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GROUNDWATER REMEDIATION USING MICRO & NANO-SIZED OF ZVI & $KMNO_4$ TO TREAT TRICHLOROETHYLENE (TCE) CONTAMINATION

by

Semienawit Berhabe Ghebrezadik

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

Department: Chemical Engineering
Major: Chemical Engineering
Major Professor: Dr. Stephanie Luster-Teasley

North Carolina A&T State University
Greensboro, North Carolina
2011

School of Graduate Studies
North Carolina Agricultural and Technical State University

This is to certify that the Master's Thesis of

Semienawit Berhabe Ghebrezadik

has met the thesis requirements of
North Carolina Agricultural and Technical State University

Greensboro, North Carolina
2011

Approved By:

Dr. Stephanie Luster-Teasley Major Professor	Dr. Leonard C. Uitenham Committee Member
Dr. Kenneth L. Roberts Committee Member	Dr. Leonard C. Uitenham Department Chairperson

Dean of Graduate Studies
Dr. Sanjiv Sarin

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Semienawit Berhabe Ghebrezadik
2011

DEDICATION

This book is dedicated to my Grandparents, Nor Asfieday & Abrihat Asfieday.

BIOGRAPHICAL SKETCH

Semienawit Berhane Ghebrezadik was born on July 25, 1984, in Asmara Eritrea, Africa. She received a Bachelor of Science degree in Chemical Engineering from North Carolina Agricultural and Technical State University in 2008. She is a candidate for the Maters of Science degree in Chemical Engineering.

ACKNOWLEDGEMENTS

First, I would like to give thanks to my savior Jesus Christ for giving me the strength to complete my work. In addition, I would like to express my gratitude to the people that have made this possible. It is hard to overstate my gratitude to my advisor Dr. Stephanie Luster Teasley for her enthusiasm, inspiration, support and great effort to explain things clearly and simply. Throughout my thesis writing period, she provided encouragement, words of advice, and lots of good ideas. I would also like to thank my committee members for their support and continuous guidance that has enabled me to finish my work successfully. Special thanks to all of my family and friends for heartfelt concern and endless support. This work was supported by National Science Foundation (NSF BRIGE Grant Number #0813631).

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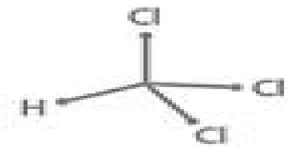
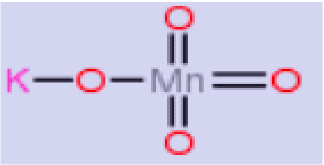
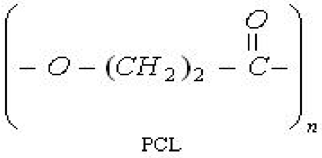
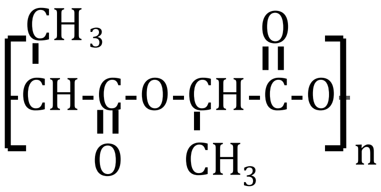
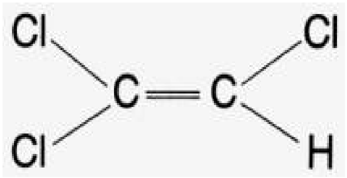
Chloroform	
Potassium Permanganate ($KMnO_4$)	
Polycaprolactone (PCL)	
Polylactic acid (PLA)	
Trichloroethylene (TCE)	

LIST OF SYMBOLS

1, 1-DCE	1-dichloroethylene
CVOCs	Chlorinated volatile organic compounds
DCE	Dichloroetheleyne
DNAPLS	Dense aqueous phase liquids
DPLA	Dissolved PLA Pellets
DPLA~ZVI	Dissolved PLA mixed with micro-size Zero-Valent Iron
DPLA~nZVI	Dissolved PLA mixed with nano-size of Zero-Valent Iron
EDTA	Ethylenediaminetetraacetic acid
EMG	$KMnO_4$ (800 micron)
EMG~MPCL	$KMnO_4$ (800 micron) mixed with Melted PCL Pellets
EMG~ DPLA	$KMnO_4$ (800 micron) mixed with Dissolved PLA Pellets
EPA	Environmental Protection Agency
FML	$KMnO_4$ (50 micron)
FML~ DPLA	$KMnO_4$ (50 micron) mixed with Dissolved PLA Pellets
FML~MPCL	$KMnO_4$ (50 micron) mixed with Melted PCL Pellets
Kob	Pseudo- order rate constant
Koc	Organic carbon adsorption coefficient
$KMnO_4$	Potassium permanganate
ISCF	In-situ chemical flushing
MnO_2	Manganese dioxide
MPCL	Melted PCL Pellets

MPCL~ZVI	Melted PCL mixed with micro-size Zero-Valent Iron
MPCL~nZVI	Melted PCL mixed with nano-size Zero-Valent Iron
nZVI	Nano-size Zero-Valent Iron
PCL	Polycaprolactone
PCE	Perchloroethylene
PLA	Polylactide acid
PSD	Particle size distribution
ppm	Parts per million
TCE	Trichloroethylene
VOC	Volatile organic compound
ZVI	Micro-size of Zero-Valent Iron

ABSTRACT

Ghebrezadik, Semienawit Berhane. GROUNDWATER REMEDIATION USING MICRO AND NANO-SIZED ZVI AND $KMnO_4$ TO TREAT TRICHLOROETHYLENE (TCE) CONTAMINATION. **(Major Professor: Dr. Stephanie Luster Teasley)**, North Carolina Agricultural and Technical State University.

Liquid and gaseous oxidants for years have demonstrated the ability to reduce or destroy organic compounds that can be harmful. Using the fundamental concepts of chemical oxidation, this research investigates the ability to develop solid structured controlled release systems that are able to deliver chemical oxidants and reduce chemicals for environmental remediation. Controlled release systems have become widely used for various applications such as in medical and agricultural industries. Applying this knowledge, micro to nano-sizes of potassium permanganate ($KMnO_4$) and zero-valent iron (ZVI) were encapsulated in two biodegradable polymers. The biodegradable polymers used were polycaprolactone (PCL) and polylactic acid (PLA). Encapsulation of oxidants within biodegradable polymers offers a novel application for environmental remediation.

The objective of this study was to study the degradation of trichloroethylene (TCE) using nano-particle zero-valent iron (nZVI) and potassium permanganate. The focus was to understand the chemical processes involved with groundwater remediation using these chemicals and develop a method to improve the controlled release remediation process by adapting the method used to encapsulate the oxidants. Both melt dispersion and a solvent based methods were investigated for chemical encapsulation.

The results show that the micro and nano-size particles released at different rates from the structures; however, the rate at which the oxidant or reducing agent released from the polymer ultimately determined the effectiveness in the remediation of trichloroethylene (TCE) in water.

CHAPTER 1

INTRODUCTION

1.1 Background and Theory

Chlorinated ethylene compounds represent a family of environmental contaminants that create a major challenge in groundwater remediation (Clark, Rao, and Annable, 2002). These compounds are a major concern because they have the potential to impact subsurface aquifers. Groundwater contamination due to chlorinated solvents is a wide spread problem in the United States and the focus for many environmental remediation projects. Since the industrial revolution, the amount of contaminated groundwater and soil from manufacturing, government use, and industrial use of chlorinated solvents has become a focus for remediation activities. The challenge for environmental remediation is to develop effective technologies able to remediate contaminated sites in a timely and cost effective manner.

Major research efforts to remediate chlorinated solvents began in the early 1980's to develop effective methods of treating or removing harmful solvents found in groundwater and soil (Bouwer, Rittmann, and McCarty, 1981). These studies primarily focused on the treatment of chlorinated ethylenes which include chemicals such as perchloroethylene (PCE), trichloroethylene (TCE), 1, 1-dichloroethylene (1, 1-DCE), and vinyl chloride (VC). The physical and chemical characteristics for chlorinated ethylene compounds include the properties of being classified as a volatile organic compound (VOC) exhibiting low solubility in water. Chlorinated solvents are colorless in appearance, have a slightly sweet odor, and possess a high affinity towards organic matter or carbon-based compounds. These solvents are also classified as dense aqueous phase liquids (DNAPLS), which are compounds that posses a specific gravity greater than water. Due to these properties, chlorinated solvents are denser than groundwater and as a result sink to the bottom of the aquifer. DNAPLS are harmful to aquatic organisms and may cause long-term effects in the aquatic environment. When plants, animals and humans are exposed to DNAPLS, the chemicals contribute to high toxicity within species.

Widespread contamination of groundwater by trichloroethylene (TCE) is challenging in the United States due to its use at airports, government facilities, gas stations, and dry cleaning businesses. Trichloroethylene (C_2HC_{l3}) is a chemical that is commonly-used as a cleaning solvent. This substance can be found in air, soil, and drinking water. TCE has garnered widespread concern due to its use in industrial cleaning processes from the 1970's to 1980's prior to scientists understanding the environmental impact of the solvent. TCE was also used in commercial and industrial applications such as a grease remover on metal parts, breaking down fats, waxes, resins, paints, and varnishes. TCE is able to migrate through the unsaturated (or vadose) zone of aquifers, which is the region between the ground surface and the groundwater level, and in some cases reach the underlying saturated zone which is shown in figure 1.1. The U.S. Environmental Protection Agency (EPA) estimates that one third of the country's drinking water contains trichloroethylene and it contains a TCE concentration of 0.3 parts per million (ppm). Human exposure to trichloroethylene contamination can occur through inhalation, absorption through the skin, drinking, and eating foods that contain this chemical. Once TCE enters the body it can affect many parts of organs like liver, kidney, blood, nervous system, cardiovascular system, reproductive system, and immune system in humans (Galant and Avramenko, 2005).

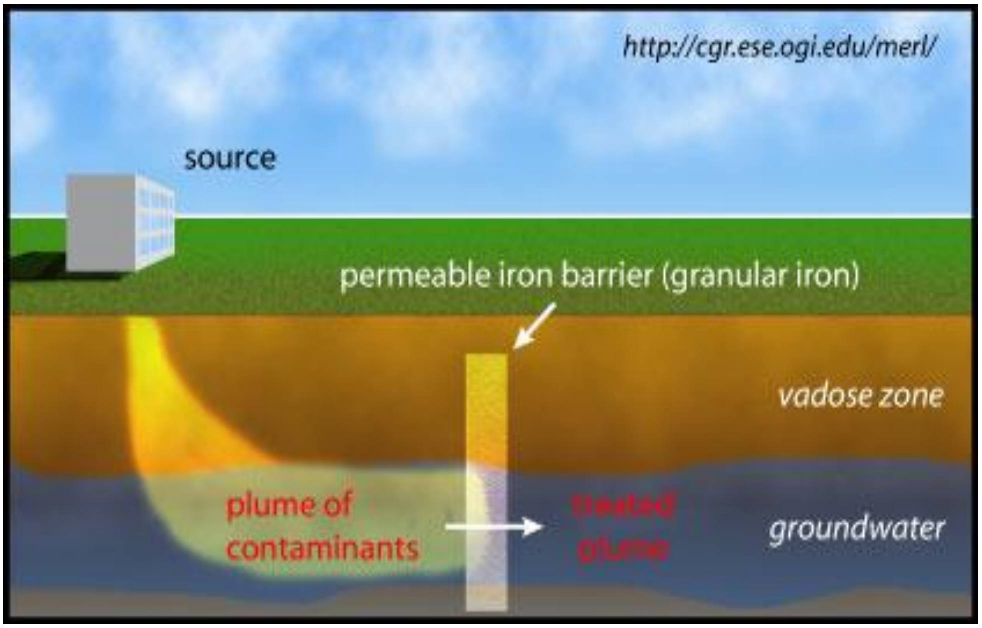


Figure 1.1. Groundwater remediation (Tratnyek and Johnson, 2005)

TCE remediation in soil and water is achieved by implementing either in-situ or ex-situ remediation at a site. In-situ treatments are processes that can be implemented at the contaminated site without the need to excavate the area. In-situ treatments consist of oxidation using potassium or sodium permanganate, ozone, peroxone oxidation, integrated remedial processes, anaerobic biological mineralization, anaerobic dechlorination, aerobic biological mineralization, modified Fenton's Reagent, and activated persulfate oxidation. The disadvantages in-situ remediation are longer treatment time periods needed to complete clean a site and less assurance about the consistency of treatment due to unpredictable behavior of water flow and soil properties subsurface in the aquifer. In-situ treatment may require permits and the effectiveness of the process may not be easy to prove. Recently, in-situ chemical oxidation has been used to remediate hazardous waste sites with soil and groundwater contaminated with organics (Environment Security Technology Certification Program, 1999). Examples of successful in-situ delivery systems for TCE oxidation treatments include: deep soil mixing, hydraulic fracturing, multi-point vertical lancing, horizontal well recirculation, and vertical well recirculation. Ex-situ treatments are used when site remediation can be achieved my pumping or excavating a site. These methods usually require shorter time periods and are considered to be more consistent methods of treatment. The disadvantages of ex-situ methods are that the groundwater needs to be pumped to the surface for treatment or contaminated soil must be excavated and transported for remediation. Ex-situ therefore requires the use of heavy equipment, qualified employees available 24-hours a day to monitor the system, and environmental permits to pump and transport hazardous waste.

In-situ chemical oxidation treatments have proven to be some of the most effective methods for site remediation. Chemical oxidation involves redox reactions that chemically transform hazardous contaminants to nonhazardous or less toxic compounds. Examples of chemical oxidants include ozone, hydrogen peroxide, hypochlorites, chlorine, chlorine dioxide, potassium permanganate, and Fenton’s Reagent. In-situ remediation using chemical oxidation compounds effective at reducing TCE contamination has proven to be effective in a number of studies (Nesheiwat, 2000). The method entails injecting oxidizing chemicals into contaminated soil and water for remediation. The major advantage to using in-situ chemical oxidation is that it is possible to complete site remediation within months. Chemical oxidation is efficient, does not produce major wastes; however, this method can be expensive due to the cost of the oxidants and the site supervision needed for safety during remediation.

Two oxidants that are effective at TCE remediation and the topics of many remediation studies in literature are potassium permanganate and zero-valent iron. Potassium permanganate ($KMnO_4$) is an example of a chemical oxidant used for TCE soil and groundwater treatment. This oxidant has demonstrated promising results for remediating sites contaminated by chlorinated alkenes solvents such as trichloroethylene (TCE) and perchloroethylene (PCE). When the reaction takes place between $KMnO_4$ and TCE, the final oxidation products are carbon dioxide, chloride salt, hydrochloric acid and manganese dioxide (MnO_2) (Yan and Schwartz, 2000). Zero-valent iron (ZVI) is a metal that is able to reduce contaminants to non-toxic forms through electron transfer at the surface of the metal. ZVI has the capability of reductive degradation of chemical pollutants, such as PCBs, TCE, pesticides and chlorinated organic solvents in biosolids (Li and Schwartz, 2004). Since the early 1990’s, zero-valent iron has been used in several field applications for groundwater remediation (Kim, Jung, Kim, and Yang, 2009). Due to its low cost and non-toxicity, zero-vale nt iron became highly used for site remediation (Park, Kanel, and Choi, 2009).

