TCE Removal Utilizing Coupled Zeolite Sorption and Advanced Oxidation

by

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Abstract

Trichloroethylene (TCE) is one of the most common groundwater pollutants in the United States. The EPA estimated that between 9% and 34% of the drinking water sources in the United States may contain TCE. The United States Environmental Protection Agency set a maximum contaminant level at 5 μg/L of trichloroethylene for drinking water.

This study investigated the feasibility of removing TCE from water by sorption to ZSM-5 and advanced oxidation to destroy the TCE on the zeolite. Aqueous oxidation of TCE with Fenton's reagent was shown to be efficient for the destruction of TCE. The quantified by-products were cis-DCE and trans-DCE. ZSM-5 rapidly removed TCE from water. A Freundlich isotherm was created for the uptake of TCE by ZSM-5. Once TCE was sorbed to ZSM-5, preliminary experiments showed that the oxidation was able to destroy the TCE while producing the same by-products.

Chapter 1 Introduction

The United States Environmental Protection Agency (EPA) set a maximum contaminant level at 5 μg/L of trichloroethylene (TCE) for drinking water. TCE was introduced into groundwater by industry; particularly though accidental spills, improper handling, leaking storage tanks and leaching from landfills (WHO, 1985). TCE has been found in rainwater, surface water, groundwater, drinking water and sea water (EPA, 2001).

TCE is one of the most frequently reported groundwater contaminants. TCE is the organic groundwater contaminant that was reported in the highest concentration in 1982 (EPA, 2001). Reported levels in water are typically between 10 and 100 μg/L (ppb) (WHO, 1985). The EPA (2001) estimates that between 9% and 34% of the drinking water sources in the United States may contain TCE. It is important to note that this estimate does not include private wells, which may also be contaminated especially if the wells are located near TCE disposal/contamination sites where leaching may occur. In California, 187 of 2,947 wells tested had TCE, with concentrations up to 440 μg/L and a median of 3.0 μg/L. TCE is commonly found at Superfund sites. At least 861 sites, of the 1,428 hazardous waste sites proposed for the EPA National Priority List (NPL), contain TCE as illustrated in Figure 1-1. TCE was also detected in 28% of 9,295 surface water reporting stations nationwide (EPA, 2001). This project evaluated (1) the feasibility of removing TCE from water with ZSM-5 zeolites and (2) the potential for destroying the zeolite-bound TCE with Fenton's oxidation.

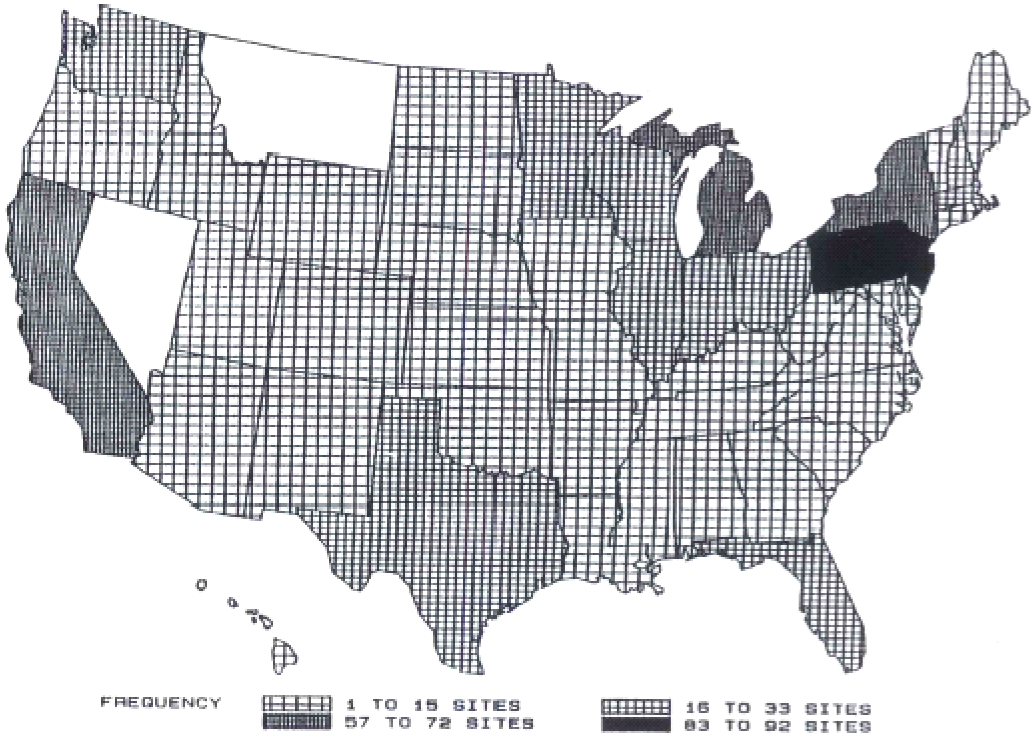

Figure 1-1: Frequency of NPL sites with TCE (EPA, 2001)

Chapter 2 Background

2.1 Trichloroethylene

Trichloroethylene (TCE) is a halogenated, aliphatic organic compound. In pure phase, it is a colorless liquid with a slightly sweet smell. TCE was used in metal degreasing, solvent extraction processes, textile cleaning and as a carrier solvent (WHO, 1985). TCE was replaced with tetrachloroethylene in the dry cleaning industry. TCE has also been discontinued in the following uses: fumigants, extractant for decaffeinating coffee, use in cosmetics and drug products (EPA, 2001). The molecular formula for TCE is C_2HCl_3 and its chemical structure is shown in Figure 2-1. TCE has several trade names including but not limited to, Chlorylea, TRI-Plus M, Triad, Vitran, Perm-A-Chlor and Dow-Tri. In the gas phase, it is relatively stable in air, but unstable in light or moisture.

The reactivity of TCE in aqueous solution varies with conditions. It is incompatible with strong caustics or alkalis. It is chemically active with metals such as barium, lithium, titanium and beryllium (EPA, 2001). Several of its properties can be seen in Table 2-1.

Table 2-1: Properties of TCE (Russell *et al.*, 1992; EPA, 2001)

Density, g/mL	1.46
Solubility, mg/L @ 20˚C	1000
Henry's Law Constant, atm-m^3/mol @ 20˚C	0.00892
Molecular Weight, g	131.4
Boiling Point	86.7˚C
Melting Point	-73˚C
Vapor Pressure @ 0˚C, mm Hg	19.9
Vapor Pressure @ 20˚C, mm Hg	57.8
Log Octanol-Water Partition Coefficient	2.42

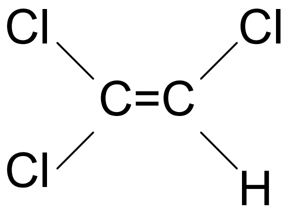

Figure 2-1: Chemical Structure of TCE

Pure TCE has a density greater than pure water. When TCE is present in pure phase, it migrates down through water due to gravitational force and forms a pool of dense nonaqueous phase liquid (DNAPL). TCE can further contaminate an aquifer by spreading via dissolution, advection and dispersion. TCE is highly oxidized, thus resists further oxidation but is readily reduced (Russell *et al.*, 1992).

Exposure to TCE is mainly through inhalation, ingestion and dermal absorption. The majority of TCE used in the United States is released to the air, primarily by vapor degreasing operations. It has also been released to the atmosphere at treatment and disposal facilities and landfills. TCE in landfill leachate can contaminate groundwater. The release of TCE by industry to the environment in the United States was approximately 55.6 million pounds in 1987, but reduced to 29.2 million pounds in 1994 (EPA, 2001).

Transformation and degradation processes of TCE in the environment are limited. TCE undergoes aerobic biodegradation in soil at a slow rate. Its half-life is estimated at six months to one year. Anaerobic biodegradation may occur but at the same slow rate as aerobic biodegradation. TCE does not absorb ultraviolet light at wavelengths less than 290 nanometers; therefore it will not directly photolyze in the atmosphere or in water. Vapor phase photo-oxidation with hydroxyl radicals, however, is believed to occur at moderate rates with a half-life between one and eleven days. Photo-oxidation in water was reported, but at a much slower rate with a half-life about 10.7 months (EPA, 2001).

2.1.1 Health Aspects

Once TCE is in the body, it is distributed and accumulates in adipose tissue. TCE exits the body unchanged in exhaled air and to a lesser degree in feces, sweat and saliva. TCE, however, may be rapidly metabolized in the liver. The symptoms of exposure to TCE are manifested in central nervous system problems (WHO, 1985). They include headache, drowsiness, hyperhydrosis and tachycardia. In more severe cases, a coma may result. Psychomotor impairment was noticed after inhalation exposure to 5,400 mg/m^3 (1,000 ppm) for 2 hours in work place conditions (WHO, 1985). TCE vapors can cause eye irritation. High oral doses, 200 mL to 300 mL, can be toxic to the liver and kidneys. The lethal dose for an adult is generally 7,000 mg/kg body weight (WHO, 1985).

2.1.2 Current Treatment Methods

Current wastewater and municipal water treatment processes, such as coagulation, sedimentation, filtration and chlorination, are ineffective for reducing TCE levels in water. Air stripping is effective in removing TCE from water, and involves using a constant stream of air for TCE to transfer into. However, large volumes of air are needed for this to be accomplished. Unfortunately, this process simply shifts the contaminant to another media. Another limitation to air stripping occurs with low concentrations of TCE as large volumes of air are needed (Russell *et al*., 1992).

Granular activated carbon (GAC) is used to adsorb TCE. However, GAC has limitations as an adsorption media. A sorbent has a finite capacity for a specific contaminant. With fixed bed adsorbents, when the sorption limit is reached the contaminant can breakthrough. It is necessary to regenerate the GAC media or replace it after breakthrough occurs. At a concentration of 1 ppm TCE at a neutral pH and 20°C, the capacity of TCE on GAC is approximately 28 mg/g (Hugh *et al*., 1992). Other organic compounds will adsorb to GAC, thus lowering the amount of TCE that can be adsorbed (Hugh *et al*., 1992).

The combination of air stripping and carbon adsorption is another method used to remediate TCE contaminated water. Air stripping can lower concentrations of TCE in water to levels that may not meet drinking water standards. However, the water may be then sent through GAC as a second treatment step. Air stripping may remove the majority of the TCE and the GAC polishes the air stripper effluent (Hugh *et al*., 1992).

Biological remediation uses bacteria to degrade TCE to CO_2, water and chloride ions. Anaerobic and aerobic degradation have been shown to work in laboratory experiments; however, readily oxidizable substrates and nutrients are required. Some bacteria species need a primary metabolite for the bacteria to produce the necessary enzymes to consume TCE (Hugh *et al*., 1992). Methanotrophs (microorganisms that oxidize methane) have been shown in laboratory experiments to use cometabolic oxidation to degrade TCE. Intermediate by products, such as dichloroethylene and vinyl chloride, have been seen in many experiments. The less chlorinated compounds, however, may be easier for the microorganisms to degrade through aerobic oxidation than TCE (Lorah *et al*., 2001).

