Bench Scale Fenton's Oxidation of TCE and By-product Formation: Revisited

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Abstract Trichloroethylene (TCE) is one of the most common groundwater contaminants in the United States. The degradation products of TCE may be more hazardous than the parent compound. With increased use of advanced oxidation and permeable barriers to treat groundwater, this research was undertaken to reevaluate the occurrence of these by-products. Fenton's oxidation was assessed for the ability to destroy trichloroethylene (TCE) in an aqueous solution over 360 minutes. TCE rapidly disappeared from the solution with a decrease of approximately 90 percent in the first 90 minutes. The degradation appeared to follow a second order reaction. Two dichloroethylene isomers (DCE) appeared in the early stages of the experiments and then began to degrade over the latter stages of the experiment following pseudo-first order reaction kinetics. This research indicates that harmful by-products are formed, but may be degradable.

Keywords Trichloroethylene, Fenton's Reagent, Dichloroethylene

1. Introduction

The focus of this paper is to assess the formation of disinfection byproducts during oxidation of trichloroethylene (TCE) which is a common groundwater contaminant. It is important to understand the production of hazardous daughter products by a remediation technique as the technique maybe deemed infeasible if the treated water is more harmful than the untreated water. The increased interest and use of reductive dechlorination via metallic nanoparticles has brought this remediation technique to the forefront of research[1,2]. Thus, the authors decided to reevaluate TCE dechlorination at the bench scale to assess the formation and disappearance of harmful daughter products.

1.1. Introduction to TCE Contamination and Advanced Oxidation

TCE is a common groundwater contaminant in the United States. TCE (C_2HCl_3) is characterized as a dense non-aqueous phase liquid (DNAPL) and tends to pool at the base of an aquifer[3,4,5,6]. TCE has low water solubility, thus the contaminant slowly dissolves from the DNAPL pool into the water causing long-term contamination of groundwater and soil[1,2]. The drinking water limit set by the US Environmental Protection Agency (EPA) is 5 $\mu\text{g/L}$ due to its potential as a health hazard. Typical levels reported in environmental water are below 200 $\mu\text{g/L}$ [5,7]. Thus, the oxidation experiments in this study were conducted with an initial TCE concentration of 500 $\mu\text{g/L}$. This concentration was chosen as it represents an environmentally relevant concentration.

1.2. Advanced Oxidation

Advanced oxidation is commonly recognized as the process of adding hydroxyl radicals to water to increase the molecular destruction of organics[4, 8]. Fenton's reagent is an aqueous mixture of hydrogen peroxide and ferrous iron. The iron cycles between the +II and +III oxidation states yielding hydroxyl radicals ($OH^\cdot$) which are characterized as indiscriminate oxidants. The intermediate steps of hydroxyl radical formation are well described in previous literature[1,2]. Fenton's oxidation is best under lower pH conditions[1,9,10,11,12]. One limitation of oxidation is the loss of hydroxyl radicals to scavenging by non-target species. In addition, the process can be limited due to inadequate amounts of iron or hydrogen peroxide in solution[9].

1.3. Evaluation of Byproduct Formation

Another potential disadvantage of advanced oxidation is the formation of daughter products that may be more hazardous than the parent compound. Dechlorination of TCE may result in the formation of cis-dichloroethylene (DCE), trans-DCE, and 1,1-DCE. DCE can further degrade to vinyl chloride (VC), which can degrade to ethylene. Finally, ethylene can degrade to the nontoxic compounds carbon dioxide and water. This process has also been seen in aerobic

and anaerobic microbial degradation of TCE[4,7,13]. The DCE isomers and VC may be more harmful to humans and therefore the production of these compounds is unwanted[14]. It is important to understand the formation of the aforementioned by-products due to their hazardous nature; however such research is lacking[11]. The drinking water limit set by the EPA is 7 µg/L for 1,1-DCE, 70 µg/L for cis-DCE, 100 µg/L for trans-DCE, and 2 µg/L for VC.

2. Materials and Methods

2.1. Materials

The following chemicals were purchased through Fisher Scientific (Fairlawn, NJ): TCE and methanol were ACS grade, 99.9% pure; the hydrogen peroxide was a 30% solution, ACS grade. A Barnstead/Thermolyne E-pure water system was used for all aqueous experiments (Dubuque, Iowa). The cis-DCE and trans-DCE were 5,000 µg/mL, the 1,1-DCE was 1,000 µg/mL, and the VC was 100 µg/mL prepared in methanol (Ultra Scientific, N. Kingstown, RI).