1.2 Thesis Outline

For this thesis work, nano-sized zero-valent iron (nZVI) and potassium permanganate are used to investigate the degradation of trichloroethylene (TCE). The primary focus of this research was to develop a controlled release chemical oxidation/chemical reduction system using polymers to slowly deliver oxidants. The work investigated the use of ZVI nano-particles and micro-sized potassium permanganate encapsulated in polycaprolactone (PCL) and polylactide acid (PLA). Using $KMnO_4$ and ZVI as the chemical oxidizing/reducing agent, the polymer delivery system was investigated to determine the best oxidizing methods. This thesis will provide in Chapter 2 a literature review to present various methods for TCE remediation, the steps taken to improve the method of remediation, and how nanotechnology plays an important role in the future of remediation. Additionally, Chapter 2 includes the literature reviews for the different technologies and summarizes publications addressing $KMnO_4$, ZVI, and ZVI nano-particles used for remediation. These papers will include the $KMnO_4$ reaction kinetics with TCE, the ability to control the precipitation of MnO_2 and methods used to reduce the MnO_2 salt formation. The literature review addresses ZVI reaction kinetics for TCE degradation, the effect of particle size on TCE degradation, and lastly the ability for encapsulated oxidants to degrade contaminants and degradation kinetics. Chapter 3 discusses the methodology used in the thesis and also discusses the details of the steps taken to evaluate the experiments. Results and discussion are presented in Chapter 4 and chapter 5 includes the conclusions and suggestion for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Chemical oxidation

Chemical oxidation has been used extensively for the treatment of pollutants in drinking water and wastewater applications for over 50 years. Chemical oxidation is a growing class of remediation technologies in which organic contaminants are degraded in a porous soil matrix by oxidants delivered to the subsurface. The chemicals used to oxidize contaminants are divided into two categories: oxidants or reducing agents depending on the standard mode of action. These chemicals are typically referred to as redox chemicals. Redox chemicals are able to remediate a site within a few months or years compared to multiple years required using solely bioremediation. As with any remediation system, however, redox treatments have several drawbacks. One such drawback is controlling the distribution of the chemical in the subsurface. Liquid or gaseous oxidants are injected subsurface by injecting the redox compound into the ground through an injection wells. The problem occurs in the movement of the chemicals to the contaminated location and the direct pathway of these contaminants produces a non-uniform distribution rendering the process incomplete. Thus the method requires repeated applications of the chemical to complete remediation efforts. Oxidation remediation requires the use of experienced contractors because the high reactivity of the redox chemicals with contaminants can lead to explosion hazards.

2.2 $KMnO_4$ Reaction Kinetics with TCE

Chemical oxidation using potassium permanganate ($KMnO_4$) is typically performed by dissolving $KMnO_4$ in water to achieve a 4% $KMnO_4$: water by volume ratio. Soil and groundwater treatments have demonstrated promising results for remediating sites using dissolved $KMnO_4$. The reaction between TCE and $KMnO_4$ results in the production of carbon dioxide, chloride salt, hydrochloric acid and manganese dioxide (Yan et al., 2000). For the chemical reaction to occur the stoichiometry requires a ratio of 2:1 for oxidant to TCE as shown below in Equation 2.1.

$$C_2HC_{l2} + 2KMnO_4 \rightarrow 2CO_{2(aq)} + 2MnO_{2(s)} + 2KCl + HCl \qquad (2.1)$$

Oxidation using $KMnO_4$ involves cleavage of carbon-carbon bonds which is often facilitated by free-radical oxidation mechanisms. Magnesium dioxide is a brown precipitate that hinders TCE remediation using potassium permanganate due to clogging that occurs in the pore space during subsurface treatment. The formation of MnO_2 precipitate decreases remediation efficiency by reducing the hydraulic conductivity of the soil in the treatment zone, thus limiting the water movement. The precipitation of MnO_2 and the formation of the CO_2 bubbles near zones of high dense non-aqueous phase liquid (DNAPLs) saturation (DNAPLs) may cause plugging of the pores in the soil media, which would contribute to low flushing efficiency and reduce the rate of DNAPL removal. Since MnO_2 is insoluble in water, this could also produce complications with the oxidative process. Schnarr, Truax, Farquhar, Hood, Gonullu, and Stickney (1998) observed in their work that this method proves to be difficult to control subsurface because permanganate injected into the surface moves along to the uncontaminated area without completing degradation at a desired site. To address this problem, Chapman Ross et al. (2005) hypothesized it would be feasible to encapsulate particles of potassium permanganate in polymer shells.

Oxidative dechlorination of chlorinated solvents by permanganate is a potential technology for the remediation of groundwater contaminated with dissolved chlorinated contaminants (Schnarr et al., 1998; Huang et al., 1999; Yan and Schwartz, 1999). Organic compounds can be oxidized by permanganate through diverse reaction pathways including electron abstraction, hydrogen atom abstraction, hydride ion abstraction and oxygen donation (Stewart, 1964; Gardner and Mayer, 1995). These reaction pathways will depend on the structure of the substrates and the acidity of the solutions, hence impacting the ability to remediate a site.

Yan et al. (1999) researched the oxidative treatment of five chlorinated ethylene compounds in groundwater using the oxidative compound potassium permanganate. The chlorinated ethylene compounds used in the research investigated trichloroethylene (TCE), tetra-chloroethlyene (PCE), and the isomers of dichloroetheleyne (DCE). This study consist of both laboratory and field experiments which were conducted to measure the remediative ability of potassium permanganate ($KMnO_4$) to eliminate five sets of chlorinate solvents. The work provided a detailed understanding of the remediation process by examining the reaction order, degradation rate and the kinetic behaviors of the chlorinated ethylene in reaction with the potassium permanganate. Additionally the study investigated the extent of dechlorination and the effects of pH and other organic compounds in TCE degradation subsurface. The experiments were conducted in sealed reaction vessels where a zero headspace was maintained at all times. Studies conducted by Yan and Schwartz (1999) also tested the adjustment of the environment by maintain a pH level between of 4 to 8. The rate of reaction experiment carried out in the research paper was done by utilizing several systems for five chlorinated ethylene compounds and then measured over time on the reaction with potassium permanganate. The study conducted by Yan et al. (1999) measured the chlorine ion concentration, pH level, temperature, and concentration of the chlorinated ethylene compounds over time. The research also investigated the consumption rate of potassium permanganate by other organic compounds, other than chlorinated ethylene, present in reactor system. Potassium permanganate was isolated by using the solution containing various percentages of landfill leachate with excess concentrations of organic compounds which would interfere or retard the ability for potassium permanganate to react only with TCE.

Yan and Schwartz (1999) proposed a model for the rate of reaction for the reaction between chlorinated ethylene compounds and potassium permanganate (Equation 2.2).

$$\alpha C_2Cl_nH_{4-n} + \beta MnO^-_4 \rightarrow \gamma\ CA + \delta MnO_2 + \xi\ Cl^- \qquad (2.2)$$

The experiment determined the reaction is a second order reaction. Equation 2.2 represents the reaction kinetics where as the reaction kinetics, k, is the rate constant and k_{ob} is the pseudo- order rate constant.

Yan et al. (1999) degradation experiment investigated five different chlorinated ethylene compound and determined the degradation behavior for the chlorinated ethylene compounds depicts a pseudo-first order rate constant. The rate constant indicates the rate at which the reaction occurs. The degradation rate is inversely proportional to the number of the chlorine ions substituted in the chlorinated ethylene. Yan and Schwartz hypothesized the steps for the reaction occurs by first with MnO_4 by attacking the double bond to form a cyclic complex. This is similar to the oxidation of ethylene in solution. The experiment conducted measured chloride concentration and showed how the measurement of TCE was based on the chlorine concentration. The concentration of TCE is inversely proportional to chlorine ions present in the system stochiometrically. This work suggest that as the chlorine concentration increases, the TCE concentration decreases over time making the TCE dependent on chlorine ion as seen in Figure 2.1.

Yan and Schwartz (1999) proposed that during the reaction of chlorinated ethylene and potassium permanganate, carboxylic acid byproducts will be formed. To prove this theory, they examined the change in acidity of the reaction. A drop in pH from 5 to 3 was observed within several minutes of the reaction. The effects of the reduction in pH were studied in the degradation of TCE. The experiment measured the rate of the reaction based on the change of the pH level. The experiment showed that the pH had no effect on the degradation of TCE. The study also showed that chlorinated ethylene can be rapidly degraded by permanganate in aqueous solutions. Extensive kinetic studies done by Yan and Schwartz proved that the reaction can be reasonably described as a second order reaction. Complete dechlorination and possibility the formation of organic acids suggests that the degradation products of chlorinated ethylene are much less harmful than the initial concentration.

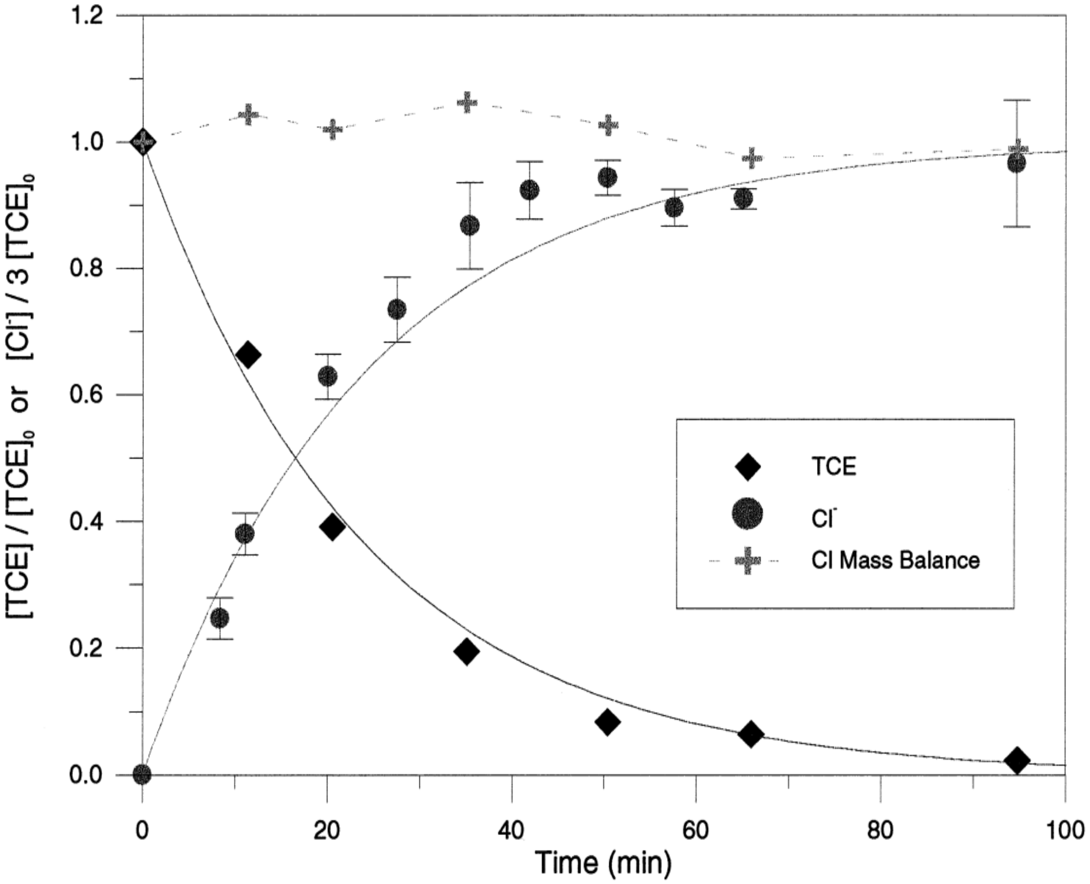


Figure 2.1. TCE oxidative reduction and production of Cl ions at pH 7 (Yan & Schwartz, 1999)

The studies indicated that reaction pathway of oxidation of TCE with $KMnO_4$ proceeds an initial step which includes a formation of a cyclic hypomanganate intermediate (Yan et al., 2000). This may lead to the formation of different carboxylic acids (i.e. formic acid, glycolic) acid, glyoxylic acid and oxalic acid depending on the reaction conditions or state. The Yan et al. (2000) study focused on: 1) The identify the reaction products, 2) clarifying the reaction pathways and their pH dependence 3) development of a kinetic model and 4) determining the kinetic parameters of $KMnO_4$ and TCE. In this their study, four carboxylic acid intermediate products were formed. These were formic, oxalic, glyoxylic and glycolic acids. Within one hour of reaction time, most of the initial TCE was converted to either formic acid or oxalic acid. It is suggested that carboxylic acid is formed because of the strong electron-withdrawing chlorine atoms in TCE. This method is believed to initiate HCl removal of α-haloalcohols and haloketones produced throughout the reaction and by enhancing the initiation of hydroxyl ions from the solvent to join the positively charged carbon atoms. The product analysis indicated that the majority of the TCE was converted to CO_2 and for this transformation to take place the pH values were between 4 to 8.

Several studies demonstrate the effectiveness of chlorinated solvent reduction by $KMnO_4$. Vella and Veronda (1992) reported that in batch experiments, $KMnO_4$ (50 mg/L) completely reduced TCE (8-10 mg/L) in tap water in about four hours. Gates and Siegrist (1995) research investigated the destruction of TCE and PCE using a 5% (by weight) solution of $KMnO_4$. This resulted in 93% and 99% destruction of PCE and TCE, respectively in artificially contaminated soil slurries. The Schnarr et al. (1998) study used in-situ chemical flushing (ISCF) by injecting $KMnO_4$ solution into artificially contaminated sheet-piling-contained soil. Literature suggests, ISCF is a realistic method from former published work that indicates that $KMnO_4$ rapidly mineralizes TCE in the aqueous phase (Vella et al., 1992).

Hoag et al. (1998) studied the kinetics of oxidation of TCE by $KMnO_4$ in a homogeneous aqueous system by using a zero headspace system. Their investigation concluded that the oxidation of TCE by $KMnO_4$ is second order overall and first order individually. The second-order rate constant and the activation energy under the experimental conditions were k = 0.83 ±0.05 M and AE = 35 ± 3 kJ/mol, respectively. It also established the reaction stoichiometry (i.e., 2 mol of $KMnO_4$ are required for the mineralization of 1 mol of TCE). The behavior of the reaction between TCE and $KMnO_4$ was modeled using an irreversible second-order model and by keeping the pH and temperature constant. The concentration reduction, or change throughout the reaction, was predicted by the model. During the reactions of TCE and $KMnO_4$, the study indicated a reasonable behavior which can be useful in predicted similar behaviors in soil system.

2.3 Removable Magnesium oxide (MnO_2)

When $KMnO_4$ is used to treat TCE, it breaks down chlorinated ethylene to CO_2 and Cl^- ions while the MnO_4^- ion reduces to MnO_2 (Yan et al., 2000). In previous studies for chemical oxidation, research indicated that in soil, TCE and $KMnO_4$ produce MnO_2 which can potentially reduce the permeability of the porous medium. To develop a method to control MnO_2 formation, Schwartz (2004), evaluated the use of citric acid, oxalic acid and ethylenediaminetetraacetic acid (EDTA). The results from this experiment have shown that EDTA provides the highest dissolution rate and nitric acid the lowest. Citric acid and oxalic acid also promotes MnO_2 oxide dissolution at a reasonable rate. Proton-promoted dissolution is slow and probably appropriate to treat problem of plugging, which nitric acid also produces proton-promoted and it important at low pH.