2.2 Zeolites

Zeolites are naturally occurring aluminosilicalite minerals that posses 3-dimensionsal structures of SiO_4^{4-} and AlO_4^{5-}. Many different types of zeolites of various chemical compositions have been synthesized in the laboratory. Zeolites have porous structures, which allow them to selectively take up molecules into their structure (Dyer, 1988). Table 2-2 lists some common zeolites and several of their properties.

Table 2-2: Common zeolites (Greene *et al.*, 1996; Anderson, 2000; Tiscareno-Lechuga *et al.*, 2003)

Zeolite	Pore Size	Characteristic properties
ZSM-5	Medium pore size, 5.3 X 5.6 Å	Pentasil family, 10-membered oxygen rings, $SiO_2/Al_2O_3 \sim 1000$, hydrophobic
Silicalite		Al-Free ZSM-5, Pentasil family, $SiO_2/Al_2O_3 \sim \infty$, hydrophobic
Zeolite Y	Large pore size, 7.4 Å	Faujasites family, 12-membered oxygen rings, $SiO_2/Al_2O_3 \sim 75$
Zeolite A	Small pore size, 4.1 Å	hydrophilic
Mordenite	6.5 X 7.0 Å	$SiO_2/Al_2O_3 \sim 200$

Zeolites may be characterized by X-ray powder diffraction (XRD). XRD uses X-ray irradiation of the zeolite powder to produce a characteristic pattern from the regular array of the atoms within the zeolite structure. These patterns provide a technique to identify zeolite material by comparison with known patterns. The International Zeolite Association (IZA) has an official registry with a list of 133 structurally different zeolites (Crabb, 2001). The following zeolites account for about 90% of the zeolite adsorbent market: Zeolite A, the Faujasites (X and Y) and the Pentasils (ZSM-5 and silicalite) are used as commercial adsorbents (Greene *et al*., 1996; Crabb, 2001).

Zeolites with high SiO_2/Al_2O_3 ratios have been shown to remove organics from water (Anderson, 2000; Giaya *et al*., 2000). These zeolites tend to be hydrophobic and therefore sorb non-polar molecules. In general, as the aluminum content decreases, the zeolites' affinity for water decreases (Pope, 1987). Selectivity for molecules is also a function of pore size and shape. Molecules which are larger than the pore diameter of the zeolite are excluded from the internal spaces (Anderson, 2000; Giaya *et al*., 2000). Molecules which are able to enter the zeolite can interact with the zeolite through van der Waals, electrostatic and other interactions. ZSM-5 is stable over elevated temperatures and under acidic conditions. It may be regenerated with the removal/destruction of the organic by heating (Anderson, 2000). ZSM-5 has medium pore sizes with 10-membered oxygen rings accompanied by two types of intersecting channels, sinusoidal and straight (Greene *et al*., 1996).

Anderson (2000) conducted experiments on the removal of TCE from water using three different zeolites and two activated carbon samples. The zeolites used included: ZSM-5 with a pore size of 5.3 x 5.6 Å; mordenite with a pore size of 6.5 x 7.0 Å; and zeolite Y with a pore size of 7.4 Å. The ZSM-5 removed greater than 97% of the TCE from a 100 µg/L TCE-MTBE-chloroform solution. The removal with mordenite was about 77%. The removal with the activated carbons was about 68% and the removal was only 9% for zeolite Y. The most effective sorbent for removing TCE from water was ZSM-5.

Giaya *et al*. (2000) studied the sorption of TCE by several different adsorbents. The sorbents were a silicalite-1 provided by Union Carbide, ZSM-5 provided by Zeolyst, silicalite-1 synthesized at Worcester Polytechnic Institute several years prior to the research, Centaur® activated carbon by Calgon, Dealuminated Y by Zeolyst, Celite® Diatomaceous Earth by Celite Corporation, Mordenite by Union Carbide, Coked zeolite X from UOP, and Engelhard catalysts by Engelhard. All of these sorbents were tested for their TCE adsorption capacity. Experiments were performed with TCE in the 100-1,000 ppb concentration range at 20°C. The two silicalite-1 samples and the ZSM-5 had the highest uptake capacity and were further tested along with Centaur® activated carbon and the dealuminated Y. The silicalite-1 was found to outperform the activated carbon for the four chlorinated organics sampled (TCE, tetrachloroethylene, carbon tetrachloride, and chloroform) and the authors claimed that the silicalite-1 pores concentrated the organics by the preferential exclusion of water (Giaya *et al*., 2000).

2.3 Oxidation via Fenton's Reagent

Fenton's reagent is a mixture of hydrogen peroxide and ferrous iron. During Fenton's oxidation iron cycles between the +II and +III oxidation states yielding hydroxyl radicals ($\cdot OH$) as shown in equation 1. Hydroxyl radicals are indiscriminate oxidants and may be used to oxidize contaminants found in water. The ferric iron (+III) can react with hydrogen peroxide to return to the +II oxidation state, as shown in equation 2. Fenton's oxidation is best under acidic conditions because at higher pHs iron has a lower solubility (Huling *et al.*, 2000; Teel *et al.*, 2001).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet \qquad (1)$$

$$2Fe^{3+} + H_2O_2 \rightarrow 2Fe^{2+} + O_2 + 2H^+ \qquad (2)$$

Other reactions may take place during Fenton's oxidation (Teel *et al.*, 2001).

$$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^- \qquad (3)$$

$$H_2O_2 + OH\bullet \rightarrow H_2O + HO_2\bullet \qquad (4)$$

$$OH\bullet + HO_2\bullet \rightarrow O_2 + H_2O \qquad (5)$$

The hydroperoxyl radical ($HO_2\bullet$) is an oxidant, but not as strong an oxidant as the hydroxyl radical. The hydroxyl radical is considered responsible for oxidizing organic contaminants in water (Chen *et al.*, 2001).

Advanced oxidation of TCE occurs with the following reaction:

$$TCE + OH\bullet \rightarrow products \qquad (6)$$

Hydroxyl radicals may also react with organics to produce another radical:

$$RH + OH\bullet \rightarrow R\bullet + H_2O \qquad (7)$$

where RH is an organic compound. These radicals can convert Fe^{3+} back to Fe^{2+}:

$$R\bullet + Fe^{3+} \rightarrow Fe^{2+} + products \qquad (8)$$

Research has been conducted on the effectiveness of Fenton's reagent for treating chlorinated organics. Teel *et al.* (2001) found that in classical Fenton's oxidation 78% of the initial TCE was degraded. 2.5 moles of H_2O_2 were consumed per mole of TCE. During this reaction, 1.9 moles of chloride were released per mole of TCE, thus not all of the chlorine was displaced from the TCE (Teel *et al.*, 2001).

Chen *et al*. (2001) found that Fenton's reagent was able to degrade aqueous phase TCE by 90% to 100%, at a $pH = 3 \pm 0.05$ and initial TCE concentration of 53 mg/L. In a sandy soil column experiment, when iron, hydrogen peroxide and TCE were all added to the column influent, the TCE was completely oxidized in the column. Fenton's reagent, therefore, was able to oxidize TCE in the presence of soil. It was also found, however, that soil-induced H_2O_2 decomposition (no iron addition) did not degrade TCE. The addition of H_2O_2 and ferrous iron and lowering the pH are necessary for the successful *in situ* application of this remediation technique (Chen *et al*., 2001).

Gates and Siegrist (1995) studied the chemical oxidation of TCE in fine grained soils. They found 98% removal of TCE within an initial TCE concentration of 1.9 mg/kg soil and the H_2O_2 dose varied from 0.1 g/kg soil (0.015%) to 28.3 g/kg soil (7.3%). The amount of iron used in the experiments was equal to the amount already existing in the soil (i.e., none was added). The removal efficiency was independent of initial TCE concentration. The amount of H_2O_2 added affected the removal efficiency; it was found that with higher H_2O_2 doses, more removal was measured (Gates and Siegrist, 1995).

In addition to the traditional Fenton's reagent there is Fenton-like oxidation employing UV light in a photo-Fenton process. Photo-Fenton oxidation is a combination of ferric iron (Fe^{3+}), H_2O_2, and UV light to produce $OH\bullet$. Engwall *et al*. (1999) used photo-Fenton oxidation to remove pentachlorophenol (PCP) and creosote from water. The constituents added were $Fe^{3+} = 1mM$, $H_2O_2 = 10mM$. Then the solution was subjected to UV light ($UV = 1.4 * 10^{-3}$ M hν min^{-1}). The pH was 2.75 and the temperature was 25°C. The molar ratio of H_2O_2:organics was about 40:1. The PCP was completely dechlorinated in 10-20 minutes, and total organic carbon decreased by 80% in 180 minutes (Engwall *et al*., 1999).

Huling *et al*. (2000) adsorbed 2-chlorophenol (2CP) to granular activated carbon (GAC) amended with fixed iron, and then regenerated the carbon by Fenton's oxidation. The treatment efficiency increased with higher amounts of iron and 2CP on the GAC. The oxidation of 2CP increased with increasing H_2O_2 concentration. The authors noted that desorption of the contaminant from the GAC and subsequent oxidation can also occur. The repeated adsorption/oxidation experiments did not change the GAC surface to a degree in which adsorption was no longer attainable. Many environmental contaminants may be removed from water by activated carbon, and can react with OH• produced from advanced oxidation. Thus, there is a range of contaminants for which the adsorption/oxidation process could work (Huling *et al*., 2000).

Unfortunately, there are limitations to Fenton's oxidation. One limitation is the reaction of the hydroxyl radicals with non-target species, also called scavenging. Scavenging can occur with nitrate and sulfate, which are common ground water constituents. Insufficient amounts of iron or hydrogen peroxide would not produce high enough concentrations of hydroxyl radicals which are necessary for oxidation to occur (Huling *et al*., 2000).

2.4 Oxidation By Products

The potential by-products of TCE degradation may be in the form of dichloroethylene (DCE) or vinyl chloride (VC). The dichloroethylenes are: cis-1,2-DCE (cis-DCE), trans-1,2-DCE (trans-DCE), and 1,1-DCE. Isomers of 1,2-dichloroethylene (cis- and trans- isomers) are formed by anaerobic microbial degradation of TCE in soil, groundwater and sediments (EPA, 2001). DCE can be anaerobically or aerobically oxidized to vinyl chloride, with half lives on the order of months (Lorah *et al*., 2001). DCE isomers are typically removed from water by volatilization. Cis-DCE has been found in Miami drinking water at 16 ppb, and at 0.1 ppb in both Cincinnati and Philadelphia (EPA, 2001). A well in Wisconsin had 83.3 ppb cis-DCE. In air, cis-DCE can react with hydroxyl radicals (photochemically produced) with a half life of 8 days. Cis-DCE is the isomer most commonly found (EPA, 2001).

