/l))	20.75
final total volume(ml)	40
final total <i>ug</i> of TCE	830
MW of TCE <i>ug</i>	131359000
final total molesof TCE	6.31856E-06
%TCE REMAINING	5.5

TCE+Persulfate+ZVI	
initial (mg/l))TCE	375
initial total volume(ml)	40
intial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
intial total molesof TCE	0.000114191
final (mg/l))	0.1
final total volume(ml)	40
final total <i>ug</i> of TCE	4
MW of TCE <i>ug</i>	131359000
final total molesof TCE	3.04509E-08
%TCE REMAINING	0.03

Appendix C: pH Experiments

pH 2		pH 2		pH 2	
initial (mg/l)TCE	375	initial (mg/l)TCE	375	initial (mg/l)TCE	375
initial total volume(ml)	40	initial total volume(ml)	40	initial total volume(ml)	40
initial total ug of TCE	15000	initial total ug of TCE	15000	initial total ug of TCE	15000
MW of TCE ug	131359000	MW of TCE ug	131359000	MW of TCE ug	131359000
initial total molesof TCE	0.000114191	initial total molesof TCE	0.000114191	initial total molesof TCE	0.000114191
final (mg/l)	20.5	final (mg/l)	15	final (mg/l)	21
final total volume(ml)	40	final total volume(ml)	40	final total volume(ml)	40
final total ug of TCE	820	final total ug of TCE	600	final total ug of TCE	840
MW of TCE ug	131359000	MW of TCE ug	131359000	MW of TCE ug	131359000
final total molesof TCE	6.24243E-06	final total molesof TCE	4.56764E-06	final total molesof TCE	6.39469E-06
%TCE DESTROYED	95	%TCE DESTROYED	96	%TCE DESTROYED	94.4
pH 3		pH 3		pH 3	
initial (mg/l)TCE	375	initial (mg/l)TCE	375	initial (mg/l)TCE	375
initial total volume(ml)	40	initial total volume(ml)	40	initial total volume(ml)	40
initial total ug of TCE	15000	initial total ug of TCE	15000	initial total ug of TCE	15000
MW of TCE ug	131359000	MW of TCE ug	131359000	MW of TCE ug	131359000
initial total molesof TCE	0.000114191	initial total molesof TCE	0.000114191	initial total molesof TCE	0.000114191
final (mg/l)	76	final (mg/l)	10	final (mg/l)	56
final total volume(ml)	40	final total volume(ml)	40	final total volume(ml)	40
final total ug of TCE	3040	final total ug of TCE	400	final total ug of TCE	2240
MW of TCE ug	131359000	MW of TCE ug	131359000	MW of TCE ug	131359000
final total molesof TCE	2.31427E-05	final total molesof TCE	3.04509E-06	final total molesof TCE	1.70525E-05
%TCE DESTROYED	80	%TCE DESTROYED	97	%TCE DESTROYED	85
pH 4		pH 4		pH 4	
initial (mg/l)TCE	375	initial (mg/l)TCE	375	initial (mg/l)TCE	375
initial total volume(ml)	40	initial total volume(ml)	40	initial total volume(ml)	40
initial total ug of TCE	15000	initial total ug of TCE	15000	initial total ug of TCE	15000
MW of TCE ug	131359000	MW of TCE ug	131359000	MW of TCE ug	131359000
initial total molesof TCE	0.000114191	initial total molesof TCE	0.000114191	initial total molesof TCE	0.000114191
final (mg/l)	69	final (mg/l)	57.5	final (mg/l)	80.5
final total volume(ml)	40	final total volume(ml)	40	final total volume(ml)	40
final total ug of TCE	2760	final total ug of TCE	2300	final total ug of TCE	3220
MW of TCE ug	131359000	MW of TCE ug	131359000	MW of TCE ug	131359000
final total molesof TCE	2.10111E-05	final total molesof TCE	1.75093E-05	final total molesof TCE	2.4513E-05
%TCE DESTROYED	82	%TCE DESTROYED	85	%TCE DESTROYED	79
pH 5		pH 5		pH 5	
initial (mg/l)TCE	375	initial (mg/l)TCE	375	initial (mg/l)TCE	375
initial total volume(ml)	40	initial total volume(ml)	40	initial total volume(ml)	40
initial total ug of TCE	15000	initial total ug of TCE	15000	initial total ug of TCE	15000
MW of TCE ug	131359000	MW of TCE ug	131359000	MW of TCE ug	131359000
initial total molesof TCE	0.000114191	initial total molesof TCE	0.000114191	initial total molesof TCE	0.000114191
final (mg/l)	148	final (mg/l)	26	final (mg/l)	6
final total volume(ml)	40	final total volume(ml)	40	final total volume(ml)	40
final total ug of TCE	5920	final total ug of TCE	1040	final total ug of TCE	240
MW of TCE ug	131359000	MW of TCE ug	131359000	MW of TCE ug	131359000
final total molesof TCE	4.50673E-05	final total molesof TCE	7.91723E-06	final total molesof TCE	1.82705E-06
%TCE DESTROYED	61	%TCE DESTROYED	93	%TCE DESTROYED	98