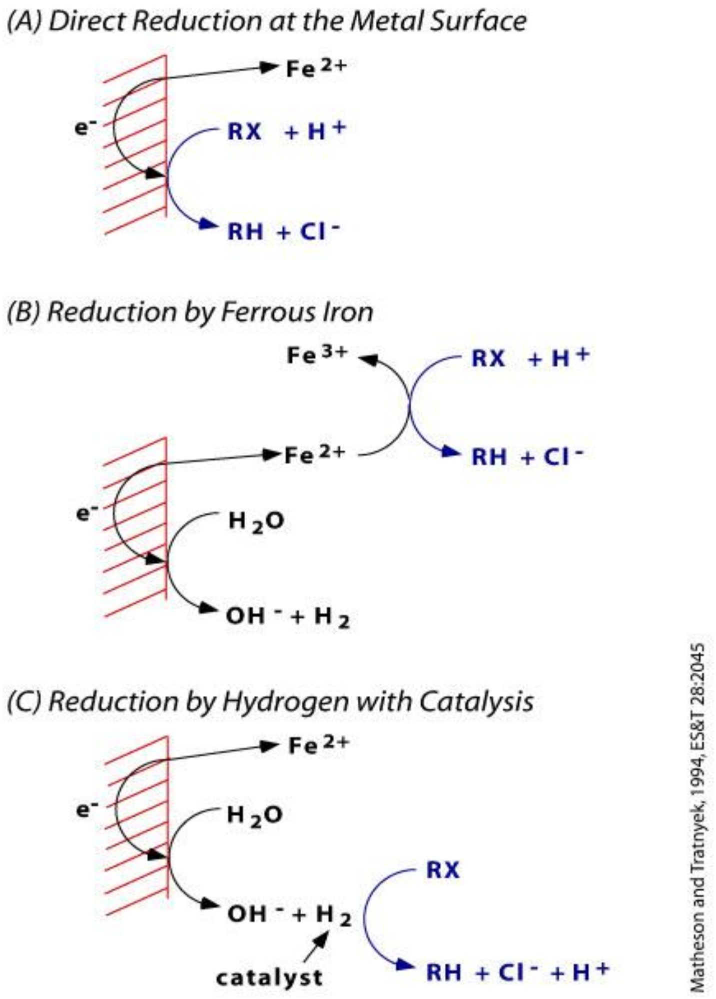
Zhaohui Li (2004) studied the enhancement of trichloroethylene (TCE) degradation by $KMnO_4$ in aqueous solution in the presence of a surfactant. Some studies have proposed that combination of surfactants improves the solubilization of DNAPLs with fast degradation rate of permanganate in one step to achieve synchronized pump-and-treat. The study evaluation process was performed through a continuously stirred batch reactor system with permanganate as the limiting reagent and free phase TCE. By continuously monitoring the amount of chloride produced and the rate of permanganate consumed, the degradation of TCE was determined. The results have shown that the production of chloride indicated that the TCE is being reduced. Previous results have shown that TCE degradation follows a pseudo-first-order reaction kinetics with respect to $KMnO_4$ in the presence of free phase TCE. The TCE in the system and $MnO_{4,}$ as the limiting reagent, followed an overall second order reaction (Yan et al., 1999; Yan et al., 2000; Huang et al., 1999). The overall second order reaction can be approximated as pseudo-first-order reaction and is presented in equation 2.3.

$$\frac{1}{3}\frac{d[Cl^-]}{dt} = -\frac{1}{2}\frac{d[MnO_4^-]}{dt} = k_{obs}[MnO_4^-] \qquad (2.3)$$

This study observed when surfactants were not present, the reaction rate constant was pseudo-first-order rate constant (kobs) where kobs = 0.08–0.19 min$^{–1}$ and the half-life (t_1=2) was 4–9 min for MnO_4. As the critical micelle concentration (CMC) was increased, the k_{obs} values increased to k_{obs} = 0.42–0.46 min and the half-life (t_1=2) reduced to 1.5–1.7 min for MnO_4. When the CMC decreased and the surfactant concentration increased, the kobs values increased to 0.56–0.58 min$^{–1}$ and the half-life (t_1=2) reduced to 1.2–1.3 min.

2.4 ZVI/nZVI Reaction Kinetics with TCE

Zero-valent iron is a chemical that is able to remediate chemical pollutants, such as PCBs, TCE, pesticides and chlorinated organic solvents in biosolids. (Li et al., 2004 ; Kim et al., 2009 ; Park et al., 2009). The reaction between a contaminant and zero-valent iron occurs at the surface of the metal where electrons are exchanged between the metal and the contaminant. The chemical pathways for TCE oxidation are demonstrated in Figure 2.2. From Figure 2.2, Pathway A depicts direct reduction of an organic contaminant at the iron surface. This pathway represents direct electron transfer from the iron (Fe) to the adsorbed halocarbon denoted as RH at the metal-water interface. This results in dechlorination and production of Fe(II). Pathway B demonstrates reduction by ferrous iron. For this reaction, Fe(II) reacts by exchanging electrons with the contaminant to result in the production of Fe(III). Pathway C represents reduction by hydrogen with catalysis. For Pathway C, H_2 transfers from the anaerobic corrosion of Fe(II) and react with RX if an efficient catalyst is present.



Matheson and Tratnyek, 1994, ES&T 28:2045

Figure 2.2. Zero-valent iron pathways reaction with organic compound (Tratnyek and Johnson, 2005)

The reaction between TCE and ZVI involves the transfer of two-electrons from the iron atom to the TCE compound. Trichloroethylene (C_2HC_{l3}) can readily accept the electrons from iron oxidation and releases chloride ions from the chemical structure resulting in the production of ethane. For corrosion of ZVI by aqueous TCE in anaerobic solutions, the anodic reaction is given by Equation 2.4 -2.6.

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (2.4)$$

$$H_2O + H^+ + 2e^- \rightarrow H_2 + OH^- \qquad (2.5)$$

$$C_2HCl_3 + 3H^+ + 6e^- \rightarrow C_2H_4 + 3Cl^- \qquad (2.6)$$

ZVI can degrade TCE much faster than biodegradation; however this process may take days with micron-sized ZVI (Gotpagar, 1998). According to Wei-xian Zhang (1998), the limitation of micro ZVI is the surface area and because the oxygen in the air reduces the ability to reduce TCE at the surface of the metal. To improve ZVI reductive dechlorination, researchers have begun investigating the use of nano-scale ZVI. Nano-particles are of interest for TCE remediation because they exhibit increased surface area, are more mobile, and more reactive when compared to micron sized iron (EPA, 2005).

According to the United States Environmental Protection Agency (USEPA), a total of 26 sites are currently using or testing nano-particles for remediation in the U.S. and Canada (USEPA, 2008). Nano-scale zero-valent iron (nZVI) is any microscopic particle less than about 100 nanometers (nm) in diameter. Nano-scale ZVI remediation has been successfully applied to degrade chemical contaminants including organic and inorganic pollutants in waste water and ground water (Wang and Zhang, 1997). Nano-scale ZVI is effective for treating pollutants such as chlorinated hydrocarbons, nitrobenzenes, pesticides, radio-nuclides, chlorinated phenols, arsenic(V), polychlorinated biphenyls (PCB’s), benzoic acid and anions to reduces it toxic end product (Hoch, Hydutsky, Hershman, Skluzacek and Mallouk, 2008).

Studies have shown that this method can be used successfully to reach contaminants dispersed in underground ponds and at much lower cost than methods which require pumping the water out of the ground for treatment. Even though the advantages of using nano zero-valent iron (nZVI) out last the disadvantages, there is still a concern with the material cost of nano-scale iron. Since the contaminants consume a large area or volume, it requires a large stoichiometric excess of iron. A normal remediation project may require thousands of pounds of nano-scale iron particles (Varadhi, Gill, Apoldo, Liao, Blackman, and Wittman, 2005). Zero valent iron can be used for remediation by creating a permeable reactive barrier by suspending iron in water and injecting the liquid, or by filling a well with iron particles and allowing groundwater flow to transport iron particles. Figure 2.3 below shows each of the three approaches for the application of iron particles in groundwater remediation. Figure 2.3(a) shows the conventional "permeable reactive barrier" treatment made with millimeter-sized construction-grade granular iron. Figure 2.3(b) shows the "reactive treatment zone" formed by sequential injection of particles to create a reactive barrier through which contaminated water will flow. Figure 2.3(c) shows the treatment of non-aqueous phase liquid (DNAPL) contamination by injection of mobile nano-particles.

According to recent studies, the poor transport properties of nano-particles in porous media such as soil and groundwater aquifers have made nano-iron relatively ineffective for in situ remediation (Hoch et al., 2008). Recent work suggests the use of polymers as “delivery vehicles” improved the transport properties of nZVI (Liu and Lowry, 2006).

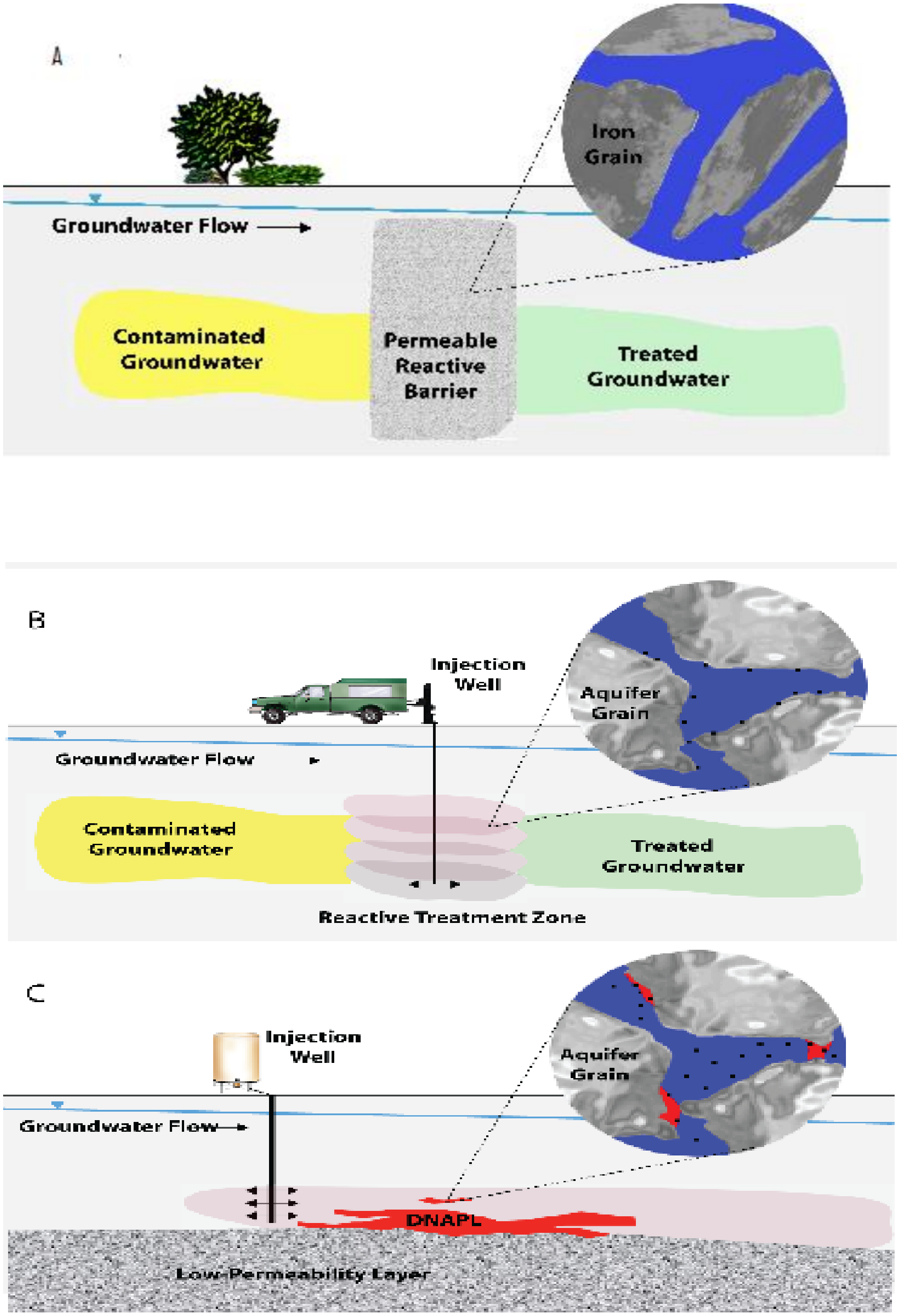


Figure 2.3. Various methods of nano-particle treatments (EPA, 2005)

The unique properties and enormous surface area of nano-particles has led to research applied to the treatment of organic contaminants in groundwater. Nano-ZVI has proven that it delivers promising results when used in the field and in the laboratory for a wide range of contaminants, including the reduction of chlorinated ethane, chlorates, nitrates, bromated and nitro-aromatic compounds. It is also effective for chlorinated methane, brominates or carbarylated pesticides, and the removal of arsenic, lead, uranium, mercury, and hexavalent chromium (Arnold and Roberts, 2000). Because ZVI is increasingly being used yearly, the USEPA has prepared a fact sheet on the uses of nanotechnology for site remediation. The USEPA overview includes information about sites where the technology has been tested and investing it energy on supporting researcher throughout the country.

Clark et al. (2003) researched the effectiveness of using the zero-valent iron in the remediation of perchloroethylene in an aqueous solution and how the presence of ethanol and modification of the iron surface altered dechlorination. The iron surface research by Clark et al. (2003) was to see if the degradation of PCE occurs when the remediation process is carried out with zero-valent iron coated with nickel plated iron, acid treated iron, or untreated iron surfaces. PCE degradation in the presence of this metallic surface was shown in the research to follow pseudo-first order kinetic reaction. The paper showed the effectiveness of the different kinds solvent fractions, which would provide useful information about designing above ground water treatment systems for chlorinated waste fluids. The paper utilized a batch reactor system for a two week period. The degradation of PCE was determined in this paper by conducting a PCE mass balance for the adsorbed phases based on equation 2.7.

$$\frac{dM_T}{dt} = \frac{d(V_W C_W + a_S \Gamma_S)}{dt} = -k a_S \Gamma_S \tag{2.7}$$

Batch tests measuring degradation of PCE in the presence of zero valence iron were conducted for both relatively high and low PCE concentrations and with different forms of zero iron. The paper demonstrated that PCE degradation followed a pseudo-first order reaction. The paper also explained that the introduction of ethanol solvents affected the degradation rate of PCE. The work demonstrates that an increase in the ethanol metallic coating would decrease the degradation of PCE and of all the coatings tested. It was shown that the iron coated by nickel provided a more suitable degradation than any order plating.

Farrell, Kason, Melitas and Li (2000) investigated the long term remedative performance of zero valent iron for remediation of TCE. Farrell et. al (2000) determined the reaction of TCE and zero valent iron followed a pseudo-first order reaction. Recent examples of in-situ chemical oxidation remediation include a former wood treatment site where pentachlorophenol water and soils were treated with ozone. The Oil Distribution Terminal site in Ilion, New York was contaminated with PAH and remediated using $KMnO_4$. Another treatment site located at Automobiles Sales and Service Center located in Bound Brook, New Jersey which were contaminated with BTEX and treated using hydrogen peroxide.

Kim and Hong (2008) studied the reductive degradation of chlorinated ethylene utilizing the zero-valent iron. The paper utilized micron-sized zero-valent iron particles with bimetallic palladium and nickel catalysts on the surface of the metal. This paper focused on the synthesis and analysis of nano-particles. The degradation of TCE concentration occurred within the first 4 hours. TCE was degraded the fastest by the ZVI coated with palladium reaching over 90% removal of TCE. The removal efficiency of TCE by ZVI immobilized membrane demonstrated that ZVI with large pore space and coating and nano-ZVI provided a more efficient means of degrading TCE.

2.5 Characterization of Encapsulated Oxidant

Controlled release techniques have attracted attention in diverse fields of studies. In environmental engineering, the concept of controlling release oxidant into subsurface environment is up-and-coming technique. This concept is important in site remediation and few studies using controlled delivery systems have been conducted, particularly for $KMnO_4$ (Siegriest et al., 1999). One of the essential steps in developing this remedial concept is manufacturing and testing the prototype using controlled release $KMnO_{4.}$ This method delivers permanganate ions in a realistically controlled fashion over a period of time. The advantage of this method of delivery is that is minimizes non-specific oxidant loss and it decreases the amount of oxidant needed for a particular cleanup (Namgoo and Hong, 2004).

By partially coating the water-soluble solid oxidant with a water-insoluble matrix, the controlled release of oxidant may be achieved. The point of the coating would be to avoid contact between the groundwater and the oxidant and thus control the suspension rate of treatment before the oxidant reaches the targeted contaminant (Siegriest et al., 2001). A coating material should include several critical characteristics: solid at ambient temperature, water insoluble, soluble in the target organic contaminant, chemically compatible and equally immiscible with $KMnO_4$, and biodegradable.

Ross et al. (2005) studies looked at the characteristics of potassium permanganate encapsulated in a chlorine-based polymer. This experiment carried out experiments with eighteen various polymers which had different formulations to create microcapsules with slower delivery system. The encapsulation process consisted of two microcapsules. One encapsulated structure included a single grain of $KMnO_4$ enveloped in polymer shell and the second is multiple grains of $KMnO_4$ in the core. The experiments were evaluated using two batch testing methods. One method examined the release rate of $KMnO_4$ by measuring its concentration over time and the second was a batch test measuring the TCE degradation as the microcapsule oxidants were suspend over time.