Trans-DCE has the same chemical formula and molecular weight as cis-DCE, however has a different physical orientation, as shown in Figure 2-2. Trans-DCE was discovered in drinking water at 1 ppb in Miami and in Illinois private wells at a median value of 8 ppb and a high concentration of 64 ppb. Monitoring wells near a degreasing plant in Connecticut had levels ranging from 1.2 ppb to 320.9 ppb. In air, trans-DCE can react with hydroxyl radicals (photochemically produced) with a half life around 3.6 days (EPA, 2001).

Another potential degradation by-product may be 1,1-DCE. This compound has the same chemical formula and molecular weight as cis-DCE and trans-DCE, however 1,1-DCE has a different orientation, as shown in Figure 2-2.

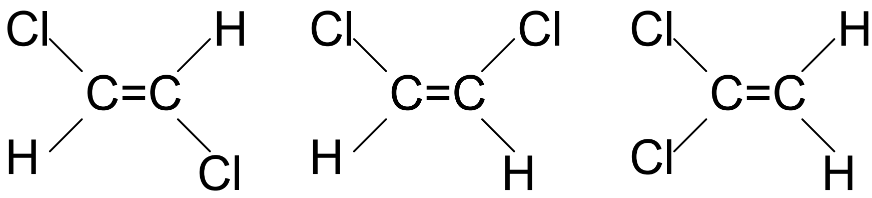

Figure 2-2: Chemical structure of trans-DCE, cis-DCE, 1,1-DCE

Vinyl chloride (VC) may also be formed from the oxidation of TCE. Vinyl chloride has the molecular formula C_2H_3Cl and the structure shown Figure 2-3. VC is a known human carcinogen and the US EPA set a drinking water maximum contaminant level of 2 µg/L for VC. The World Health Organization guideline is 0.5 µg/L for drinking water (Yamamoto *et al*., 2001). Therefore this is an unwanted by-product of TCE remediation.

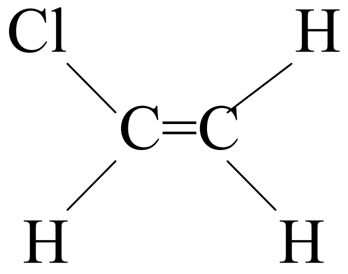

Figure 2-3: Chemical Structure of Vinyl Chloride

Eventually these by-products should degrade to ethylene then to carbon dioxide and water. These final products are wanted because they are nontoxic end products.

2.5 Hypothesis and Objectives

There were three hypotheses formulated:

- TCE can be destroyed by Fenton's oxidation.
- TCE can be removed from water by zeolites, specifically ZSM-5.
- The TCE on the zeolite can be destroyed by oxidation.

To evaluate these hypotheses, the objectives of this research were:

- To conduct aqueous phase Fenton's oxidation of TCE.
- To measure the extent and rate at which zeolite ZSM-5 was able to remove TCE from water.
- To conduct experiments to oxidize the TCE from the zeolite following sorption.

Chapter 3 Materials and Methods

3.1 Materials

The following chemicals were all from Fisher Scientific (Fair Lawn, NJ). The TCE and methanol were A.C.S. grade with an assay of 99.9%. The hexane was HPLC grade with an assay of 99.9%. And the 30% hydrogen peroxide was A.C.S. grade. The water (E-pure) was tap water sent through an RO Pure ST reverse osmosis system, followed by an E-pure system supplied by Barnstead/Thermolyne (Dubuque, Iowa). The cis-DCE (5,000 μg/mL), trans-DCE (5,000 μg/mL), 1,1-DCE (1,000 μg/mL) and VC (100 μg/mL) standards, all diluted in methanol, were from Ultra Scientific (N. Kingstown, Rhode Island).

The zeolite used in all experiments was ZSM-5 provided by Grace-Davidson (Columbia, Maryland). A thermogravimetric analysis was run on an as-received sample of ZSM-5. The thermogravimetic analysis (TGA) was a Hi-Res TGA 2950 Thermogravimetric Analyzer by TA Instruments. The experiments were run in a heat and hold method with a temperature range from room temperature (about 23 °C) to 550 °C and then held at 550 °C for ten minutes. The temperature increase rate was 5 °C per minute. Nitrogen was the carrier gas. Figure 3-1 shows the results of the thermogravimetric analysis. A template would result in a weight loss around 14%. Between the two plateaus, where any weight loss would have been, is less than 10 % which indicates that this sample does not contain a template. An EDX analysis was run on a sample of the zeolite in Washburn Shops at Worcester Polytechnic Institute in Worcester, MA. The results showed 6.43 weight percent Al_2O_3 and 93.57 weight percent SiO_2. The percent of oxygen was 66.25, of the aluminum was 2.53 and the silica was 31.23, assuming these three elements make up 100% of the composition. The following four analyses were completed with the EDX: spot stoichometry analysis, area stoichometry analysis, spot scan analysis, and area scan analysis.

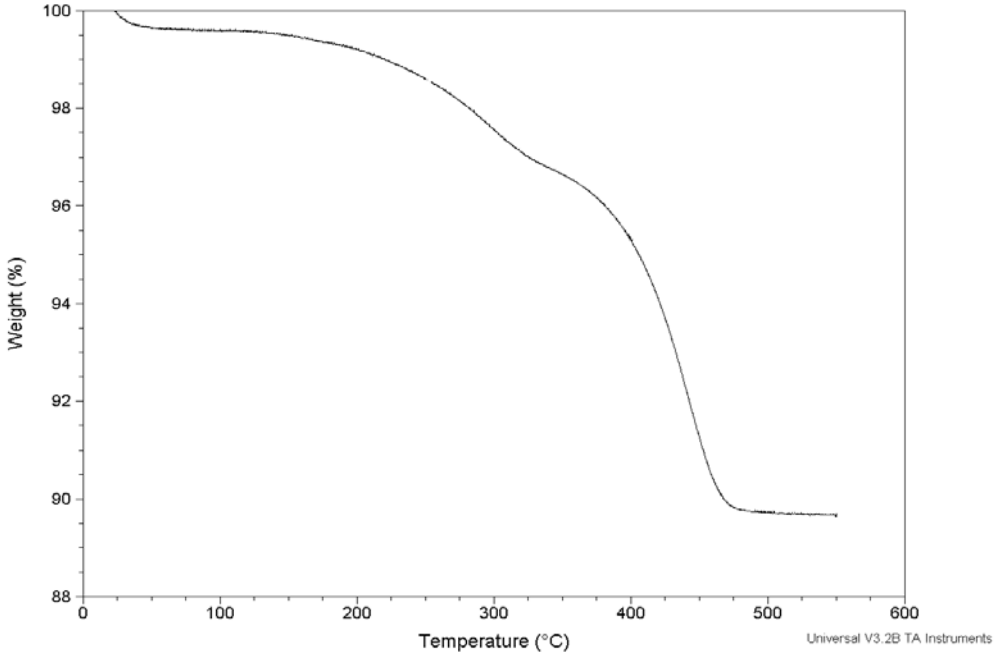

Figure 3-1: Thermogravimetric Analysis of ZSM-5 sample

3.2 Methods

All glassware was washed by first soaking in Alconox® detergent overnight. The glassware was rinsed four times in tap water and once in E-pure, then immersed in 20% nitric acid overnight. It was soaked in E-pure water then air dried. Finally the glassware was rinsed with hexane and oven dried at 105˚C for at least 8 hours.

Stock solutions were kept in a 4˚C refrigerator until use. The hydrogen peroxide was diluted 99 parts water to 1 part 30% H_2O_2.

The 100 ppm (mg/L) as Fe^{2+} stock was obtained by adding solid $FeSO_4 \cdot 7H_2O$ to E-Pure water. The amount of $FeSO_4 \cdot 7H_2O$ needed to make 100 ppm as Fe^{2+} was determined via the following equation.

$$100\frac{mg}{L}\,Fe^{2+}\times\frac{mmol\ Fe^{2+}}{55.8\ mg\ Fe^{2+}}\times\frac{1\ mmol\ FeSO_4}{1\ mmol\ Fe^{2+}}\times\frac{278.02\ mg\ FeSO_4}{1\ mmol\ FeSO_4}= 498.2\,\frac{mg}{L}\,FeSO_4 \quad (9)$$

The TCE was also kept as a 100 ppm stock. The amount of pure TCE needed was determined by the following equation. The density of pure TCE is 1.456 g/mL.

$$100\,\frac{mg}{L}\,TCE\ =\frac{(x, mL)\left(1.456\,\frac{g}{mL}\right)\left(1000\,\frac{mg}{g}\right)}{.250\,L} \qquad (10)$$

Solving for x, or the amount of TCE to add to 250 mL bottle of solution, gives a volume of 17.1 μL measured with a syringe. Once the stock was made, it was necessary for the solution to mix for 24 hours in order to ensure complete mixing. A 1.6 mg/L stock was kept of TCE, cis-DCE, trans-DCE, 1,1-DCE and VC (all five chemicals in one solution). An example calculation of the dilution of the stock chemicals is shown with the following equation:

$$mL\ of\ 100\,\frac{mg}{L}\,TCE\ stock=\frac{(250mL)*(1.6mg/L)}{100mg/L}=4mL \qquad (11)$$

where the mL of TCE is the amount of 100 ppm TCE solution needed to make a 250 mL bottle of 1.6 mg/L solution of TCE. This dilution procedure was used to make a calibration curve for each experiment.

3.2.1 Equipment

3.2.1.1 Gas Chromatograph (GC)

The gas chromatograph used for these analyses was an Agilent Technologies 6890 Series Gas Chromatograph supplied with ChemStation software by the Hewlett-Packard Company. The column was a fused silica column with a length of 30 meters, an inside diameter of 0.32 mm and a film thickness of 0.25 μm provided by J & W Scientific (Folsom, CA). The inlet of the GC was set to splitless mode with the purge valve set to 0.4 minutes. The inlet temperature was set to 240˚C and a pressure of 5 psi. The inlet sleeve was a 0.75 mm inner diameter glass sleeve which was to be used with SPME fibers and was supplied by Supelco, Inc. (Bellefonte, PA). The carrier gas was nitrogen. The oven temperatures were as listed in Table 3-1.

The retention times for TCE, cis-DCE, trans-DCE, 1,1-DCE and VC were found by running a known standard of each compound separately through the GC. The retention time for TCE was 10.9 minutes, cis-DCE 9.05 minutes, trans-DCE 7.4 minutes, 1,1-DCE 6.2 minutes and VC 3.9 minutes. Standard curves were created for each of the five chemicals, which can be seen in Appendix A. Hypothesis testing was conducted on a triplicate of the lowest concentration and a triplicate of a sample blank to determine the method detection limit for each of the five chemicals. The method detection limit for TCE was 1 ppb; cis-DCE 1 ppb; trans-DCE 1 ppb; 1,1-DCE 1 ppb; and VC 1 ppb. The results from the hypothesis testing are in Appendix A.