pH 6	
initial (mg/l)TCE	375
initial total volume(ml)	40
initial total ug of TCE	15000
MW of TCE ug	131359000
intial total molesof TCE	0.000114191

final (mg/l))	118
final total volume(ml)	40
final total ug of TCE	4720
MW of TCE ug	131359000
final total molesof TCE	3.59321E-05

%TCE DESTROYED **69**

pH 7	
initial (mg/l)TCE	375
initial total volume(ml)	40
initial total ug of TCE	15000
MW of TCE ug	131359000
intial total molesof TCE	0.000114191

final (mg/l))	38
final total volume(ml)	40
final total ug of TCE	1520
MW of TCE ug	131359000
final total molesof TCE	1.15713E-05

%TCE DESTROYED **90**

pH 8	
initial (mg/l)TCE	375
initial total volume(ml)	40
initial total ug of TCE	15000
MW of TCE ug	131359000
intial total molesof TCE	0.000114191

final (mg/l))	80
final total volume(ml)	40
final total ug of TCE	3200
MW of TCE ug	131359000
final total molesof TCE	2.43607E-05

%TCE DESTROYED **79**

pH 9	
initial (mg/l)TCE	375
initial total volume(ml)	40
initial total ug of TCE	15000
MW of TCE ug	131359000
intial total molesof TCE	0.000114191

final (mg/l))	150
final total volume(ml)	40
final total ug of TCE	6000
MW of TCE ug	131359000
final total molesof TCE	4.56764E-05

%TCE DESTROYED **60**

pH 6	
initial (mg/l)TCE	375
initial total volume(ml)	40
initial total ug of TCE	15000
MW of TCE ug	131359000
intial total molesof TCE	0.000114191

final (mg/l))	16
final total volume(ml)	40
final total ug of TCE	640
MW of TCE ug	131359000
final total molesof TCE	4.87214E-06

%TCE DESTROYED **96**

pH 7	
initial (mg/l)TCE	375
initial total volume(ml)	40
initial total ug of TCE	15000
MW of TCE ug	131359000
intial total molesof TCE	0.000114191

final (mg/l))	57
final total volume(ml)	40
final total ug of TCE	2280
MW of TCE ug	131359000
final total molesof TCE	1.7357E-05

%TCE DESTROYED **85**

pH 8	
initial (mg/l)TCE	375
initial total volume(ml)	40
initial total ug of TCE	15000
MW of TCE ug	131359000
intial total molesof TCE	0.000114191

final (mg/l))	80.5
final total volume(ml)	40
final total ug of TCE	3220
MW of TCE ug	131359000
final total molesof TCE	2.4513E-05

%TCE DESTROYED **79**

pH 9	
initial (mg/l)TCE	375
initial total volume(ml)	40
initial total ug of TCE	15000
MW of TCE ug	131359000
intial total molesof TCE	0.000114191

final (mg/l))	96
final total volume(ml)	40
final total ug of TCE	3840
MW of TCE ug	131359000
final total molesof TCE	2.92329E-05

%TCE DESTROYED **74**

pH 6	
initial (mg/l)TCE	375
initial total volume(ml)	40
initial total ug of TCE	15000
MW of TCE ug	131359000
intial total molesof TCE	0.000114191

final (mg/l))	12
final total volume(ml)	40
final total ug of TCE	480
MW of TCE ug	131359000
final total molesof TCE	3.65411E-06

%TCE DESTROYED **97**

pH 7	
initial (mg/l)TCE	375
initial total volume(ml)	40
initial total ug of TCE	15000
MW of TCE ug	131359000
intial total molesof TCE	0.000114191

final (mg/l))	13
final total volume(ml)	40
final total ug of TCE	520
MW of TCE ug	131359000
final total molesof TCE	3.95862E-06