The study suggested encapsulation is a promising method of controlling the release rate of the oxidant, which this was one of the observations also included in studies by ORNL (1997) and Schnarr et al. (1998). The results from the degradation test have indicated that TCE should be exhausted within a week for the mass of microcapsules that were added. The release of $KMnO_4$ was shown at early stages of the reaction, but over time the release rate slowed with time. The initial release rate of $KMnO_4$ decreased over time and the duration of the release ranged from 3 to 80 days. The byproduct of MnO^-_4 was visually seen as the reation of $KMnO_4$ and TCE took place. The results from Ross et al. (2005) have shown that it is possible to encapsulate $KMnO_4$ in a polymer and deliver oxidants in-situ for remediation.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The experimental methods for this thesis were developed to compare controlled release of encapsulated $KMnO_4$ and zero-valent iron (ZVI) for the remediation of groundwater. Both $KMnO_4$ and zero-valent iron are treatment methods currently used for remediating TCE was discussed in the literature review. This thesis investigates encapsulation of micro and nano-size $KMnO_4$ and zero-valent iron using two types of polymers. Two types of biodegradable polymers were used in encapsulation of the oxidants. These were polycaprolactone (PCL) and polylactic acid (PLA).

3.2 Materials

The experiments focused on using various sizes of $KMnO_4$ and ZVI particles which were encapsulated within the polymer structure. Potassium permanganate ($KMnO_4$) was purchased from Fisher Scientific and will be referred to by the acronym EMG. The EMG $KMnO_4$ was processed by grinding the crystals using a mortar and pestle to reduce the size of the crystals. A sieve with fine mesh screens ranging from 0.074 mm (sieve mesh no 10.) – 2 mm (sieve mesh no. 200) was used to separate ground EMG particles by size. The ground EMG particles that were 50-microns or less in size were collected and encapsulated within the polymers for the studies. The 50-micron

$KMnO_4$ particles will be referred to for the remainder of the document using the acronym FML.

The reducing chemical, zero-valent iron, was purchased in two size ranges from Hoeganaes Corporations (H-200 plus Iron powder) and NanoPure in Austin, TX. The two zero-valent iron samples ranged from micro to nano-size samples. The polymers used to encase the oxidants were polycarprolactone (PCL) (DuPont and Solvay Chemical) and polylactic acid (PLA) obtained from Dr. J Lou in the Department of Chemical Engineering at North Carolina Agricultural and Technical State University. Trichloroethylene was purchased from Fisher Scientific. Chloroform was used as a solvent to solubalize or dissolve the polymers to make CRBP when melting was not the method used.

3.3 Method for Preparing $KMnO_4$ Controlled Release Polymers

Potassium permanganate was encapsulated by blending 0.1g of the oxidant into 0.5g of PCL. PCL is a low temperature polymer that melts at approximately 58-60^oC temperature. To form pellets, the polymer was melted using a hot plate. After the PCL was melted, the $KMnO_4$ was blended into the polymer. The polymer-oxidant was then formed into a coil and pellets ranging in size from 0.2 cm^2 to 0.4 cm^2 were cut using a razor blade. Polymers produced by melting polycaprolatone will be refered to using the acronym MPCL for melted polycaprolactone. A different encapsulation process was used to produce $KMnO_4$ encapsulated polylactic acid (PLA). Because, the melting point for PLA was significantly higher than PCL, a solvent was used to dissolve the polymer for encapsulation. This method of encapsulating oxidant into the polymer in this case PLA will be referred from this point forward as dissolved polylactic acid (DPLA).

3.4 Method for Preparing ZVI Controlled Release Polymers

Zero-valent iron (ZVI) both micro and nano sizes were encapsulated in PLA. Chloroform was used to solubalize the polymer to encapsulate the iron. The controlled release polymers with iron were produced using 0.5 g PLA added to a 50 mL of beaker. A volume of 10-15 mL of chloroform solvent was added to the beaker under a hood. In approximately about 2-hrs, all the PLA was dissolved and approximately 75% of the 10 – 15 ml of chloroform had evaporated as the polymer hardened. Next, 0.1g of ZVI was added to avoid reaction between chloroform and oxidant. Using a spatula, the polymer and ZVI were well mixed and then scraped it out of the beaker and placed between two glass slides or plastic Petri-dishes. The remaining chloroform was allowed to evaporate and the polymer was cut to small pellets using scissors. Pellets ranged in size from 0.2 cm^2 to 0.4 cm^2. The pellets were made the same day of the experiment to insure that the aging of the pellet would not affect the treatment and pellets. This method of encapsulating oxidant to the polymer, in this case PLA, will be referred to as dissolved polylactic acid (DPLA).

3.5 Experiment Setup

The experiments were conducted using 300 ml bottle for the batch reaction vessels. Polymers pellets containing 0.1 g $KMnO_4$ or ZVI and 0.5 g biodegradable polymers (PLA and PCL) were add to clean reaction vessels. For the oxidant release test, 150 mL of distilled (DI) water was added bottle containing the pellets and then the bottle was sealed. Every 5 minutes, about a volume 0.1 ml of sample was pipetted from the bottle and diluted with distilled water. Diffusion of the oxidant from the polymer shell was measured for one hour. To understand the degradation of TCE, solution of 200 ppm TCE was prepared in distilled water. TCE was dissolved in distilled water using a sealed volumetric flask and stir plate for approximately for 20-30 minutes to ensure the chemical was completely dissolved. For the experiments, serum bottles were over-filled with the 200 ppm TCE solution and crimp clamped sealed to prevent headspace in the bottles. The reactions were allowed to proceed at room temperature and all samples were extracted from the sealed bottle using a syringe.

3.6 Gas Chromatography

Gas chromatography (GC) is a type of chromatography used in analytic chemistry for analyzing and separating compounds that can be vaporized without decomposition. GC includes the testing of purity particular substance, or separating the different components of a mixture for quantification. In some situations, GCs may help in identifying the unknown compound. For this study, a Shimadzu GC-2010 equipped with a flame ionization detector (FID) and Electron Capture Detector (ECD) was used to analyze samples. The GC FID column was operated using ultra pure hydrogen, nitrogen and air. The ECD column is used hydrogen and nitrogen. For this study, both FID and ECD were used to quatinfy TCE concentrations in the samples. The sensitivity of ECD is

10-1000g/ml more sensitive than FID; therefore, very small concentrations of TCE could be detected in samples.

The columns used in the GC were Shimadzu SHRXI-5MS columns (15 m length, 0.25 mm film thickness, and 0.25 mm ID). Ultra pure gases were purchased from Air Gas Corporation (Greensboro, NC). A headspace analysis of TCE was conducted by sampling the TCE vapor from the headspace in screw top vials in the GC auto sampler. The GC system parameters are provided in table 3.1 and table 3.2.

Table 3.1. Parameters GC Column and Gas Flow

Temperature:	250 °C
Injection Mode:	Split
Pressure:	47.8 kPA
Control Flow Mode:	Linear Velocity
Total Flow	12.0 ml/min
Column flow:	1.0 ml/min
Linear Velocity:	29.5 cm/sec
Purge Flow:	1.0 ml/min
Split:	10

Table 3.2. Temperature program for columns

Program Temperature Profile		
Temperature Increment (degrees/min)	**Temperature (Degrees °C)**	**Hold Time (minutes)**
0	50	2
6	80	2
20	110	0

3.7 Release Test

3.7.1 $KMnO_4$ Release Test

A spectrophotometer was used to analyze the absorption of each sample. It is a device used for measuring light intensity as a function of color or more specifically the wavelength of light. To analyze the samples, the instrument was set up to 525 nm wavelength. Using the calibration curve, the concentration of $KMnO_4$ was determined by comparing the absorbency to the mass of $KMnO_4$ present in solution from the calibration curve.

Batch experiments were carried out to study the release of the $KMnO_4$ with various sizes of $KMnO_4$ in two types of biodegradable polymer as identified DPLA and MPCL. These studies were designed to measure the release of $KMnO_4$ in deionized water. This provided an understanding of the diffusion of $KMnO_4$ from the pellets. Pellets were prepared using 0.1 g of oxidant blended with 0.5 g of polymer. The experimental setup for the release test and is described in experimental setup section above. By applying the data collect from this test into equation (3.1), the reaction stoichiometry could be used to calculate the theoretical TCE degradation.

$$C_r = \frac{CV}{M} \tag{3.1}$$

This is degradation rate can then be used to predict the behavior of TCE during treatment using the encapsulated $KMnO_4$. In the equation, Cr represents the concentration ratio, C represents the concentration of KMnO4 in water, V is the volume of water, and M is the mass of permanganate added to the batch reactor..

3.7.2 ZVI Release Test

The release of ZVI was examined using a HACH iron test kit. This kit is a colormetric method used to determine the levels of iron present in water. The analysis was performed by filling one test tube with 5 ml of DI (control) and a second test tube with the sample containing iron. The iron encapsulated pellets were prepared using 0.1 g of oxidant blended with 0.5 g of polymer. A mass of 0.1 g pellets was added to the sample test tube with 5 ml of DI. One HACH FerroVer Iron Reagent Powder Pillow was added to the test tube which has the pellets. The reagent was allowed to dissolve for two to minutes and if iron was present in the water sample, an orange color would develop. To determine the iron levels, the tubes were placed lengthwise into a viewing adapter provided in the kit to compare the control to the sample. A viewing adapter was read by holding the apparatus towards a light source to view the color change through the front opening of the comparator and by rotating the disc to read the iron concentration in the sample. The iron concentration could then be read and recorded in units of mg/L or concentration.

3.8 $KMnO_4$/ZVI kinetics

A measured amount of 0.01 g of $KMnO_4$ or ZVI was encased in either polycaprolactone or polylactic acid. The oxidants were encased in the polymer through either melting or dissolving process and mixing the oxidant to the polymer when it was in liquid form. TCE degradation was measured by taking 1 ml out of the reactor bottle every 5 min, adding 20 μL of sodium thiosulfate to the sample to stop the reaction, and sealing the vial. The vial was heated for 6 min and allowed to cool for an hour for the vapor and liquid in the vial to reach equilibrium. The vial headspace was measured to determine the TCE present in the treated sample. Controls for DI and the initial TCE concentration were run prior to the treated samples.

3. 9 MnO_2 formation test

This study investigated the formation of MnO_2 in the system when using 800 µm particles of $KMnO_4$ (EMG) and 50 µm size particles (FML). Both melted polycaprolactone (MPCL) and dissolved polylactic acid (DPLA) were used for this study. Four bottles were used for this experiment. The first bottle evaluated MPCL encapsulating 800 µm oxidant (MPCL~EMG), the second bottle contained MPCL with 50 µm oxidant (MPCL~FML), the third consisted of DPLA encapsulating 800 µm oxidant (DPLA~EMG), and in the fourth bottle contained DPLA encapsulating 50 µm oxidant (DPLA~FML) was present. The weight each pellet was collected by placing them into the bottle. The sample containing 200 ppm TCE in water was added to the bottle with no headspace and crimp sealed. The solid reaction precipitate (MnO_2) was filtered and weighed over a 5 day period to measure the amount of precipitate forming in the reaction vessel.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 $KMnO_4$ Release Test/Melted Polymer

The release test was carried out to compare the release of $KMnO_4$ encapsulated in a polymer shell to control or retard the release of the oxidant. The purpose of this experiment was to formulate a reasonable comparison of how the size of the oxidant affects the release of the oxidant from the polymer shell. Table 4.1 shows the release of $KMnO_4$ from the samples. For the experiment, samples were collected every 5 minutes for a total of 45 minutes to monitor the $KMnO_4$ concentration. For the first 10 minutes, the results show that the release occurred faster with the smaller particle size of FML (50 µm). After 10 minutes, the concentration of EMG (800 µm) was 0.000243 mg/l $KMnO_4$ compared to 0.000251 mg/L $KMnO_4$ for FML. Therefore the results show that smaller particle sizes are released faster. This experiment provided an insight into diffusion of encapsulated $KMnO_4$ when placed in water. At the end of the 45 minutes, the $KMnO_4$ concentration measured was higher in water containing the FML pellets compared to water containing the EMG pellets.

Table 4.1, table 4.2 and figure 4.1 below are graphical representations of the $KMnO_4$ release test. These tables compare the release of $KMnO_4$ from the different particle sizes with time. The graph shows that $KMnO_4$ for both particle sizes increase over time at different rates. The release of the FML occurred faster than the EMG. After

45 minutes, the concentration of EMG was at 0.000299 mol /L compared to the concentration of FML at 0.000328 mol/L of $KMnO_4$.

Table 4.1. $KMnO_4$ release FML (50 µm) ~MPCL

Time (min)	**Concentration $KMnO_4$ mg/L**	**Concentration of TCE remaining(A)**	**In(A)**	**% TCE REMOVED**
5	0.0019	200.00	5.30	100.00
10	0.0020	184.05	5.22	98.43
15	0.0020	167.58	5.12	96.66
20	0.0021	150.91	5.02	94.68
30	0.0022	133.21	4.89	92.33
35	0.0025	114.79	4.74	89.52
40	0.0026	93.83	4.54	85.71
45	0.0030	72.35	4.28	80.81

Table 4.2. $KMnO_4$ release EMG (800 µm) ~MPCL

Time (min)	**Concentration $KMnO_4$ mg/L**	**Concentration of TCE remaining (A)**	**ln(A)**	**% TCE REMOVED**
5	0.001899	200.00	5.30	100.00
10	0.001918	184.25	5.22	98.45
15	0.00193	168.35	5.13	96.75
20	0.001974	152.35	5.03	94.86
30	0.001986	135.99	4.91	92.72
35	0.002098	119.52	4.78	90.28
40	0.002225	102.13	4.63	87.32
45	0.002364	83.68	4.43	83.56

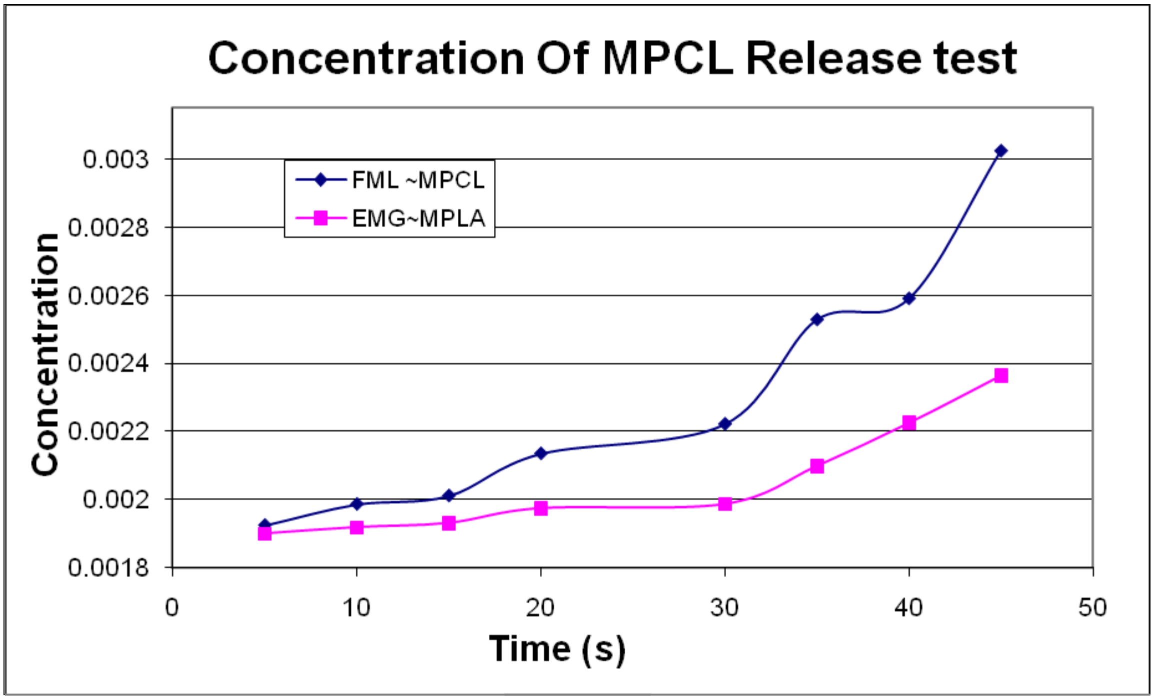


Figure 4.1. Compares the $KMnO_4$ released in FML compared to EMG

4.1.1 Iron (Fe) Release Test /Melted (MPLA)

The size comparison experiment measured the release of Fe particles. The experiment utilized two Fe encapsulated polymer samples. The first oxidant used was nano-Fe sized iron particles and the second was a micro sized-Fe particle processed in the lab. The experiment sought to compare the rate at which these two Fe sizes would be released from the polymer. The polymer was designed to slowly release the oxidant over time; therefore, the experiment related how these oxidants being released from the polymers over time.