An Agilent 7683 Series Injector autosampler was used with the GC for the hexane extraction analysis in the sorption/oxidation experiments. The oven settings of the GC are shown in Table 3-1. A FID was used and its settings are shown in Table 3-2. The sampling depth was set to 5 mm and the injection volume was 2 μL.

Table 3-1: GC oven settings

	Rate, °C/min	Final Temperature, °C	Hold time, min
Initial		35	1
1	7.50	50	2
2	20	90	2
3	340	200	7

Table 3-2: GC detector settings for hexane extraction

Parameter	Setting
Temperature	250 °C
Hydrogen Flow	40.0 mL/min
Air Flow	450.0 mL/min
Makeup Flow	30.0 mL/min
Makeup Gas	Nitrogen

3.2.1.2 Total Organic Carbon

The total organic carbon was measured with a Shimadzu TOC-5000A Analyzer. Approximately 20 mL of sample, acidified with 6 N HCl, was placed in a TOC vial and covered with parafilm that was secured with a plastic ring. The vials were placed in an autosampler tray. The machine was run in TOC mode with the sparge turned off. The calibration curve consisted of three TOC standards made from potassium hydrogen phthalate (KHP) and a second calibration curve of three inorganic carbon standards made of sodium carbonate/bicarbonate. The gas used throughout the run was "Ultra Zero" grade air.

3.2.1.3 pH

The pH was measured with an Orion model 420A pH meter equipped with an Orion pH probe. The meter was calibrated each day with buffer solutions of pH 4.00, pH 7.00 and pH 10.00 (Fisher Scientific, Fair Lawn, NJ).

3.2.1.4 Solid Phase Micro Extraction (SPME)

SPME incorporates a fused silica fiber attached to a wire plunger that is pushed through a syringe to be immersed in the liquid sample. The silica fiber is coated with 85 μm Carboxen/polydimethylsiloxane. During GC injection the compounds are thermally removed from the fiber in the heated injection sleeve of the GC.

New fibers were conditioned by putting them in the inlet of the GC at 260ºC for one hour. E-pure samples were extracted with each fiber until it was stable (typically six times). If the fiber was not used for one day or more, it was reconditioned by placing it in the inlet of the GC at 260ºC for a half hour.

The initial step was to assemble the vial holder by inserting a Teflon septum with a hole into the bottom of the vial holder with the Teflon side down. 43 mL of the sample was dispensed into a 43 mL vial with a small Teflon stir bar; the vial was screwed into the vial holder and placed on a magnetic stirring table. After turning on the stirring plate, the Supelco© fiber assembly, with the fiber set at 3.6 cm line, was placed into the top of the vial holder. The fiber handle was pushed down and locked into place. The fiber stayed immersed in the solution for 25 minutes. After 25 minutes, the fiber assembly was unlocked and brought back to its original position. The fiber was manually placed in the GC for analysis and left in the inlet of the GC for 10 minutes. This procedure was based on work by Theis (2002).

Other researchers reported using up to 25% NaCl to extract the contaminant (Black and Fine, 2001), however NaCl was not used here as it caused premature breakage of the fiber and caused fouling of the GC column (Theis, 2002). The fibers can be reused approximately 50 times before being discarded (Santos *et al*., 1996; Theis, 2002).

3.2.1.5 Miscellaneous Equipment

An Eppendorf Centrifuge 5804 was used. The spectrophotometer used in these experiments was a Varian Cary 50 Scan UV-Visible Spectrophotometer in combination with Cary WinUV software.

3.2.2 Experiments

There were a number of experiments that were conducted to investigate the hypotheses discussed earlier. The first experiments were to investigate aqueous phase Fenton's oxidation of TCE. The second set of experiments were to quantify the sorption kinetics for the removal of TCE from water by ZSM-5. Isotherms for TCE removal from water by ZSM-5 were created for equilibrium conditions. Oxidation of TCE bound zeolites was the final stage to this research. Silicalite synthesis was conducted in parallel with the other experiments.

3.2.2.1 Aqueous Fenton's Oxidation of TCE

A 1600 mL solution of 0.25 mg/L as Fe^{2+} was prepared by adding 4056 µL of 100 ppm as Fe^{2+} stock to E-pure water to make a 1600 mL solution. The pH was adjusted using 10% sulfuric acid. 200 mL of this solution was transferred using a graduated cylinder to each of the 8 reaction vessels (250 mL amber bottles). 1.0 mL of 100 ppm TCE was added to each vessel using an automatic pipette to achieve a concentration of 500 ppb TCE. The bottles were wrapped in aluminum foil to prevent degradation by UV light. After stirring for one hour, 0.392 mL of 0.3% H_2O_2 was added to each vessel for a H_2O_2: TCE ratio of 50:1. At the predetermined time approximately 30 mL of solution was removed from the vessel. 0.525 mL of 6 N HCl was added to the 30 mL in order to drop the pH below 1 for samples used in the TOC analyzer. 0.810 mL of methanol was added to the remaining solution in the vessel in order to obtain a concentration of 3,000 mg/L. The methanol is a hydroxyl scavenger (Teel et al., 2001; Theis, 2002) and quenched the reactions. This solution was used in the GC with SPME to quantify the TCE, DCEs and VC, and to determine the pH of the solution.

3.2.2.2 TCE Sorption Kinetics

After adding 0.1 gram of zeolite to each of 14 43 mL vials, the vials containing the zeolite plus a cap were weighed on a scale. The vial was filled with a 500 ppb TCE solution and the weight recorded. The temperature of the TCE solution was measured. The vials were wrapped in aluminum foil to prevent UV degradation of the TCE and placed on their sides on a shaker table set to 125 rpm. At specified times (0 minutes, 15 minutes, 20 minutes, 30 minutes, 60 minutes, 90 minutes, 120 minutes and 180 minutes) two vials were sacrificed by centrifuging at 3,000 rpm for 10 minutes. The times recorded were the time the vials were on the shaker table plus the time the vials were in the centrifuge (10 minutes). 21.5 mL from two of the sacrificed vials was transferred to a clean, 43 mL vial. The supernatant was analyzed using SPME/GC for TCE.

Preliminary experiments were conducted to determine the proper centrifuge speed and time. To determine the centrifuge time, 43 mL glass vials were placed in the centrifuge and spun at different speeds until the vial broke. The appropriate centrifuge speed to avoid fracture was 3,000 rpm. The time required to separate the liquid and solid by centrifuging was determined by allowing vials with zeolite to come in contact with a 500 ppb TCE solution for 24 hours on a shaker table. The vials were removed and centrifuged for the following times at 3,000 rpm: 0 minutes, 10 minutes, 13 minutes, 15 minutes, 20 minutes and 25 minutes. The optical density of the supernatant was measured using a spectrophotometer and plotted as shown in Figure 3-2. The optical density of E-pure water was also taken (0.0600) and was used as the “zero” point for the optical density of the supernatants; i.e. the optical density of the E-pure was subtracted from the optical densities of the supernatants to account for interferences by the E-pure water as opposed to the interferences by the zeolite. There was no difference in the clarity of the liquid after a ten minute centrifuge time so that was the amount of time that all of the vials were centrifuged throughout the experiments.

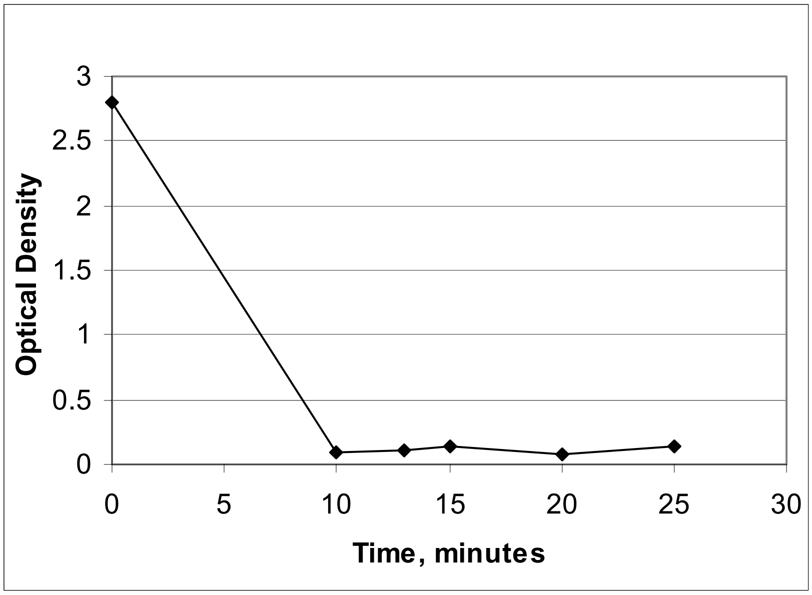

Figure 3-2: Optical density versus centrifuge time

Preliminary experiments were conducted to determine the amount of zeolite and the length of the sorption experiments. 1.0 g of zeolite was used in each of the 43 mL vials filled with 500 ppb TCE. The experiments were conducted with the same procedure as for the sorption kinetics, except the times at which the vials were sacrificed were: 0 minutes, 30 minutes, 60 minutes, 120 minutes, 240 minutes, 480 minutes, 960 minutes and 1440 minutes. Figure 3-3 depicts the results of this experiment. The TCE sorbed very quickly to the ZSM-5, thus it was difficult to see the kinetics. So the amount of zeolite was reduced to 10 percent (0.1 gram) per vial. The graph also descends rapidly at the beginning so it was determined that more points needed to be taken before the 30 minute mark. Therefore, vials were sacrificed at 15 and 20 minutes. These were the shortest times possible because the total time is the time on the shaker table plus the time in the centrifuge. The TCE and zeolite needed enough time on the shaker table to come in contact (about 5 minutes). As shown Figure 3-3, the sorption extent did not change after 1 hour, so the experiment run time was altered to end at 3 hours.