2.2. Aqueous Fenton's Oxidation

A reaction vessel (250 mL amber jar) was filled with a 0.25 mg/L Fe^{2+} aqueous iron solution. The pH was adjusted using 10% sulfuric acid until the desired pH was obtained (2.5, 3.5, or 4.5). TCE was added to the reaction vessel to achieve a concentration of 500 µg/L and left to equilibrate for one hour on a stir plate (Fe^{2+} :TCE molar ratio of 1.2:1). After equilibration, hydrogen peroxide was added to achieve a H_2O_2 :TCE molar ratio of 50:1 (approximate 14:1 weight ratio). At predetermined times methanol was added to the vessel to achieve a concentration of 3,000 mg/L; the methanol is a hydroxyl scavenger and its addition to the solution quenched the oxidation of TCE[10]. The reaction times were 5, 10, 20, 40, 90, 180, and 360 minutes. The pH of the solution was recorded for each time interval with an Orion model 420A pH meter equipped with an Orion pH probe.

2.3. Quantification

An Agilent Technologies 6890 Series Gas Chromatograph (GC) equipped with a flame ionization detector and a J & W Scientific DB-1, 30 m X 320 µm X 0.25 µm, fused silica column (Folsom, CA) was used to quantify the organic chemicals[6]. The inlet temperature of the GC was 240°C at 5 psi. The initial temperature in the oven was 35°C and held for one minute; the first temperature rate was 7.5°C/min to a final temperature of 50°C which was held for 2 minutes; the next rate was 20°C/min to a final temperature of 90°C which was held for 2 minutes; the final rate was 340°C/min to a final temperature of 200°C which was held for 7 minutes. The carrier gases were hydrogen at 40 mL/min and air at 450 mL/min. The carrier gas was nitrogen at 30 mL/min. Supelco® Solid Phase Micro Extraction (SPME) fibers were

used to concentrate the organics from the aqueous solution for improved detection with GC[15]. The silica fibers were coated with 85 µm Carboxen/polydimethylsiloxane. Virgin fibers were conditioned at 260°C for one hour in the GC inlet, then contacted with purified water until the fiber was stable. The SPME fiber was equilibrated in the sample for 25 minutes to concentrate the organics, then placed into the GC inlet for ten minutes to ensure all organics were removed. The inlet temperature was 240°C.

Hypothesis testing in the form of analysis of variance (ANOVA) was conducted on triplicates of each chemical and triplicates of a blank solution to determine the analytical detection limits. The detection limit was the lowest concentration found to be statistically different than the blank. For TCE, DCE isomers, and VC the detection limit was 1 µg/L.

3. Results

Initially three pH solutions were evaluated (2.5, 3.5, and 4.5). One experiment was conducted for each of the three pH solutions. The experiment at an initial pH of 3.5 was found to be the most effective for TCE removal over the 6 hour experiment (Figure 1). Thus, two additional experiments at this pH were conducted for determining TCE reduction kinetics and byproduct formation (i.e. triplicates). Error bars represent the 95 percent confidence interval.

Figure 1. Percent Reduction of TCE by pH

The TCE concentration rapidly decreased with Fenton's oxidation at a pH = 3.5. The majority of degradation occurred in the first 30 minutes (Figure 2).

Figure 2. TCE degradation using Fenton's Reagent at pH = 3.5

3.1. Reaction Kinetics

Reaction kinetics was evaluated for the triplicate samples of the oxidation experiment at an initial pH of 3.5. Zero, pseudo-first, and second order reaction kinetics equations were evaluated. The best fit was the second-order reaction with a resulting $R^2 = 0.69$. The rate constant was $0.00003 \text{ (mg/L)}^{-1} \text{ s}^{-1}$ when the entire data set was used. If only the first four points are used (the rapid degradation portion) the R^2 was 0.69 and the reaction rate was $0.0004 \text{ (mg/L)}^{-1} \text{ s}^{-1}$.

3.2. By-product Formation

Figure 3. DCE isomer formation and disappearance at pH = 3.5

Figure 4. TCE and DCE isomers at pH = 2.5

Figure 5. TCE and DCE isomers at pH = 4.5

The DCE isomers appeared and then degraded over the 6 hour experiment at a pH = 3.5. The 1,1-DCE and VC were below the detection limit for almost all reaction times

(Figure 3). For comparison the experiments conducted at an initial pH of 2.5 and 4.5 are presented in Figure 4 and Figure 5, respectively. The TCE did not decrease as greatly in the pH = 2.5 experiment, but the DCE isomers increased to a higher level compared to the pH = 3.5 experiments. In addition, the DCE isomers did not appear to decrease over the 360 minutes when the initial pH was 2.5. The pH = 4.5 experimental results were similar to the pH = 3.5 experimental results. The TCE degraded to lower concentrations than the pH = 2.5 experiments and the DCE isomers increased to lower concentrations.