The figures below show the comparison of the two different iron particles. The graph shows over time, the increase of nano-particles demonstrated a larger increase of

Fe concentration compared to the micro size-Fe particles. The comparison proved that the initial concentration of the nano-iron was at 4.5 mg/l compared to the micro-iron particle that measured at approximately 2.0 mg/l. Results collected for ZVI release using micro/nano~MPCL oxidant are shown in the Table 4.3 and Table 4.4. Figure 4.2 graphically compares the two sizes.

Table 4.3. ZVI release test ZVI ~MPCL

Time (min)	Concentration ZVI mg/L	Concentration of TCE remaining(A)	In(A)	% TCE REMOVED
4	4.6	200.00	5.30	100.00
6	5.9	139.86	4.94	69.93
8	7.0	62.72	4.14	31.36

Table 4.4. ZVI release test nZVI ~MPCL

Time (min)	Concentration ZVI mg/L	Concentration of TCE remaining(A)	In(A)	% TCE REMOVED
2	1.8	200.00	5.30	100.00
4	3.8	176.47	5.17	88.23
6	7.9	126.79	4.84	63.39

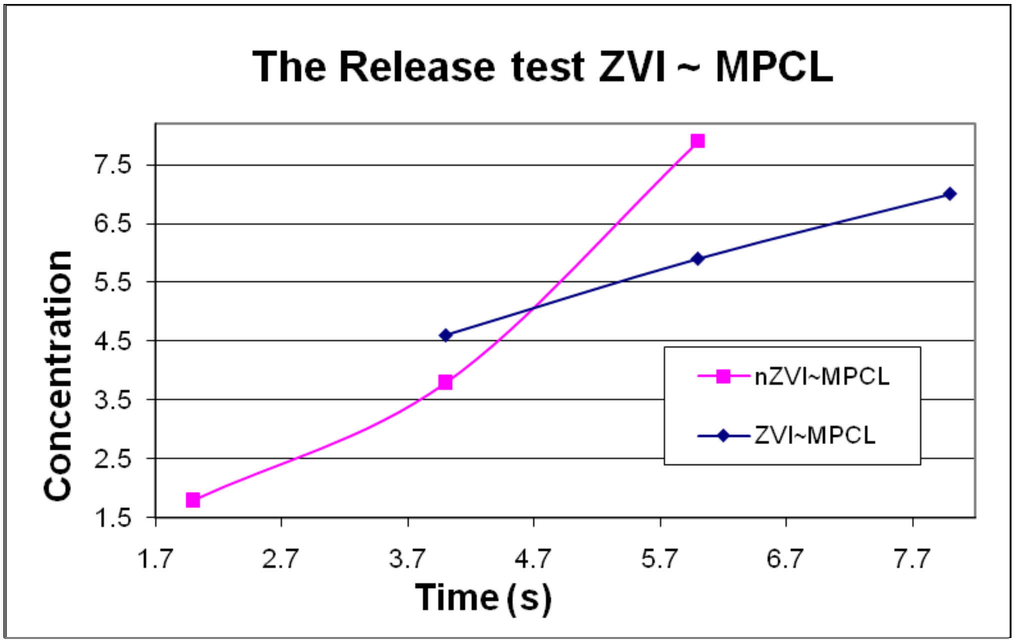


Figure 4.2. Compares the ZVI released in nano-sized particle compared to micro-sized particles

This experiment showed the amount of iron released differed such that the nano-particle concentration reached 8 mg/l compared to the micro size particle concentration which reached 4 mg/ L. These results show that iron released from the polymer occurs faster when these articles are in nano form.

4.1.2 $KMnO_4$ Release Test/Dissolved Polymer

These experiments investigated the preparation of the polymer where chloroform was used to solubalize the PLA (DPLA). For this part, DPLA was used to encapsulate the nano and micro-particle sizes to investigate the degradation of TCE. The results show that the degradation of TCE still occurred more efficiently with the 50 µm particles when placed in a different polymer types. For the micro-sized particles, 37% of TCE was left after using the 50 µm particles compared to the 800 µm particles which degraded the contaminant TCE with 87% remaining. Results collected for $KMnO_4$ release using FML/EMG~DPLA oxidant are shown in the table 4.5 and table 4.6. Figure 4.3 shows a graphical comparison of the two sizes.

Table 4.5. Release test of FML~DPLA

Time (min)	Concentration $KMnO_4$ mg/L	Concentration of TCE remaining (A)	In(A)	% TCE REMOVED
5	0.00199	200.00	5.30	100.00
10	0.00199	183.48	5.21	91.74
15	0.00200	166.91	5.12	90.97
20	0.00213	150.29	5.01	90.04
25	0.00217	132.64	4.89	88.26
30	0.00227	114.69	4.74	86.46
35	0.00228	95.86	4.56	83.58

Table 4.6. Release test of EMG~DPLA

Time (min)	Concentration $KMnO_4$ mg/L	Concentration of TCE remaining(A)	In (A)	% TCE REMOVED
5	0.00212	200.00	5.30	100.00
10	0.00215	182.40	5.21	91.20
15	0.00217	164.60	5.10	90.24
20	0.00230	146.59	4.99	89.06
25	0.00233	127.50	4.85	86.98
30	0.00239	108.16	4.68	84.83
35	0.00246	88.35	4.48	81.69

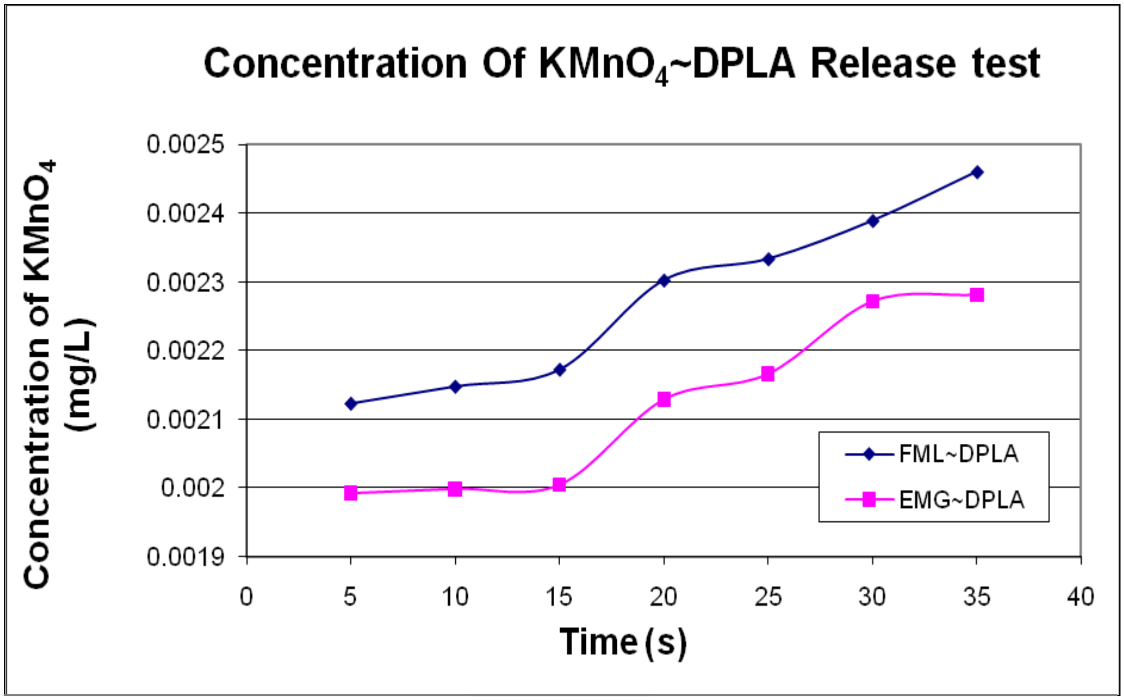


Figure 4.3. Compares the $KMnO_4$ released in FML compared to EMG

4.1.3 Fe Release Test/Dissolved Polymer

This test demonstrates similar trends with the results of the other release tests. The release occurs greater when the smaller particle size is utilized. Table 4.4 below shows that the smaller particle size released faster and degrades faster after 6 minutes. The degradation of TCE reached 37.8 mg/l for FML~DPLA compared to the other particle size of Fe which was 158.8 mg/L for EMG~DPLA. Results collected for Fe release using micro/nano ~DPLA oxidant are shown in the Table 4.7 and Table 4.8. Figure 4.4 is a graph comparing the two sizes.

Table 4.7. Release test of FML~DPLA

Time (min)	Concentration ZVI mg/L	Concentration of TCE remaining (A)	In(A)	% TCE REMOVED
2	0.5	200.00	5.30	100.00
3	2.0	193.51	5.27	96.76
4	4.1	167.57	5.12	83.79
5	5.9	114.40	4.74	57.20
6	6.7	37.87	3.63	18.94

Table 4.8. Release test of EMG~DPLA

Time (min)	Concentration ZVI mg/L	Concentration of TCE remaining (A)	In(A)	% TCE REMOVED
1	0.4	200.00	5.298	100.00
2	0.7	194.81	5.27	97.41
4	1.0	185.73	5.22	92.87
6	1.1	172.76	5.15	86.38
8	1.5	158.50	5.07	79.25

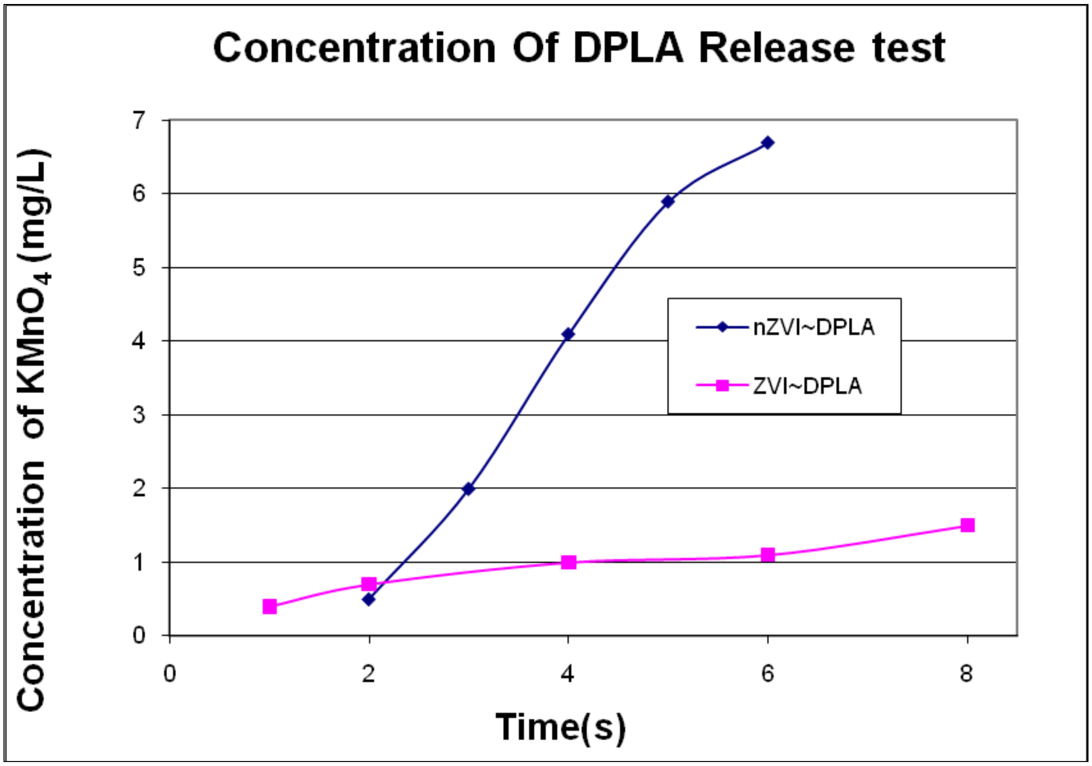


Figure 4.4. Compares the ZVI Dissolved released in nano and micro-sizes

4.2 Theoretical TCE Degradation Test /$KMnO_4$

The experiment was done utilizing the release test conducted for the $KMnO_4$ reaction between the EMG 800 µm and FML 50 µm. TCE degradation test was done to monitor the concentration of TCE over time utilizing the stoichiometric ratio of TCE and $KMnO_4$. The tables below represent the TCE degradation with time for both samples. The results show the degradation of TCE occurred more rapidly with the $KMnO_4$ with the 50 µm particle size. A comparison of both result shows at certain time intervals, the concentration of TCE was different. At the 40 minute time point in the experiment, the concentration for the 50 µm was at 93.82 mg/l compared to the 800 µm particle size which had a concentration of approximately 102 mg/l TCE in the sample. Table 4.9 and 4.10 provide the data and the graphical comparison is shown in figure 4.5.