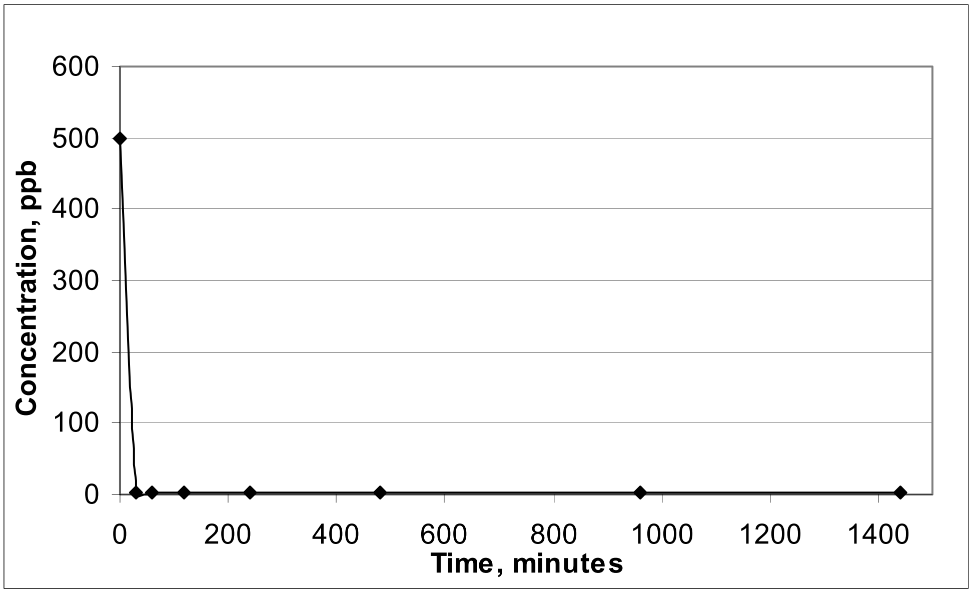

Figure 3-3: Preliminary TCE sorption experiment for 1.0 g of ZSM-5

3.2.2.3 TCE Adsorption Isotherm on ZSM-5

A sorption isotherm was created by sorbing different concentrations of TCE to 0.1 gram of ZSM-5. The TCE was allowed to sorb to the zeolite for 24 hours on a shaker table. After 24 hours, the vials were centrifuged for ten minutes at 3,000 rpm. The supernatant was transferred to clean 43 mL vials. The weight of the supernatant was measured and the temperature of the supernatant taken in order to convert the mass of supernatant transferred to a volume using the density of pure water at the measured temperature. The concentration of TCE in the supernatant was measured on the GC using SPME. The vials containing the zeolite were filled with E-pure, the water weight recorded, and placed on the shaker table for an additional 24 hours. The vials were centrifuged and the supernatant transferred to vials. The TCE in the supernatant was measured using the SPME/GC method. The initial concentrations of TCE were 500 ppb; 1,000 ppb; 1,250 ppb; 1,500 ppb; 2,500 ppb; 3,000 ppb; 12,000 ppb and 20,000 ppb TCE.

In order to create an equilibrium adsorption isotherm for sorption of TCE to zeolite ZSM-5 the following equations were used. The amount of TCE sorbed to the zeolite was the original mass added to the vial minus the mass remaining in the supernatant. The q (mass sorbed/mass of sorbent) was determined by the following equation:

$$q = \left(\frac{M_0 - M_e,\ mg}{mass\ of\ zeolite,\ g} \right) \tag{12}$$

The amount of TCE in mg in the supernatant was determined by equation 13.

$$Me = mg\ TCE = (g,\ liquid) * \left(\frac{1}{\rho(g/mL)} \right) * \left(\frac{\mu g}{L} TCE \right) * \left(\frac{1\ L}{1{,}000\ mL} \right) * \left(\frac{1\ mg}{1{,}000\ \mu g} \right) \tag{13}$$

Where ρ is the density of pure water at the temperature of the solution.

3.2.2.4 Hexane Extraction of the Zeolite After Sorption/Oxidation

Hexane extraction was done to quantify the mass of TCE sorbed to the zeolite. After equilibrating 500 ppb TCE with 0.1 g zeolite in a 43 mL glass vial for 24 hours an a shaker table set to approximately 125 rpm with no headspace hexane extraction was conducted. After 24 hours, the vials were centrifuged for 10 minutes at 3,000 rpm. The supernatant was transferred to a clean 43 mL vial and the amount of water was converted to a mass (grams) by using the density of pure water at the temperature of the water. 4 mL of hexane was added to the zeolite and left on the shaker table for 4 hours as per Teel *et al.* (2001). The zeolite/hexane mixture was then passed through a 0.45 µm nominal pore size filter (Osmonics cameo 17 mm syringe filter and a 3 mL syringe with luer locks both from Fisher Scientific, Fair Lawn, NJ), and one mL of the hexane extraction solution run on of the GC. This extraction was also done to the zeolite after sorption and oxidation.

3.2.2.5 TCE Sorption/Oxidation

These experiments were conducted by sorbing the TCE to ZSM-5, then adding iron and hydrogen peroxide to the zeolite solution to initiate Fenton's oxidation. A 500 ppb TCE solution was contacted with 0.1 g of ZSM-5 for 24 hours on a shaker table. A solution of iron and H_2O_2, adjusted to pH = 3.5, was added to the zeolite. The vials were left on a shaker table for 24 hours. The supernatant was then removed and measured with SPME/GC for TCE and potential by-products and the zeolite was subjected to hexane extraction with 4 mL of hexane as described in the previous section.

3.2.2.6 Zeolite Synthesis (Silicalite)

The mole oxide ratio for silicalite is: 60 $(NH_4)_2O$ – 90 SiO_2 – 6 $(TPA)_2O$ – 994.4 H_2O (Gonthier and Thompson, 1994). The ingredients used were ammonium hydroxide (30% in water), Ludox AS-40, tetrapropylammonium bromide (TPA), and E-pure water. Synthesis was carried out in sealed, 10 mL teflon-lined Morey-type autoclaves without agitation placed in a laboratory oven set to 180ºC and autogenous pressure. The autoclaves were left in the oven for seven day incubations and for eight day incubations. The autoclaves were removed and quenched in cold water. The samples were rinsed with E-pure water while being filtered to clean the samples (Gonthier and Thompson, 1994).

Chapter 4 Results and Discussion

The first Results section discusses the aqueous Fenton's oxidation of TCE. The second Results section covers the kinetics of TCE removal from water by ZSM-5. The third Results section presents the adsorption results of TCE by ZSM-5. The fourth section presents the results from the sorption/oxidation experiments. The final section discusses the synthesis of silicalite (aluminum free ZSM-5).

4.1 Aqueous Fenton's Oxidation of TCE

Aqueous Fenton's oxidation of TCE was conducted at three different pHs: 2.5, 3.5, and 4.5. These values were chosen based on previous work (O'Brien and Tremblay, 2002). The H_2O_2:TCE molar ratio was 50:1 and the Fe^{2+}:TCE molar ratio was 1.2:1. The TCE reduction at the three different pHs is shown in Figure 4-1.

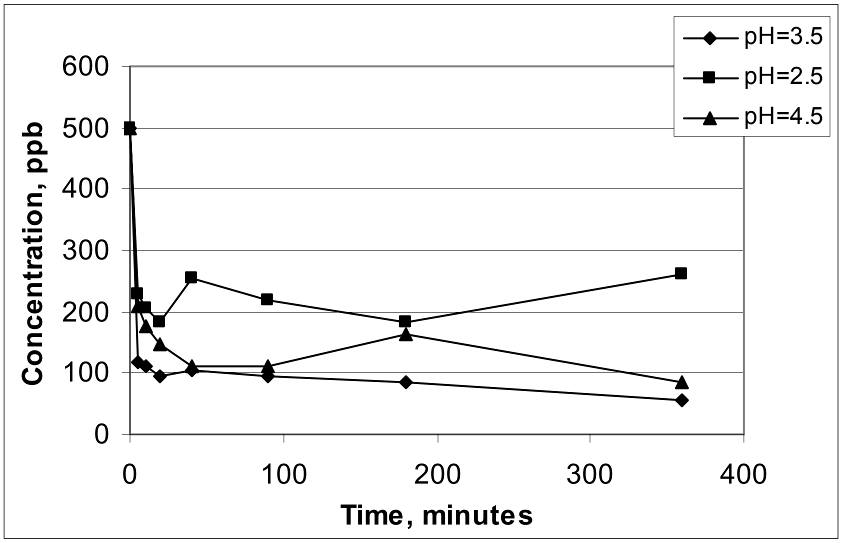

Figure 4-1: Aqueous Fenton's oxidation of TCE at different pHs

Figure 4-2 depicts the percent reduction of TCE after Fenton's oxidation at the three pH values after 6 hours.

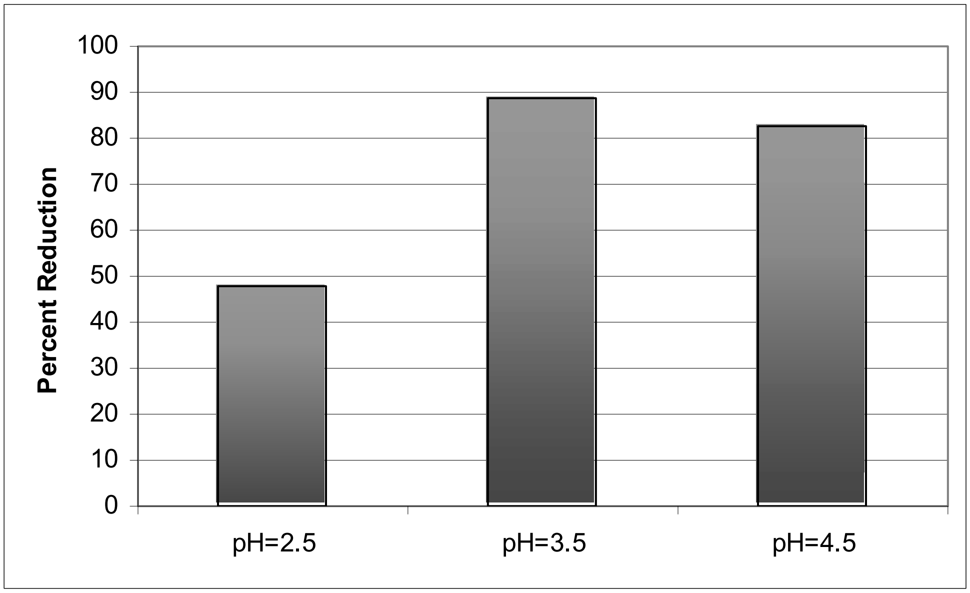

Figure 4-2: Percent removal of TCE by aqueous Fenton's oxidation at different pHs with a H_2O_2:TCE molar ratio of 50:1 and an iron:TCE molar ratio of 1.2:1

Fenton's oxidation was more effective at pH = 3.5 than at pH 2.5 or 4.5 as seen in Figure 4-1 and Figure 4-2, which agreed with work by others (O'Brien and Tremblay, 2002). Therefore, Fenton's oxidation of TCE was further investigated at pH 3.5. However, the kinetics of TCE reduction at the other pH values were also evaluated and are presented later in this section. The byproducts cis-DCE, trans-DCE, 1,1-DCE and VC were also measured over time as shown in Figure 4-3 and Figure 4-4. This experiment was done in triplicate and the average concentration at each point and 95 % confidence intervals are shown on the graphs.