The reaction kinetics was analyzed for the degradation of cis-DCE and trans-DCE over the later part of the experiment. In the first 90 minutes of the experiment, cis-DCE and trans-DCE were formed and in the remaining 270 minutes the DCE isomers were degraded (Figure 3). The degradation of both isomers followed pseudo-first order reaction kinetics for the experimental time after 90 minutes to the completion of the experiment at 360 minutes. The R^2 for cis-DCE was 0.93 and R^2 was 0.92 for trans-DCE. The reaction rate for cis-DCE was 0.0022 min^{-1} and the reaction rate for trans-DCE was 0.0029 min^{-1} .

3.3. Solution pH

The initial pH of the oxidation experiment was 3.5, however the pH quickly rose to 3.6 and remained at 3.6 for the experiment. The pH of the experiments conducted at an initial pH of 2.5 decreased. The final pH was 2.16. The experiment with an initial pH = 4.5 increased to a final pH of 4.96.

4. Discussion

In this study the TCE concentration decreased with Fenton's oxidation at a pH = 3.5 with the majority of degradation in the first 30 minutes (Figure 2). This is in agreement with the Chen et al.[11] study which also showed a rapid decrease of TCE followed by a slower trend in batch experiments. Xin-De et al.[4] studied Fenton's reagent on artificially contaminated soil slurries and found that the reduction in TCE was rapid with the experimental duration from 10 to 60 minutes. The study also showed over 80 percent reduction in TCE concentration at pH values 3 and 5.

4.1. Reaction Kinetics

Kao et al.[16] conducted laboratory experiments to evaluate the use of potassium permanganate to oxidize TCE and found the TCE degradation followed second order reaction kinetics. Zhimin et al.[17] evaluated kinetics of Fenton's reagent for the destruction of TCE. The authors determined that the degradation followed second-order reaction models, however the study went further to determine the reaction rates based on a time-squared model and only reported such values which cannot be directly

compared to this data.

For comparison, this data was modeled as a pseudo-first order reaction using the first four data points and the R^2 was 0.31 with a rate constant of 0.11 min^{-1} . The Chen et al.[11] study found that the data followed a pseudo first order reaction and the rate constant was 0.0057 min^{-1} which is three orders of magnitude different than this study. The differences could be due to different experimental setups and also to different molar ratios of TCE and H_2O_2 between the studies.

4.2. By-product Formation

Jeong et al.[14] studied TCE degradation using mackinawite (FeS) in the presence of Fe-hydroxides. The study showed that cis-DCE was formed as a degradation product of TCE, then proceeded to degrade, which was also found in this study. The degradation was modeled as a pseudo-first order reaction with a resulting reaction rate constant of $1.6 \times 10^{-3} \text{ hr}^{-1}$ [14]. This value is about three orders of magnitude higher than the reaction rate found in this study. The difference could be due to the different types of reagents used and also different molar concentrations of TCE and iron.

At this time the authors could not find data to directly compare to these reaction rates.

4.3. Solution pH

The results from this study are in contrast to the findings of Chen et al.[11] who found that pH decreased while using Fenton's reagent. In the aforementioned study, the initial pH was 3.01 and the ending pH was 2.77. The reason was allotted to the production of H^+ ions in the final cycling of Fe^{2+} to Fe^{3+} . In this study only the experiments with an initial pH of 2.5 decreased, with a final value of 2.16. This experiment was in agreement with the Chen et al.[11] study. The differences in pH changes may be due to the initial pH conditions being different between the experiments or in the iron cycling conditions in the experiments which are related to pH[12].

5. Conclusions

In conclusion, Fenton's oxidation shows promise as a remediation strategy for aqueous TCE contamination. The daughter products cis-DCE and trans-DCE formed during remediation, but they were oxidized with additional reaction time. The oxidation of DCE is not as rapid as for TCE which could be due to a lack of $\text{OH}^\cdot$ radicals remaining in solution following the oxidation of TCE. The applicability of Fenton's reagent appears to be feasible and is in fact used in the United States, however monitoring of by-products maybe necessary. It is important to note that this work was conducted with purified water and not groundwater. Due to physiochemical differences in the properties of purified

water versus groundwater, a direct extrapolation is not feasible.

Appendix

Appendix Figure 1. Second-order reaction kinetics

Appendix Figure 2. Pseudo-first order reaction kinetics

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