Table 4.9. Theoretical TCE degradation of FML~DPLA Release test

Time (min)	Abs	Concentration $KMnO_4$ (mg/ml)	kmol/ L	C_r =CV/M	Mass of TCE (mg)	TCE remaining (ppm)	% remaining
5	0.64	1.92	0.24	0.00845	0.15	200.00	100.00
10	0.66	1.99	0.25	0.00873	0.14	184.05	92.02
15	0.67	2.01	0.26	0.00883	0.13	167.58	91.05
20	0.71	2.13	0.27	0.00938	0.12	150.91	90.05
30	0.74	2.22	0.28	0.00976	0.10	133.21	88.27
35	0.84	2.52	0.32	0.01110	0.08	114.79	86.17
40	0.86	2.59	0.32	0.01130	0.07	93.83	81.73
45	0.99	3.02	0.38	0.01330	0.05	72.35	77.10

Table 4.10. Theoretical TCE degradation of EMG~DPLA Release test

Time (min)	Abs	Concentration $KMnO_4$ (mg/ml)	kmol/L	C_r =C_V/M	Mass of TCE (mg)	TCE remaining (ppm)	% remaining
5	0.63	1.89	0.24	0.00834	0.15	200.00	100.00
10	0.63	1.91	0.24	0.00840	0.14	184.25	92.12
15	0.64	1.93	0.24	0.00848	0.13	168.35	91.37
20	0.66	1.97	0.25	0.00867	0.12	152.35	90.49
30	0.66	1.98	0.25	0.00873	0.10	135.99	89.25
35	0.70	2.09	0.26	0.00922	0.09	119.52	87.89
40	0.74	2.22	0.28	0.00978	0.07	102.13	85.44
45	0.78	2.36	0.30	0.01039	0.06	83.68	81.94

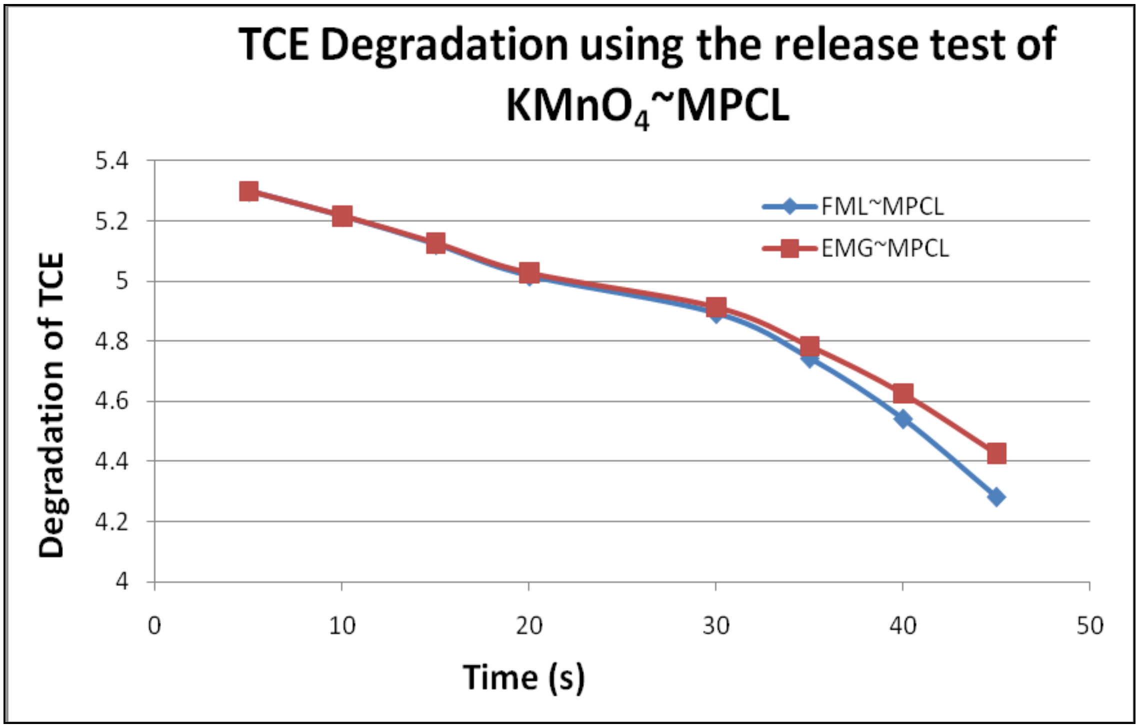


Figure 4.5. **Compares the TCE Degradation using $KMnO_4$ Melted released in FML compared to EMG**

The table also shows the percent degradation of TCE at the end of the experiment. The experiment shows that with the 50 µm size 77% of the original TCE concentration remained compared to the concentration of the 800 µm where 81% of the TCE remained. This proves that the smaller the particle size is more efficient the degradation of TCE.

4.2.1 Theoretical TCE Degradation Test ZVI and nZVI

The reduction of TCE using the reducing agent Fe was also examined using the release test from the previous experiment. TCE degradation was examined based on the effect of particle size. The table below shows TCE degradation using iron. Unlike the $KMnO_4$ degradation, TCE degraded faster with Fe than $KMnO_4$. The experiment lasted approximately 8 minutes. The degradation showed that within the first 6 min, the concentration dropped to 31% for the nano-Fe and 63.5% for the micro-Fe. At the end of the experiment, the results showed that degradation occurred more rapidly when the nano-Fe was applied. Results collected for ZVI theoretical TCE degradation of nZVI/ZVI~DPLA oxidant are shown in the Table 4.11 and Table 4.12. Figure 4.6 graphically compares the two sizes.

Table 4.11. Theoretical TCE degradation of nZVI ~ DPLA Release test

Time (min)	Abs	Concentration $KMnO_4$ (mg/ml)	kmol/L	$C_r = C_V/M$	Mass of TCE (mg)	TCE remaining (ppm)	% remaining
4	4.6	0.08	0.0014	0.23	200.00	5.30	100.00
6	5.9	0.11	0.0018	0.16	139.86	4.94	69.93
8	7.0	0.13	0.0021	0.07	62.72	4.14	31.36

Table 4.12. Theoretical TCE degradation of ZVI~DPLA Release test

Time (min)	Conc ZVI	kmol/L	C_r =CV/M	Mass of TCE (mg)	TCE remaining ppm	In(A)	% TCE
2	1.8	0.03	0.00054	0.23	200.00	5.30	100.00
4	3.8	0.07	0.00110	0.23	176.47	5.17	88.23
6	7.9	0.14	0.00240	0.23	126.79	4.84	63.39
8	9.5	0.17	0.00280	0.23	23.50	3.16	11.75

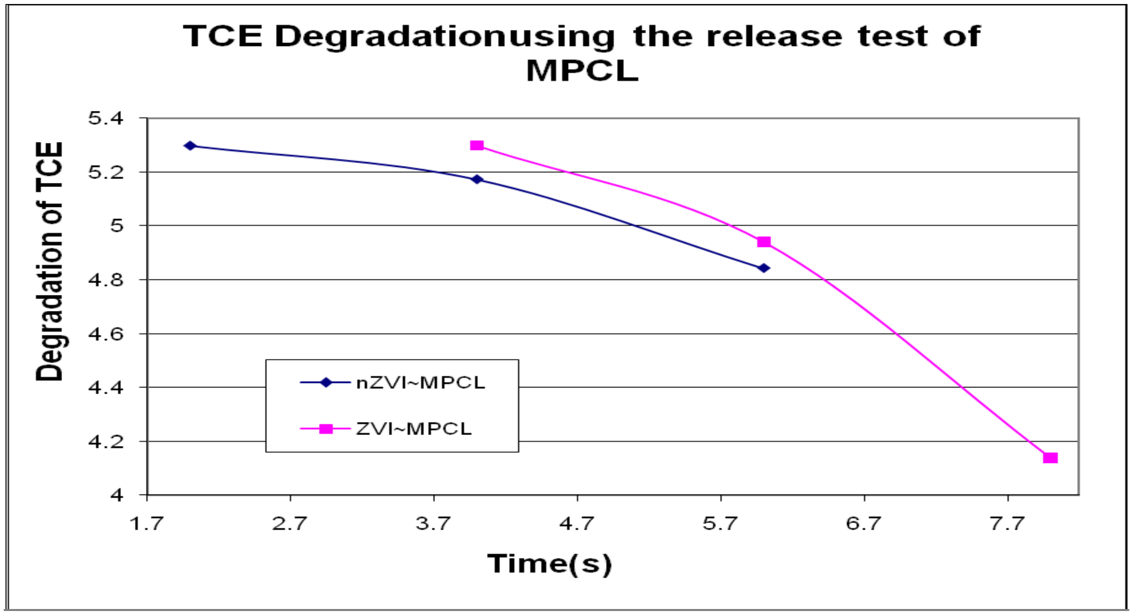


Figure 4.6. Compares the TCE Degradation using ZVI Melted released in nano-sized particles compared to micro-sized particles

4.2.2 Comparison of Dissolved and Melted Polymer in Fe

This experimental comparison was done to show which of the two polymer delivery systems provided a feasible method in the remediation of TCE. The experiment looked at which of the two polymer systems, dissolved polymer system with chloroform or the melted polymer would remediate the most effectively. The results displayed below show that the pellets made using the dissolved polymer encapsulation method released the fastest. By the end of the 45 minute experiment, the release occurred more rapidly with the concentration of TCE at 0.14 mg/l for the DPLA and for the MPLA, TCE concentration recorded at the end of the experiment reached 0.0023 mg/l. The $KMnO_4$ dissolved and melted pellets are demonstrated similar results for the Fe. The results proved the $KMnO_4$ dissolved polymer method released faster than the melted polymer method.

4.3 Kinetics

Yan sand Schwartz (1999) studied the degradation of five chlorinate ethylene compounds and determined the degradation behavior for the chlorinated ethylenes depicts a pseudo-first order rate constant. Farrell et al. (2000) investigated the long term performance of zero valence iron for the remediation of TCE and indicated that zero valence iron follows a pseudo-first order reaction. Hoag and Huang (1998) studied the kinetics of oxidation of TCE by $KMnO_4$ in a homogeneous aqueous system by using a zero headspace system. The investigation concluded that the oxidation of TCE by $KMnO_4$ is second order overall and first order individually. Combining the reaction rate with mass balance, the rate equation for particle system, or the reaction order, can be determined. The overall the reaction mixture can be express or written as shown in equation 4.1-4.3.

$$aA + bB \rightarrow cC \tag{4.1}$$

$$r = \frac{d[A]}{dt} = -k[A]^a[B]^b \tag{4.2}$$

Therefore if B is the reactant whose concentration is constant, then

$$r = k'[A]^a \tag{4.3}$$

where $k'=k\,[B]^b$

This means the second order rate equation has been reduced to a pseudo-first order rate equation and it is an elementary reaction with respect to reaction A. Therefore k is the first order rate constant with units of 1/time. This makes an integrated rate equation that is easier to use and it is shown below in equation 4.4.

$$\ln[A] = -kt + \ln[A_0] \tag{4.4}$$

Equation 4.11 can also be written in the form of exponential decay shown equation 4.5.

$$A = A_0 e^{-kt} \tag{4.5}$$

The k value was obtained by plotting the ln [A] vs. time, which gives a straight line with the slope of –k. By plugging in the k-value to equation 4.6, the half-life for the first order reaction can be calculated. The half-life for this order is dependent of the initial concentration.

$$t_{\frac{1}{2}} = \frac{\ln(2)}{2} \tag{4.6}$$

Using equations 4.8 to 4.13, the degradation of TCE was determined for all conditions. The results for some of the experiments run during this thesis are shown below. Based on equation 4.9, the reaction between TCE and the two oxidants follow pseudo-first order kinetics. For each experiment the time it took for TCE to degrade was determined using equation 4.13. The half-life and the rate of the reaction are shown in Figures 4.7 through 4.10.