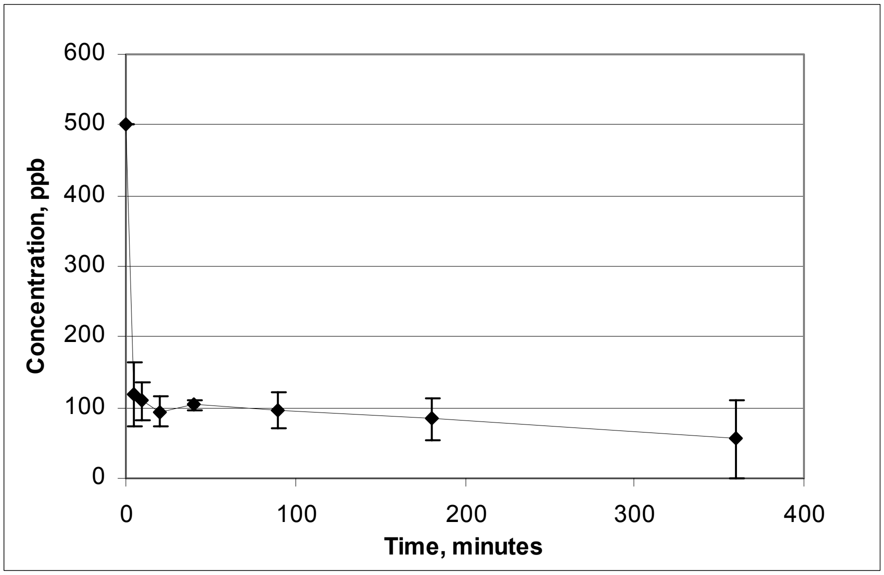

Figure 4-3: Aqueous Fenton's oxidation of TCE at pH=3.5 with a H_2O_2:TCE molar ratio of 50:1 and an iron:TCE molar ratio of 1.2:1

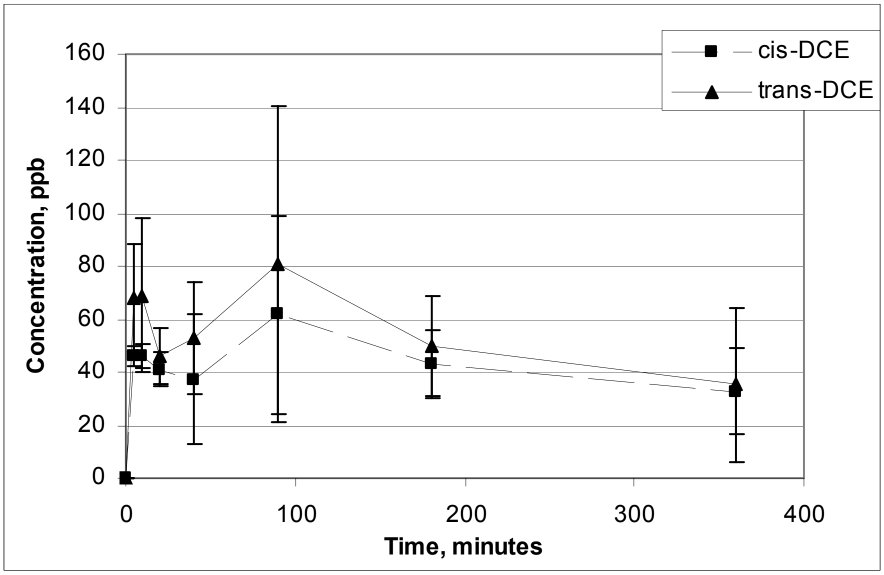

Figure 4-4: By product formation from aqueous Fenton's oxidation of TCE at a pH = 3.5 with a H_2O_2:TCE molar ratio of 50:1 and an iron:TCE molar ratio of 1.2:1

The TCE concentration decreased quickly with these reaction conditions. The concentrations of cis-DCE and trans-DCE increased, and then decreased with the reaction time. The concentrations of 1,1-DCE and the VC were below the method detection limit in almost all reaction times and therefore are not shown on Figures 4-3 or 4-4. Teel *et al.* (2001) found similar results, 78% reduction of TCE with a molar ratio of H_2O_2:TCE of 0.005:0.001. Chen *et al.* (2001) explored Fenton's oxidation of TCE in ground water samples with a pH = 3.0 ± 0.05. In 5 hours, the TCE had degraded between 90% and 100%. The mole ratio of H_2O_2:TCE was approximately 37.5 and the Fe^{2+}:H_2O_2 mole ratio was about 0.67. Chen *et al*. (2001) found that the reaction rates were rapid in the first 30 minutes and then slowed toward the end of the experiment. Our data agreed with the data from Chen *et al.* (2001).

The kinetics for the removal of TCE was determined by assuming the following reaction:

$$\bullet OH + TCE \xrightarrow{k_{TCE}} products \tag{14}$$

Assuming an elementary reaction:

$$r_{TCE} = -k_{TCE} C_{\bullet OH} C_{TCE} \tag{15}$$

The reaction can be simplified to a pseudo-first order equation:

$$r_{TCE} = -k' C_{TCE} = \frac{dC_{TCE}}{dt} \tag{16}$$

Integrating this equation:

$$\ln\left(\frac{C_{TCE}}{C_{0,TCE}}\right) = -k' t \tag{17}$$

The $\ln\left(\frac{C_{TCE}}{C_{0,TCE}}\right)$ expression was plotted versus time. The slope of the regressed line is -k'. For this research only the first four points were used in the regression line. This is because, as shown in Figure 4-3, the destruction of TCE occurred early in the experiment, and then leveled off. When these points were linearized that trend was even more evident. Figure 4-5 shows the linearized graph of the first four points that were used to determine the reaction rate constant. The pseudo first order reaction rate constant is 0.1061 min^{-1}.

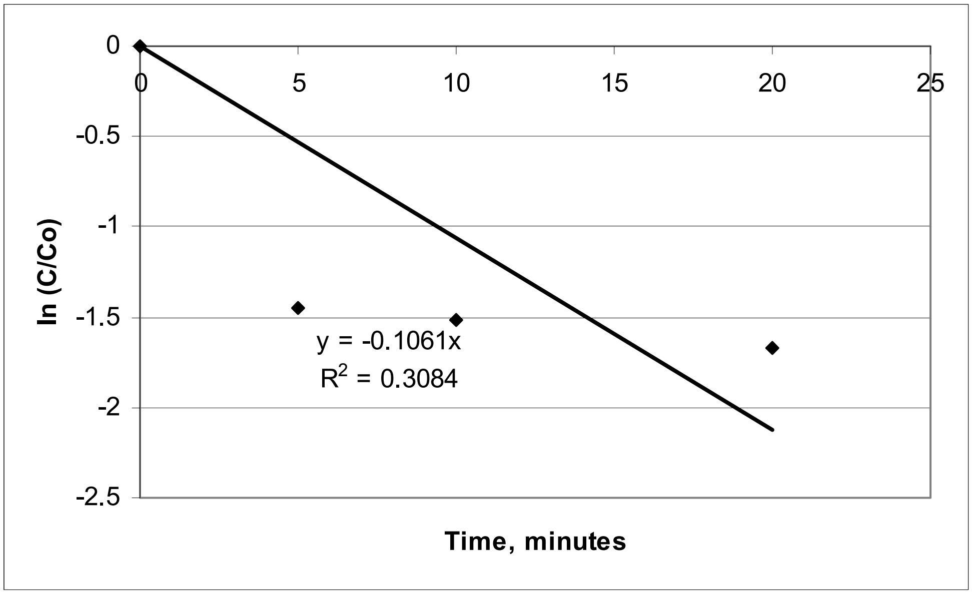

Figure 4-5: Plot of ln C/Co versus time for aqueous Fenton's oxidation

O'Brien and Tremblay (2002) reported a rate constant, k', for TCE disappearance with Fenton's oxidation of 0.0289 min^{-1}. This differs from the value obtained in this research by less than an order of magnitude. Chen *et al*. (2001) found a rate constant for TCE disappearance of 0.0057 min^{-1} which is further from our value. The decreases in TCE concentration occurred rapidly at the beginning of the experiments and then slowed down.

The Fenton's oxidation experiment was also run at pH = 4.5 and pH = 2.5. These experiments were only run once. The results of the degradation of TCE and the formation of its byproducts at pH = 4.5 and pH = 2.5 are shown in the following Figures 4-6 and 4-7.

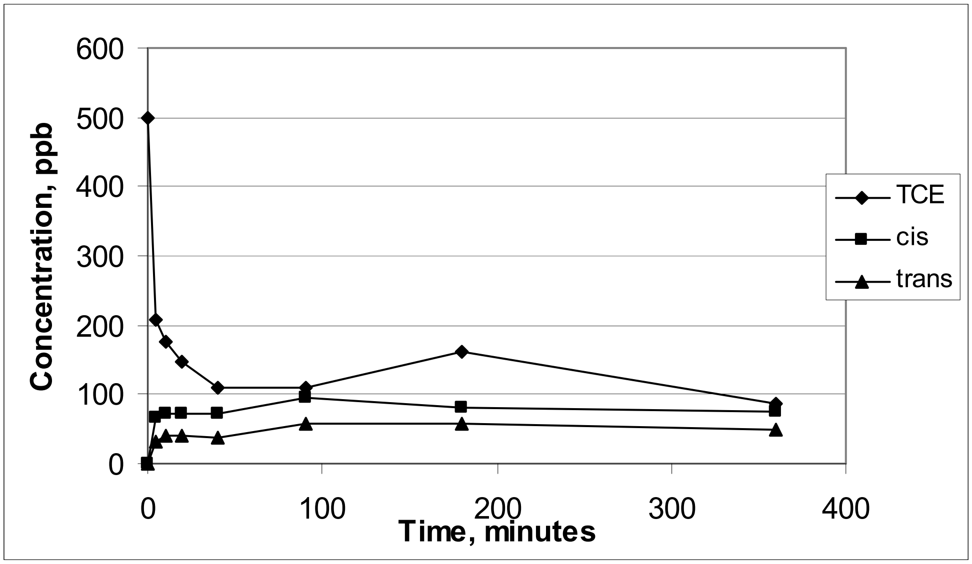

Figure 4-6: Aqueous Fenton's oxidation of TCE at pH = 4.5 with a H_2O_2:TCE molar ratio of 50:1 and an iron:TCE molar ratio of 1.2:1