%TCE DESTROYED **97**

pH 8	
initial (mg/l)TCE	375
initial total volume(ml)	40
initial total ug of TCE	15000
MW of TCE ug	131359000
intial total molesof TCE	0.000114191

final (mg/l))	21
final total volume(ml)	40
final total ug of TCE	840
MW of TCE ug	131359000
final total molesof TCE	6.39469E-06

%TCE DESTROYED **94**

pH 9	
initial (mg/l)TCE	375
initial total volume(ml)	40
initial total ug of TCE	15000
MW of TCE ug	131359000
intial total molesof TCE	0.000114191

final (mg/l))	284
final total volume(ml)	40
final total ug of TCE	11360
MW of TCE ug	131359000
final total molesof TCE	8.64806E-05

%TCE DESTROYED **24**

pH 10		pH 10		pH 10	
initial (mg/l))TCE	375	initial (mg/l))TCE	375	initial (mg/l))TCE	375
initial total volume(ml)	40	initial total volume(ml)	40	initial total volume(ml)	40
initial total ug of TCE	15000	initial total ug of TCE	15000	initial total ug of TCE	15000
MW of TCE ug	131359000	MW of TCE ug	131359000	MW of TCE ug	131359000
initial total molesof TCE	0.000114191	initial total molesof TCE	0.000114191	initial total molesof TCE	0.000114191
final (mg/l))	300	final (mg/l))	231	final (mg/l))	40
final total volume(ml)	40	final total volume(ml)	40	final total volume(ml)	40
final total ug of TCE	12000	final total ug of TCE	9240	final total ug of TCE	1600
MW of TCE ug	131359000	MW of TCE ug	131359000	MW of TCE ug	131359000
final total molesof TCE	9.13527E-05	final total molesof TCE	7.03416E-05	final total molesof TCE	1.21804E-05
%TCE DESTROYED	20	%TCE DESTROYED	38	%TCE DESTROYED	89

Appendix D: Persulfate Experiments

Molar 1/1/1	
initial (mg/l))TCE	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total molesof TCE	0.000114191

final (mg/l))	284
final total volume(ml)	40
final total <i>ug</i> of TCE	11360
MW of TCE <i>ug</i>	131359000
final total molesof TCE	8.64806E-05

%TCE DESTROYED 24

Molar 10/1/1	
initial (mg/l))TCE	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total molesof TCE	0.000114191

final (mg/l))	14
final total volume(ml)	40
final total <i>ug</i> of TCE	560
MW of TCE <i>ug</i>	131359000
final total molesof TCE	4.26313E-06

%TCE DESTROYED 96

Molar 30/1/1	
initial (mg/l))TCE	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total molesof TCE	0.000114191

final (mg/l))	0
final total volume(ml)	40
final total <i>ug</i> of TCE	0
MW of TCE <i>ug</i>	131359000
final total molesof TCE	0

%TCE DESTROYED 100

Molar 5/1/1	
initial (mg/l))TCE	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total molesof TCE	0.000114191

final (mg/l))	54
final total volume(ml)	40
final total <i>ug</i> of TCE	2160
MW of TCE <i>ug</i>	131359000
final total molesof TCE	1.64435E-05

%TCE DESTROYED 86

Molar 20/1/1	
initial (mg/l))TCE	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total molesof TCE	0.000114191

final (mg/l))	40
final total volume(ml)	40
final total <i>ug</i> of TCE	0
MW of TCE <i>ug</i>	131359000
final total molesof TCE	0

%TCE DESTROYED 100

Molar 40/1/1	
initial (mg/l))TCE	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total molesof TCE	0.000114191

final (mg/l))	0
final total volume(ml)	40
final total <i>ug</i> of TCE	0
MW of TCE <i>ug</i>	131359000
final total molesof TCE	0

%TCE DESTROYED 100

Molar 45/1/1	
initial (mg/l))TCE	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total molesof TCE	0.000114191

final (mg/l))	0
final total volume(ml)	40
final total <i>ug</i> of TCE	0
MW of TCE <i>ug</i>	131359000
final total molesof TCE	0

%TCE DESTROYED **100**

Molar 50/1/1	
initial (mg/l))TCE	375
initial total volume(ml)	40
initial total <i>ug</i> of TCE	15000
MW of TCE <i>ug</i>	131359000
initial total molesof TCE	0.000114191

final (mg/l))	0
final total volume(ml)	40
final total <i>ug</i> of TCE	0
MW of TCE <i>ug</i>	131359000
final total molesof TCE	0

%TCE DESTROYED **100**