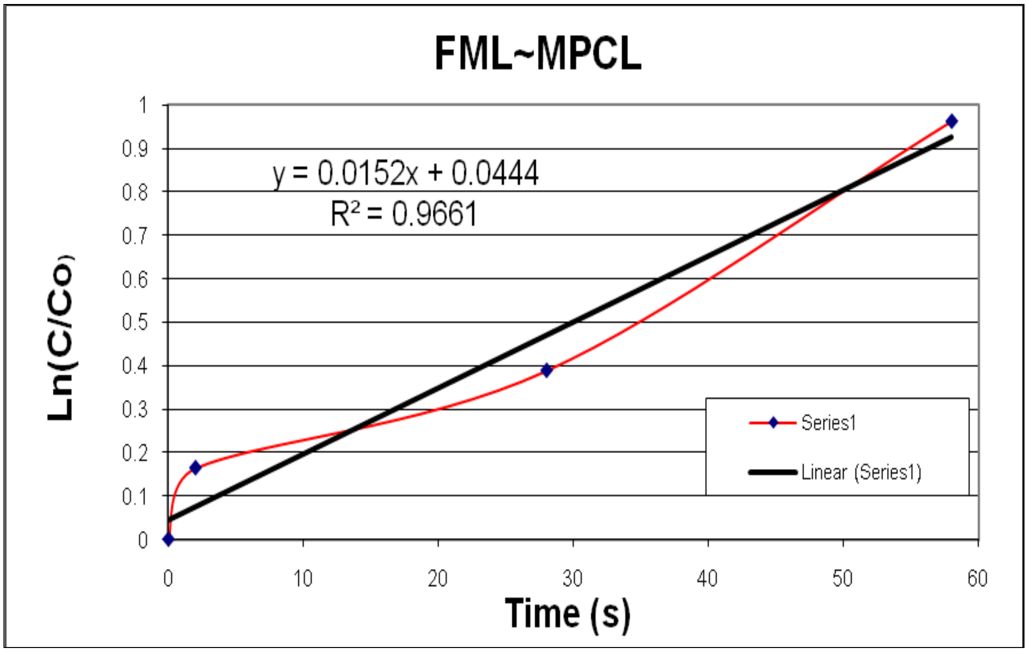


Figure 4.7. Reaction kinetics displaying a pseudo-first order for FML~MPCL

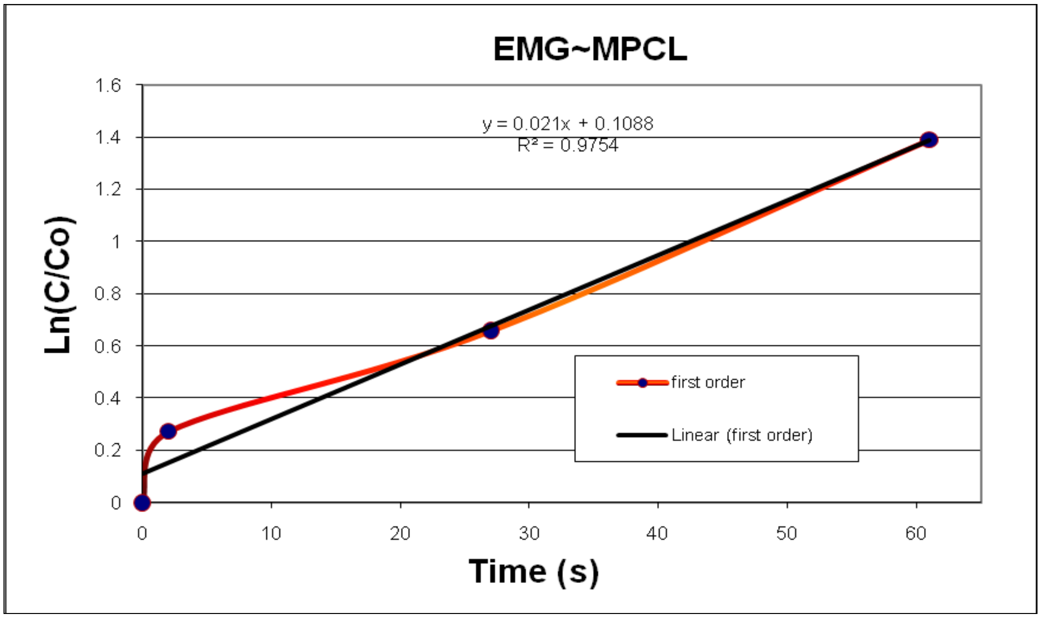


Figure 4.8. Reaction kinetics displaying a pseudo-first order for EMG~MPCL

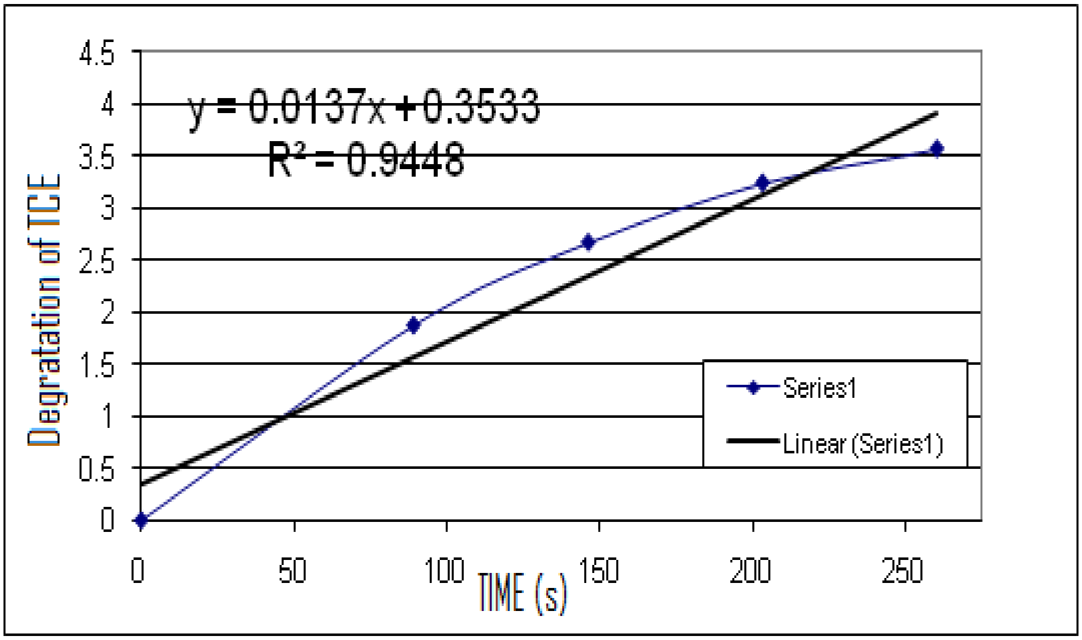


Figure 4.9. Reaction kinetics displaying a pseudo-first order for micro ZVI~DPLA

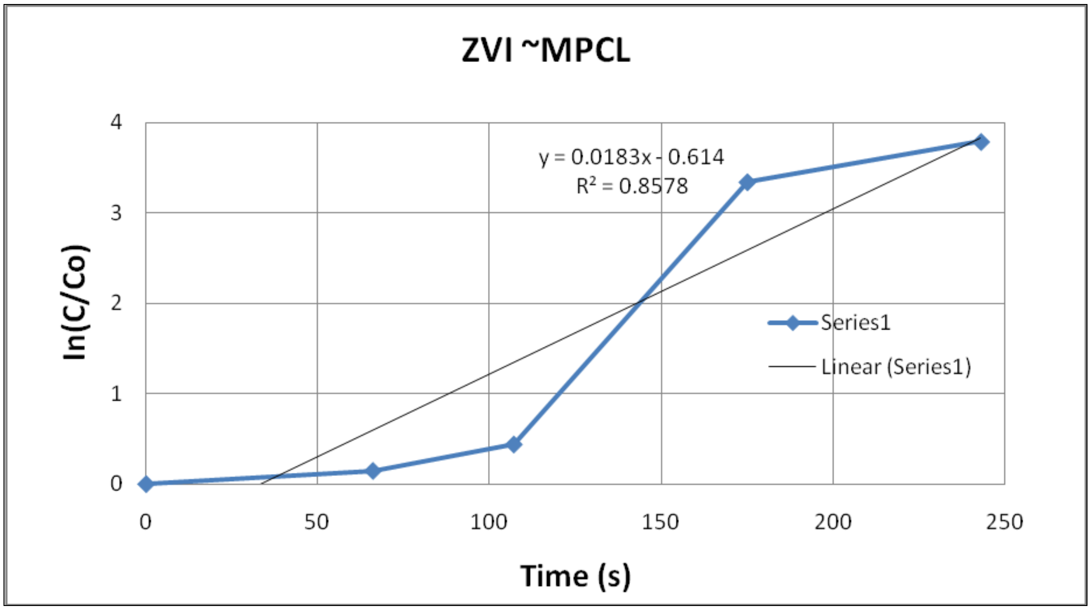


Figure 4.10. Reaction kinetics displaying a pseudo-first order for microZVI~MPCL

Table 4.13. Half-life of the remediative process utilizing the polymers process and oxidant sizes

Oxidant & Polymers	K (1/s)	$t_{1/2}$ (s)	TCE
EMG~MPCL	0.000350	1980.412	50 ppm
FML~MPCL	0.000250	2772.590	50 ppm
ZVI~DPLA	0.000310	2235.959	50 ppm
ZVI~MPCL	0.000228	3035.681	50 ppm

4.4 TCE Calibration Method

For the gas chromatography, the calibration was set up using four to five TCE standard concentrations. The area under the GC spectrum represents the specific retention time for the sample and the concentration. Therefore the retention time and size of the peak can be used to measure the amount of TCE in the treated systems. There were two methods that were used for this study: (1) liquid-liquid extraction and (2) headspace. The only difference between the two methods was the phase extracted for the GC sample. liquid-liquid samples were collected from the sample vial in the liquid phase and the headspace sampling method collected the vapor at the headspace sample.

4.4.1 Reaction Kinetics in Batch System between $KMnO_4$ (EMG~MPCL) and ZVI~MPCL

For this experiment, $KMnO_4$ and ZVI MPCL were compared for TCE remediation. Figure 4.11 and Figure 4.12 compare the degration of TCE using $KMnO_4$

EMG and ZVI with in MPCL. The results show that TCE degrades faster when zero-valent iron (ZVI) is encapsulated in polymers compared to encapsulated $KMnO_4$. Since the the reaction between TCE and ZVI is a reduction reaction, it demonstrates that the degration of TCE using the reduction agent is more effective than oxidation reaction with $KMnO_4$. For the first hour of the reaction, both the $KMnO_4$ and ZVI demonstrated a simular rate of TCE degradation. The initial concentration of TCE was 200 ppm, after one hour, the concentration for $KMnO_4$ pellets was 179.23 ppm and ZVI pellets was 157.5 ppm. After an hour, the concentration of TCE using ZVI was 16 ppm and 92 ppm using $KMnO_4$. Tables 4.14 and 4.15 show the calculations for first order kinetics.

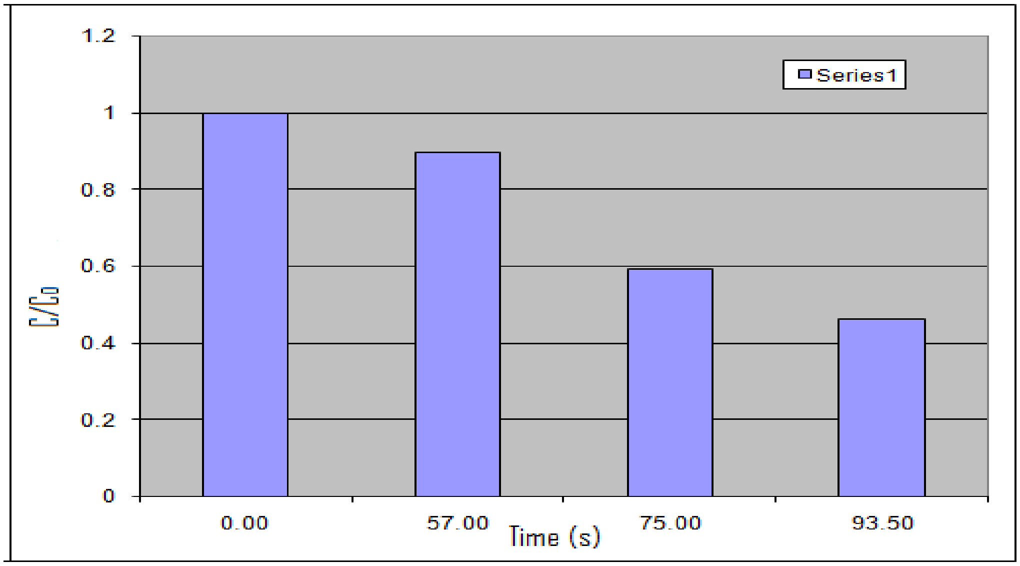


Figure 4.11. Degradeation of TCE using $KMnO_4$ in MPCL~EMG over time

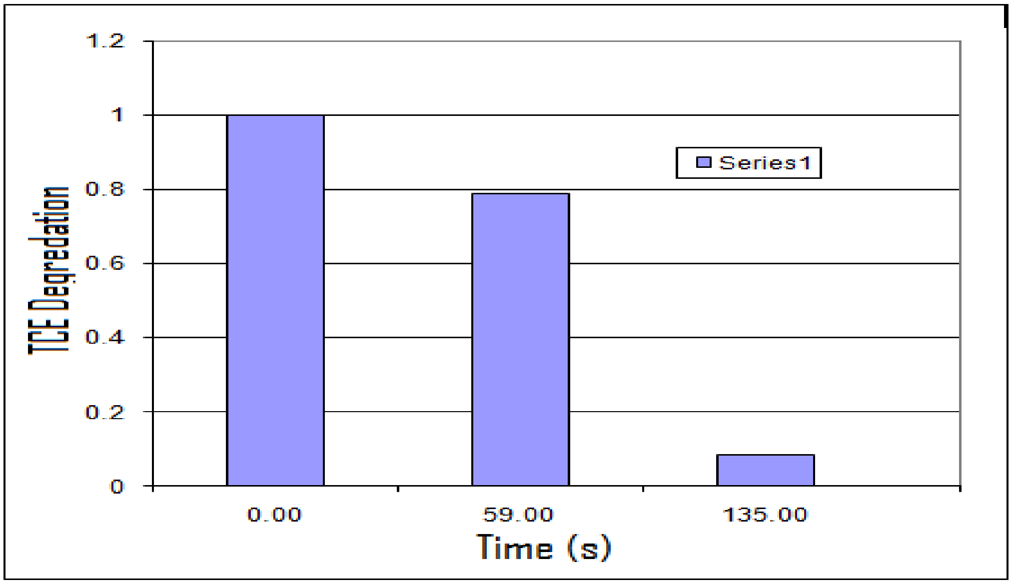


Figure 4.12. Degradeation of TCE using ZVI in MPCL over time

Table 4.14. Data for TCE using $KMnO_4$ in MPCL_EMG over time

Average time (minutes)	Average C/Co	Concentration (ppm)
0	1.00	200.00
57	0.896	179.24
75	0.591	118.38
94	0.460	92.18

Table 4.15. Degradeation of TCE using ZVI in MPCL over time

Average time (minutes)	Average C/Co	Concentration (ppm)
0	1.00	200.00
59	0.79	157.58
135	0.08	16.58

4.4.2 Reaction Kinetics in Batch System Comparing the various $KMnO_4$ particle sizes (EMG ~ MPCL and FML~MPCL)

For this experiment, the degradation of TCE over time was examined utilizing different particle sizes of $KMnO_4$. This method was tested using a batch reactor system and the GC analysis using a liquid-liquid extraction. The results shown in table 4.16 and table 4.17 are the degradation comparison of EMG ~ MPCL and FML~MPCL.

Table 4.16. Degradation of TCE using EMG~MPCL

Time Step	Area	TCE Concentration	First Order
0	703025.30	50.12	0.00
74	190934.50	14.43	1.25
119	146484.80	11.33	1.49
176	126909.40	9.97	1.62
233	123133.90	9.70	1.64

Table 4.17. Degradation of TCE using FML~MPCL

Time Step	Area	TCE Concentration	First Order
0	703025.30	50.12	0.00
88	365189.90	26.57	0.63
149	196170.60	14.79	1.22
214	165161.10	12.63	1.38

Using EMG pellets, the TCE concentration was 30% lower than FML. This is hypothesized to be the result of the particles being larger which means the $KMnO_4$ is being released on larger scale than FML. When plotting the concentration vs. time, the *k* value was found to be 0.00015 s^{-1} or 0.009 min^{-1} and the half-life was calculated to be 75 minutes for EMG. Using FML, the *k* value was 9.333E-05 s^{-1} or 0.006 min^{-1} and half-life was 124 minutes. FML has a higher decay rate than EMG. This result could be because FML is a smaller particle and lasts longer.

4.4.3 Reaction Kinetics in Batch System between Melted and Dissolved of (ZVI) particle sizes

The delivery system for the polymers was investigated using ZVI encapsulated particles. The results shown in Figure 4.13 and Figure 4.14 represent the degradation of TCE over time using the GC results. TCE using ZVI~DPLA exhibited a peak within the 1.74 – 1.84 minutes of retention time. Over time as the concentration of TCE is seen to decrease, the concentration of chlorine increases at the 1.3 minute retention time. When comparing DPLA and MPCL for ZVI, the extra chlorine formation is only seen if the polymer is dissolved to encapsulate the iron. The MPCL has the potential to degrade TCE faster than DPLA and the hypothesis is that there is a side reaction between chloroform remaining in the pellets and the TCE sample resulting in the extra peak seen at the 1.3 retention time.

Figure 4.15 is an SEM image of the dissolved polymer (DPLA) surface. It shows that the oxidants of ZVI are packed inside the polymer. For the MPCL, the oxidant is seen on the surface of the polymer. Figure 4.16 shows the oxidant on the surface as well as inside the pellet. From this SEM image, it can be concluded that the reaction would take place inside and outside for $KMnO_4$~ MPCL which can result in the reaction occurring faster.

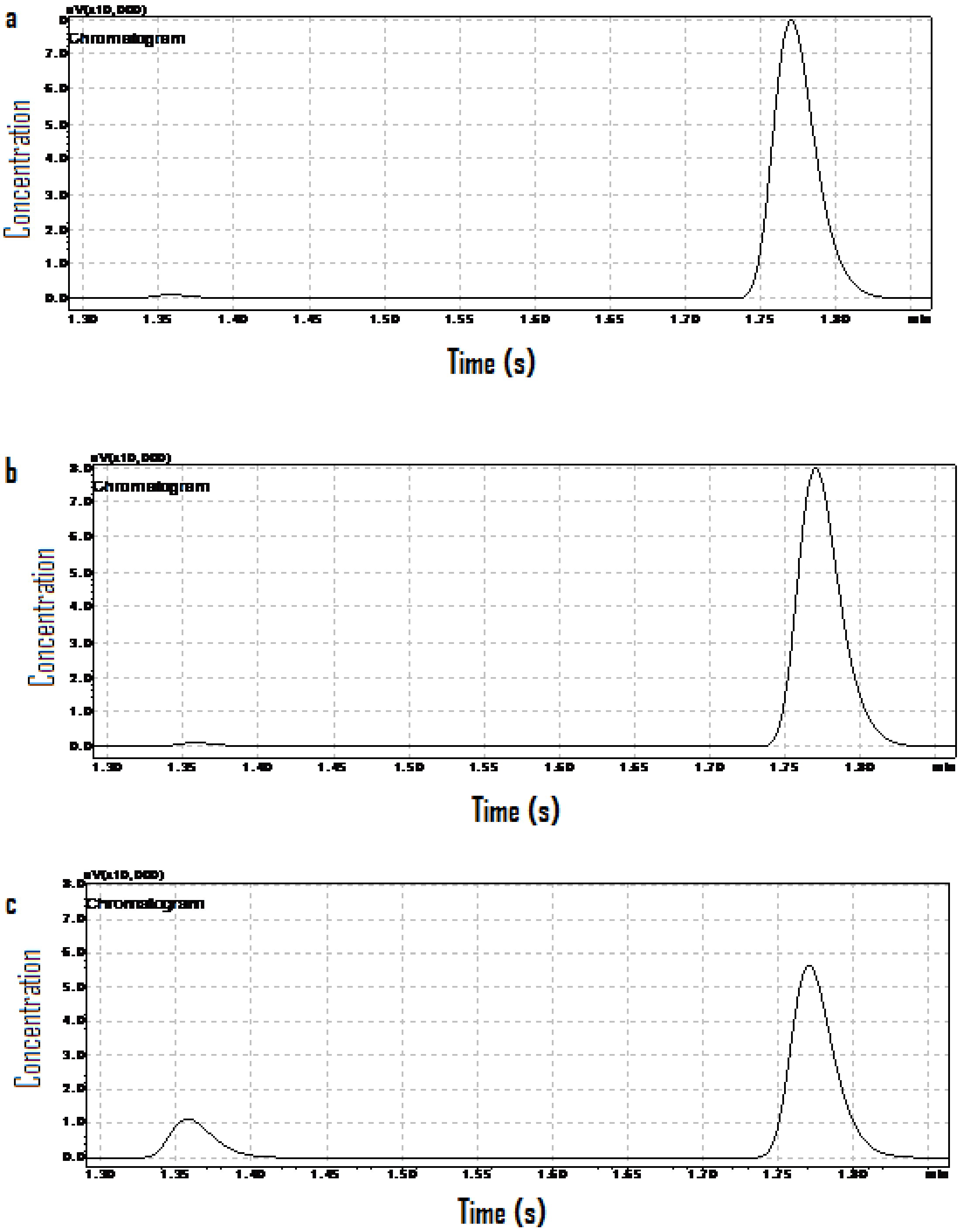


Figure 4.13. Degradation of TCE over time comparing Dissolved and melted of ZVI (a) 0 sec, (b) 10 sec, (c) 20 sec