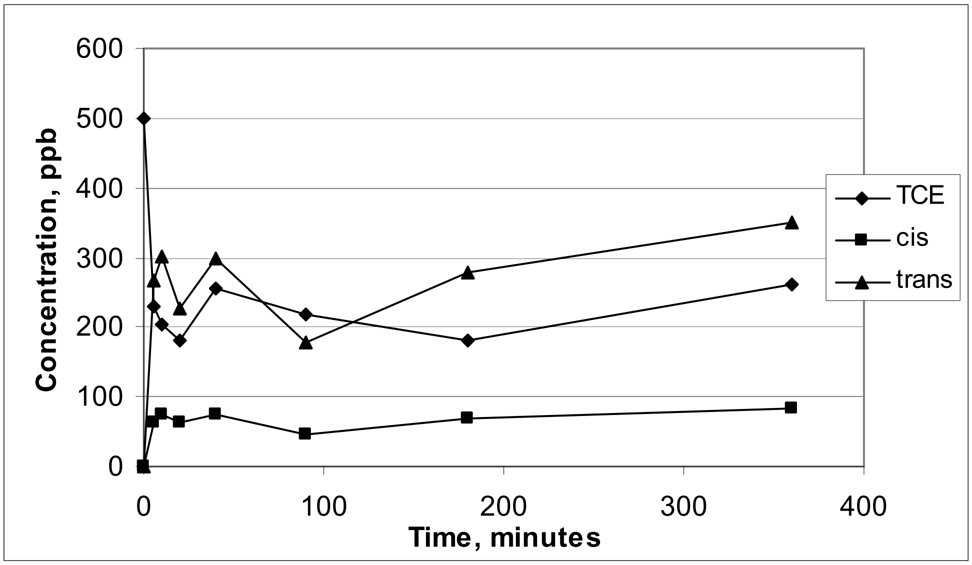

Figure 4-7: Aqueous Fenton's oxidation of TCE at pH = 2.5 with a H_2O_2:TCE molar ratio of 50:1 and an iron:TCE molar ratio of 1.2:1

In the experiments at pH = 2.5 and pH= 4.5, the cis-DCE and trans-DCE concentrations increased with reaction time. In the experiments at pH = 2.5 and pH= 4.5, the 1,1-DCE and VC were below the method detection limit at all times. The highest value of trans-DCE concentration was observed when the experiment was run at a pH of 2.5. The byproducts 1,1-DCE and VC were not seen throughout either of the six hour experiments. The k' values for these two experiments were determined in the same manner as the experiments conducted at a pH of 3.5. The k' value of the experiments run at a pH = 4.5 was 0.0025 min^{-1}, and at a pH = 2.5 was 0.0003 min^{-1}.

The pH of the aqueous Fenton's oxidation experiments was measured throughout the experiments. Figure 4-8 shows the results of the pH measurements at pH = 3.5 with the three different runs as well as the average results. The highest standard deviation between data points of different runs at the reaction time was 0.28. The pH could change due to the addition of chemicals to the water.

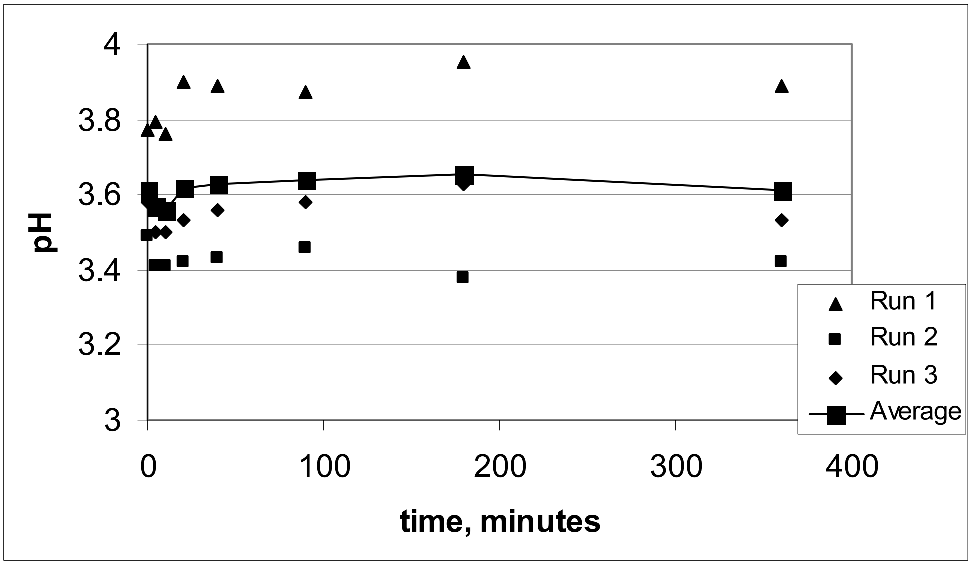

Figure 4-8: pH values during aqueous Fenton's oxidation with an initial pH of 3.5 ± 0.1 and a H_2O_2:TCE molar ratio of 50:1

The pH slightly increased with time, however by a maximum of only 0.5 pH unit (based on the average results). These results contradict those of O'Brien and Tremblay (2002) who reported a decrease in the pH over time. The initial pH was 3.5 and the ending pH was approximately 2.8. Chen *et al*. (2001) also showed the pH to decrease with reaction time. In their experiments, the initial pH was 3.01 and the ending pH was 2.77, thus a decrease of 0.24 pH units. In this research, when the initial pH was 2.5, the pH decreased at each reaction time, for an average pH of 2.2. When the initial pH was 4.5, the pH increased slightly with an average value of 4.9.

TOC analysis was run for each sample throughout all the aqueous Fenton's oxidation experiments. The analysis was determined to be inconclusive. To use the available TOC analyzer vials that could hold approximately 60 mL of liquid were filled with only 20 mL of liquid and covered with parafilm, not lids. This method left a large amount of headspace, and due to the nature of TCE, there is a good chance that the TCE could volatilize into the headspace, thus causing invalid readings.

4.2 TCE Sorption Kinetics

A 500 ppb TCE solution was contacted with 0.1 gram of zeolite for increasing contact times. At predetermined times, the vials were centrifuged and the supernatant extracted and measured via SPME/GC. Figure 4-9 shows the decrease in TCE in the aqueous phase after being in contact with ZSM-5. The error bars are 95% confidence intervals and the experiments were conducted in triplicate.

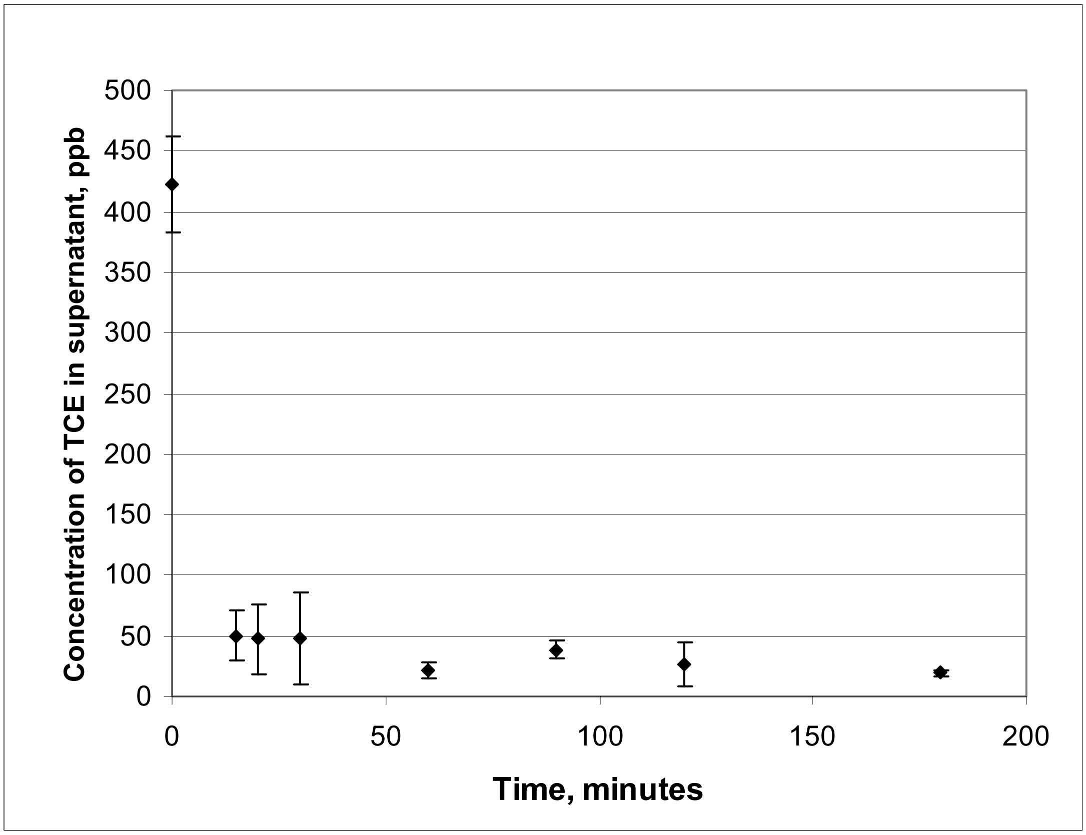

Figure 4-9: Sorption kinetics for the removal of TCE from water by 0.1 gram of ZSM-5

The ZSM-5 rapidly removed the TCE from the water. After 20 minutes the aqueous concentration of TCE was less than 50 ppb. The aqueous concentration of TCE decreased slightly over time. The percent removal of TCE at 180 minutes was about 95%.

The sorption kinetics were characterized in the same manner as the TCE degradation in the aqueous Fenton's oxidation experiments and a first order sorption rate constant was determined to be 0.0105 min^{-1}. At the time of this research, no information was found regarding the kinetics of ZSM-5 sorption of organic contaminants.

4.3 TCE Sorption Isotherm

An equilibrium adsorption isotherm was constructed for the sorption of TCE to ZSM-5. Different concentrations of TCE were left in contact with 0.1 gram ZSM-5 for 24 hours on a shaker table. After centrifuging the vials and removing the supernatant, the supernatant was measured for TCE by SPME/GC. The mass sorbed, q, was plotted versus the equilibrium aqueous concentration, Ce, as shown in Figure 4-10.

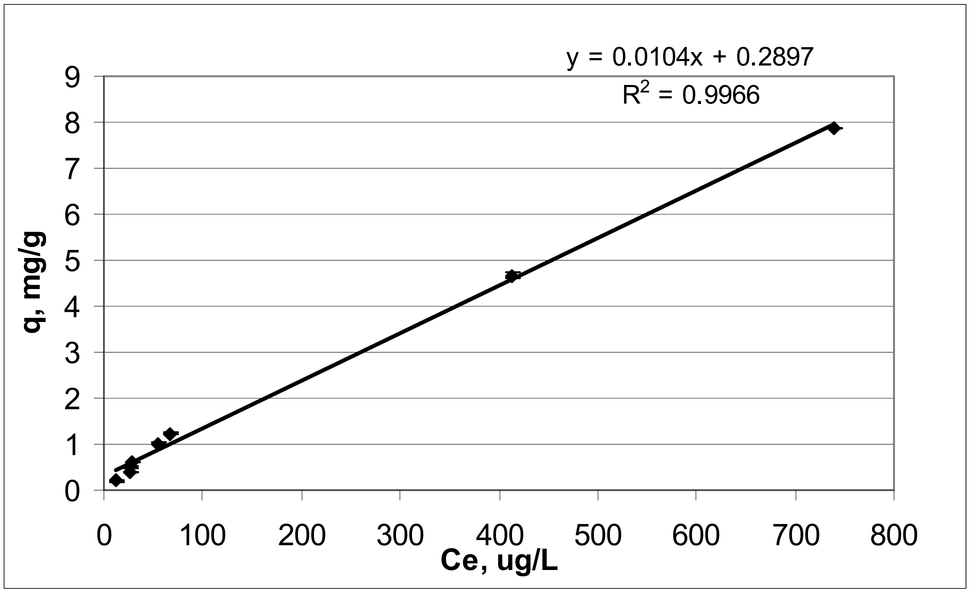

Figure 4-10: Isotherm for the uptake of TCE by 0.1 gram of ZSM-5

The following figure is an enlarged view of the isotherm at the lower concentration points.