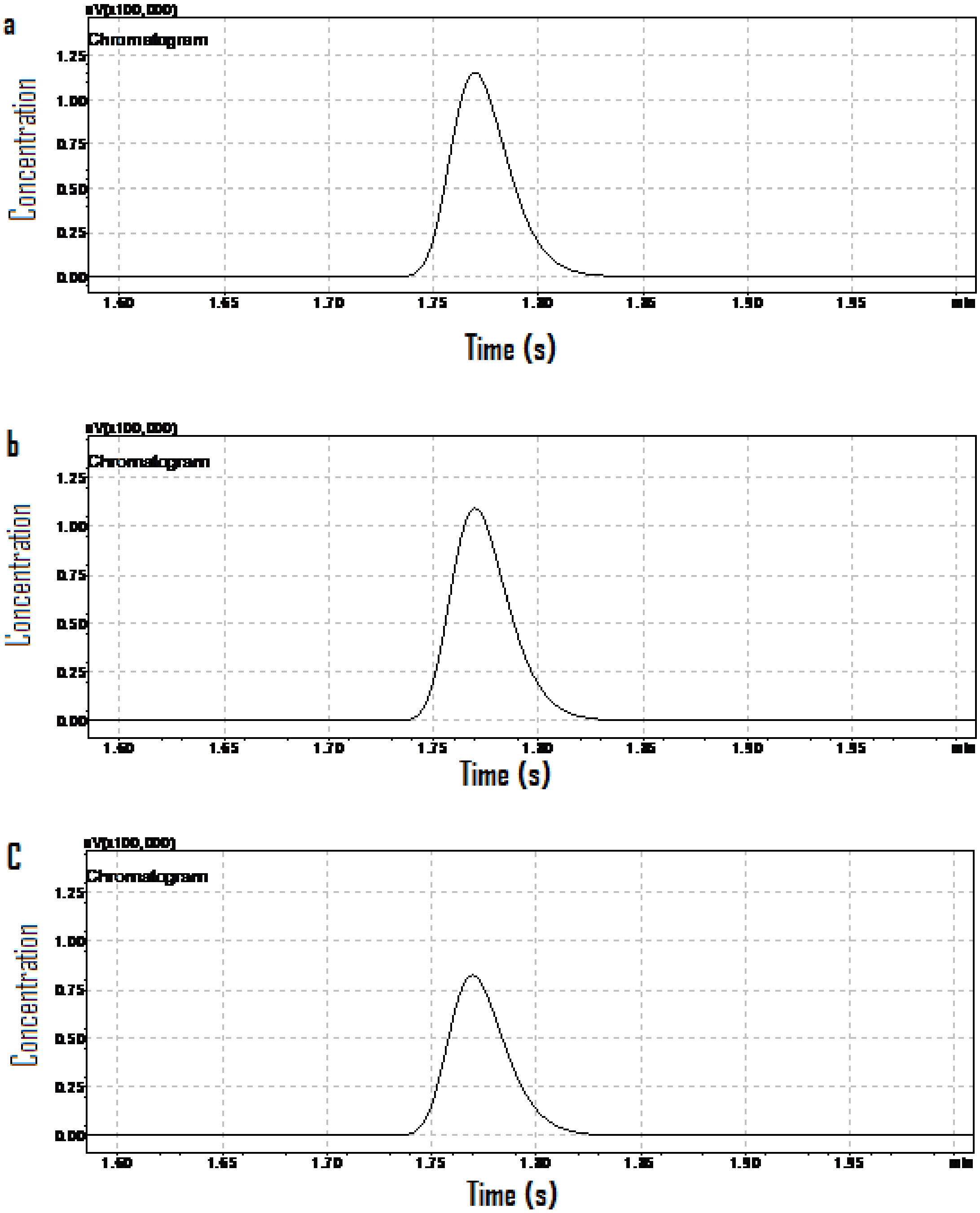


Figure 4.14. Degradation of TCE over time Melted ZVI; a) 0 sec b) 10 sec c) 20 sec

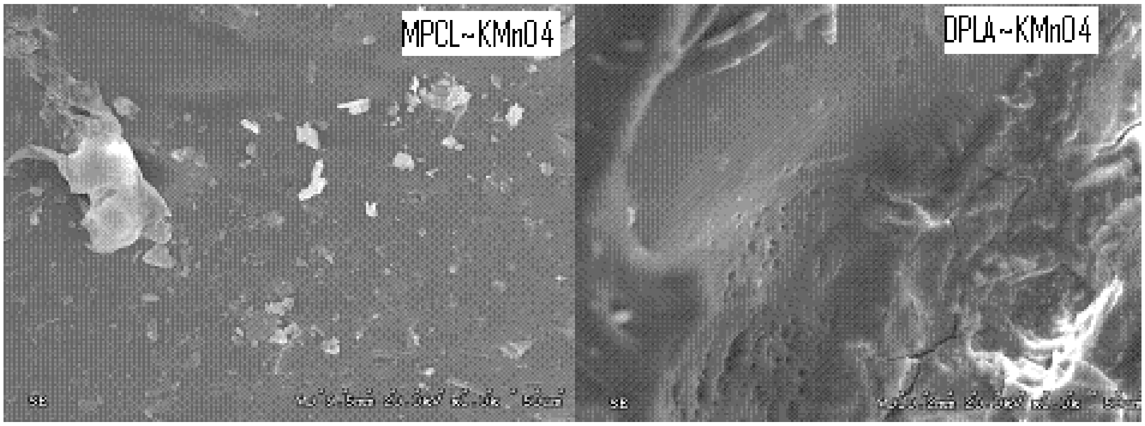


Figure 4.15. Comparison of SEM image for DPLA and MPLA surfaces

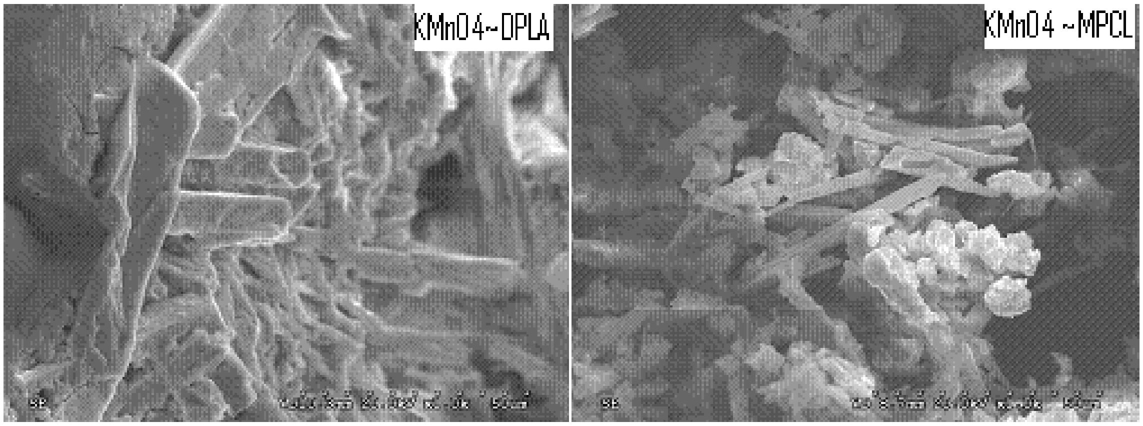


Figure 4.16. SEM images of $KMnO_4$ inside the two polymers

4.5 MnO_2 Production

4.5.1 MnO_2 Production

One of the major problems associated with the oxidation reaction using $KMnO_4$ is the production of manganese oxide (MnO_2). This problem arises when TCE reacts with

$KMnO_4$. Production of MnO_2 results in the production of a solid precipitate that will block delivery of $KMnO_4$ during subsurface remediation. The goal of this experiment was to formulate a solution to reduce $MNnO_2$ formation. The experiment used organic acids as a means to eliminate the formation of MnO_2. The experiment measured the production of MnO_2 over time. Figure 4.17 presents photos of batch systems containing organic acids to reduce MnO_2 build up. The EMG~MPCL resulted in MnO_2 production around the polymer and suspended MnO_2 in the solution resulting in a brown discoloration of the water sample. EMG~DPLA did not result in suspended MnO_2 and water discoloration; but it resulted in precipitate build-up around the polymer. FML~DPLA had significantly more MnO_2 precipitate than FML~MPCL. EMG~MPCL with nitric acid resulted in a reduction in the formation of suspended precipitate compared to the EMG~MPCL without the nitric acid present.

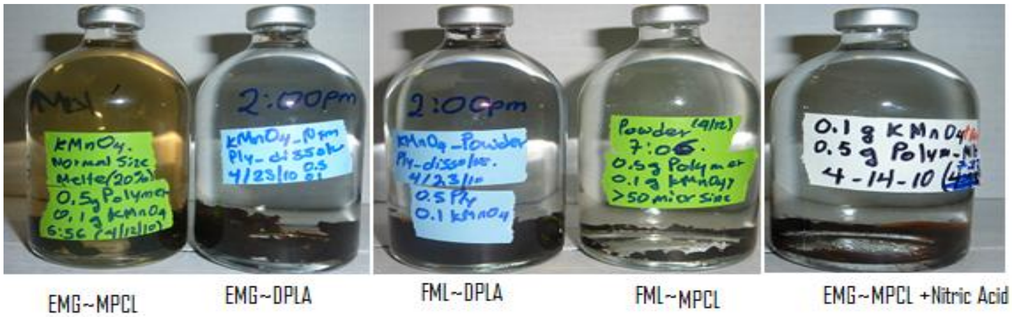


Figure 4.17. The formation of MnO_2 with various polymers and oxidants

4.5.2 Nitric acid

The results displayed below in the tables are a representation of the buildup of MnO_2 during the reaction of TCE and $KMnO_4$. Table 4.18 shows the results for MnO_2 reduction.

Table 4.18. The formation of MnO_4 utilizing EMG and FML oxidants with DPLA and MPCL

$KMnO_4$ Samples	**EMG MPCL Mass (g)**	**FML MPCL Mass (g)**	**EMG DPLA Mass (g)**	**FML DPLA Mass (g)**	**EMG MPCL + nitric acid Mass (g)**
Polymer + MnO_2 precipitate	0.932	0.698	0.520	0.500	0.511
Pellet mass	0.503	0.498	0.502	0.493	0.497
MnO_2 precipitate on polymer	0.429	0.200	0.018	0.007	0.014

The experiment showed the relationship between the different polymers and the particle sizes. The experiment ran for approximately for 42 days. The largest buildup of MnO_2 occurred during the remediation of TCE when the EMG~MPCL was used. Approximately 0.429 g of MnO_2 was produced and less precipitate was formed when using the dissolved form of the polymer with a smaller particle size. The mass of MnO_2 produced was 0.007g. Therefore this supported the hypothesis that the smaller particle of $KMnO_4$ would produce less MnO_2. This experiment also looked at the use of nitric acid to reduce the production of MnO_2 using the EMG~ MPCL. EMG~MPCL without nitric acid demonstrated the highest production of MnO_2, therefore, the goal was to see if the nitric acid would effectively reduce precipitate production. The EMG~MPCL without nitric acid resulted in 0.492 g of MnO_2 compared to the EMG~MPCL sample with nitric acid which resulted in the production of only 0.014g and a 98.368% reduction of MnO_2.

4.6 Release Modeling

Models can prove to be very useful tools to visualize and identify the behavior of the contaminants without the need to conduct experiments. Modeling has also been used in literature to evaluate the relationship between source zone and future distributions, to optimize the well field process to accomplish capture, and containment of the zone of organic compound contamination. The most important parameter needed for modeling is the diffusion rate which was obtained from the release test for the $KMnO_4$ and zero-valent iron studies. In studies by Desai et al. (1965) and Kydonieus (1980), the researchers based their model equations on diffusion of a chemical from a sphere of solute dispersed in a liquid matrix. Using this model as the basis, the equations can be applied using the data from this thesis. Their assumption was that (1) a pseudo-steady state exists; (2) the $KMnO_4$ particles are small compared to the average distance of diffusion; (3) the diffusion coefficient of the matrix is constant; and (4) a perfect sink condition exists in external media. The final assumption comes from Kydonieus (1980) indicates that the final concentration was slightly less than expected. By using these assumptions, the equation can be modified to equations 4.7 and 4.8.

$$t = \frac{C_o r^2}{2SD}\left[1 - \left(\frac{C_r}{C_{r,\max}}\right)^{\frac{2}{3}} - \frac{2}{3}\left(\frac{C_r}{C_{r,\max}}\right)\right] \tag{4.7}$$

$$C_r = \frac{C_{r,\max} t}{t_{O,S} + t} \tag{4.8}$$

Where C_0= the initial concentration of the solute in the matrix, r^2 is the radius of the pellets, and D = diffusivity of the solute through the matrix. The empirical functions can be used to characterize the release each permanganate pellets using equation (4.8). Based on Ross et al. (2001), if diffusion is assumed to be one-dimensional from the core containing a saturated solution of $KMnO_4$ though the shell into the water concentration $C_{W,}$ equation 4.9 can be used.

$$C_w = c_{sat}\left(1 - e^{-\left(\frac{3DHw}{TryV_w}\right)t}\right) \tag{4.9}$$

Where H= partitioning coefficient for $KMnO_4$ between shell and the water, w = initial mass of $KMnO_4$ in the soil phase, t= time, T= thickness of the shell, r= radius of the core, Y= unit weight of the particles (g cm^{-3}), and V_3= volume of water in the bottle. C_{sat} =63.8 g L^{-1} at 20 ^{0}C for $KMnO_4$ (Weast, 1987). Therefore future studies can be conducted to determine the model for remediation capabilities using $KMnO_4$ and ZVI encapsulated in polymers.

CHAPTER 5

CONCLUSIONS

This research suggests that using nano-size oxidant particles for the remediation of TCE is very promising technology. Not only does encapsulation with the polymer help reduce the formation of MnO_2 when using $KMnO_4$ oxidants, but it also has the ability to control the release of oxidant since it release low concentration. The release tests showed that the release of FML~MPCL is faster at the beginning of reaction but it slows down over time. This could suggest that the reaction between the oxidant or reducing chemical and TCE takes place at the surface of the polymer. When looking at the release of EMG~MPCL, it is slower at the beginning of the reaction but over time it increases. The half life of FML~MPCL is higher than FML~MPCL due to the concentration (i.e. smaller particle release lower concentrations of the $KMnO_4$ and bigger particles of the $KMnO_4$ does the opposite). When the polymer is dissolved and $KMnO_4$ is being encapsulated, it demonstrated a different behavior compared to the melted polymer. The degradation of TCE is not impacted by the particle size however the concentration of oxidant released over time is impacted based on processing method.

The ZVI encapsulated particles behaved differently depending on the polymer process used during encapsulating the chemical. The best delivery system compared to all the methods tested in this thesis was the nZVI~DPLA. Results indicated there was chloroform remaining in the dissolved polymer and this was confirmed by the GC analysis. This may have interfered with the reaction and caused the reaction to start at a faster rate. The interesting part of this is that when melting the polymer, EMG~MPCL had the most promising results. The formation of MnO_4 could be controlled by applying smaller sizes of oxidants, since the release of the oxidant occurred at the beginning at a fast rate. When comparing the melted and dissolve, the FML~DPCL shows less formation of MnO_4 when using the EMG ~ DMPLA then FML~DMPLC.

This study has shown that there are different options to select for controlled release chemical oxidant development. These choices are oxidant or reducing agent size, polymer type, and encapsulation method. For example when ZVI is used, the results from this thesis suggest it is best to use melting encapsulation process. This thesis demonstrated that for nZVI, it is better to use DPLA because of the side reaction which occurs in the system. For future research, it is recommended that batch experiments be conducted using the pellets which contain both ZVI and $KMnO_4$ encapsulated in the pellets. A future study of kinetics in both water and soil contaminated with TCE can be conducted using a bench scale system. The pellets can be arranged to create a permeable reactive barrier in a saturated and unsaturated system. This can be used to compare the efficiency for TCE remediation. Future studies can additionally investigate modifications which can be made to the polymer structure such as geometry, chemical layering, and use of hydrophilic polymers to extend the release time of the oxidant or reducing agent and control its degradation.

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