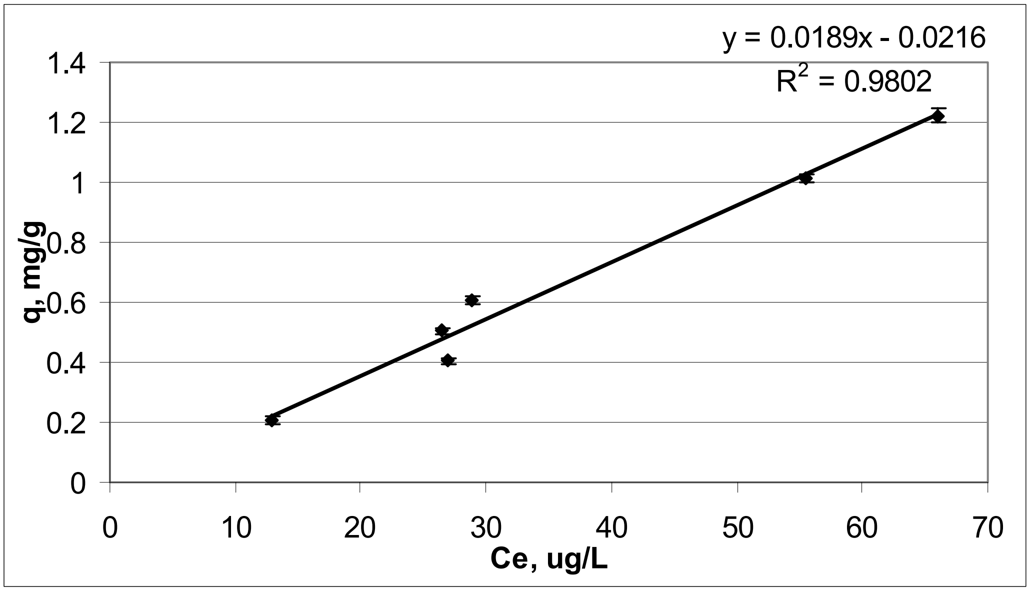

Figure 4-11: Low concentration isotherm for the uptake of TCE by 0.1 gram of zeolite

The equilibrium adsorption data was linearized to determine if the isotherm follows a Freundlich adsorption model or a Langmuir adsorption model. The Freundlich model follows the equation:

$$q_e = KC_e^{1/n} \tag{18}$$

where q_e is the equilibrium sorbed concentration, C_e is the equilibrium concentration and K and 1/n are characteristic constants. The Freundlich model is linearized to the following equation:

$$\log q_e = \log K + \frac{1}{n}\log C_e \tag{19}$$

The Langmuir model has the equation:

$$q_e = \frac{abC_e}{1+bC_e} \tag{20}$$

where C_e is the effluent concentration, q_e is the q value at equilibrium, a and b are constants. The Langmuir model is linearized to the following equation:

$$\frac{C_e}{q_e} = \frac{1}{ab} + \frac{C_e}{a} \tag{21}$$

The following two figures are the plots of the linearized models.

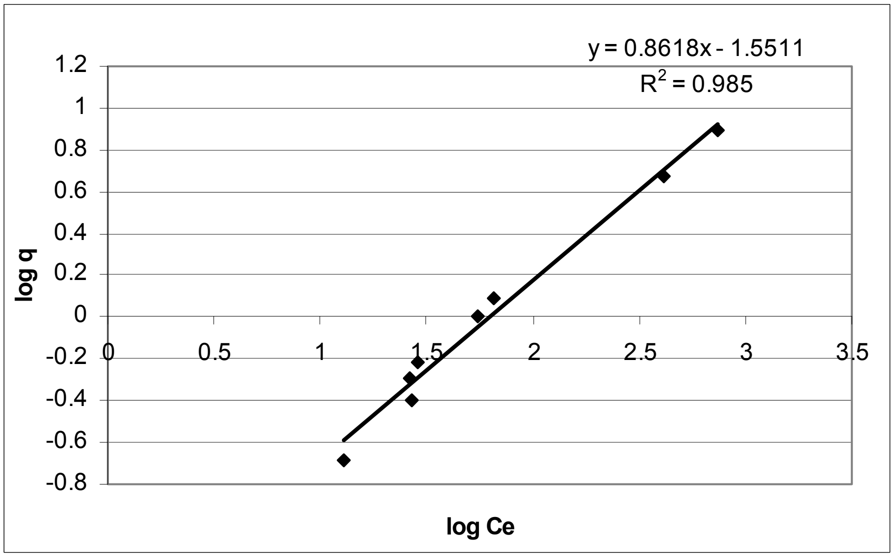

Figure 4-12: Freundlich model for the sorption of TCE to 0.1 gram of ZSM-5

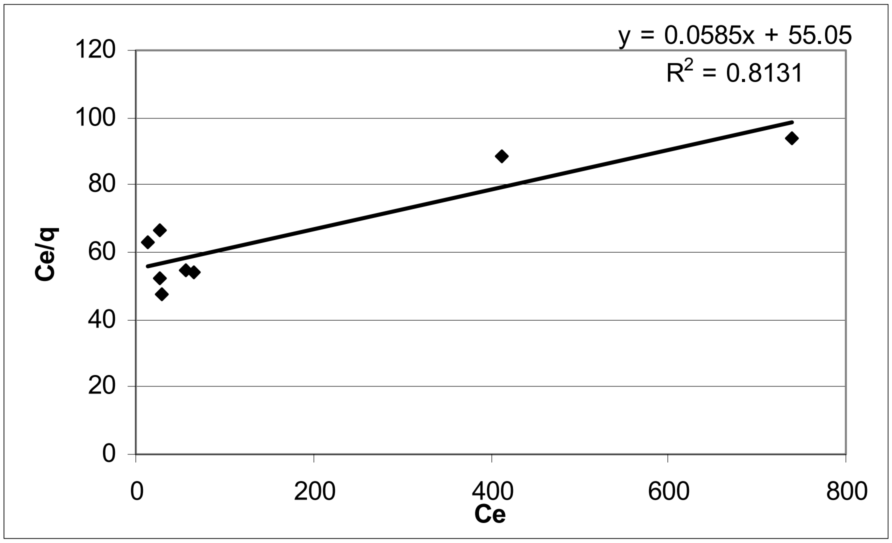

Figure 4-13: Linearized Langmuir model for the sorption of TCE to 0.1 gram of ZSM-5

The data has a higher correlation for the linear model and the linearized Freundlich model than the linearized Langmuir model. The linear isotherm had a higher correlation than the Freundlich model by 0.0116 units. Sorption in this lower concentration range may therefore follow a linear model. If the sorption experiments are extended to include higher concentrations, it could deviate from the linear form and follow the Freundlich model more closely.

In the Freundlich model, the 1/n value is a measure of cumulative magnitude and distribution of energy associated with the sorption process. The slope of the line is the 1/n value and is 0.8618. K is characteristic of the sorption capacity (Weber, 2001). It is the y-intercept of the linearized Freundlich model and was found that log K=-1.55, thus the K is 0.028. The Freundlich model is:

$$Q_e = 0.028\, C_e^{\,0.8618} \tag{22}$$

Giaya *et al*. (2000) also determined that the adsorption of TCE on silicalite followed a Freundlich model. The 1/n value was 0.702 and K was 0.43. Silicalite is similar to ZSM-5, but it has no aluminum in it. The saturation capacity for ZSM-5 and silicalite has been shown to be very similar for a variety of sorbates (Pope, 1987). Giaya *et al*. (2000) showed that ZSM-5 and silicalite are similar in the range tested here, as shown by Figure 4-14 (the three top lines). The K determined by Giaya *et al*. (2000) for silicalite was about 15 times larger than the Freundlich K of ZSM-5. These values could differ because the zeolites could have slightly different properties (i.e. composition). This phenomenon has been noticed before as reported by Pope (1987). Pope (1987) found that the water uptake by a silicalite sample was only half that of the water uptake reported by another silicalite researcher. However the benzene and n-hexane saturation concentrations did not significantly differ. The conclusion was that there were slight composition differences between the two samples.

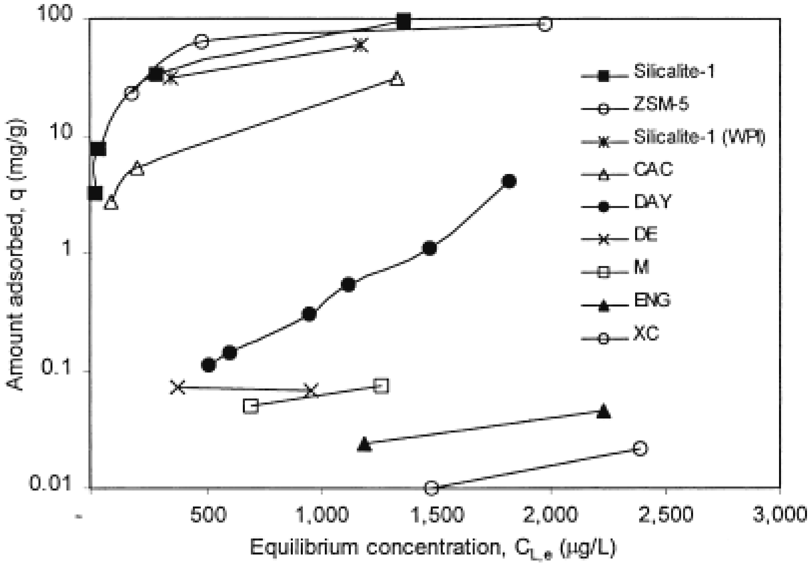

Figure 4-14: Adsorption isotherm of ZSM-5 and silicalite (Giaya *et al.*, 2000)

After the supernatant was removed after adsorption, the vials containing the zeolite were filled with E-pure water. The vials were put back on the shaker table and left to equilibrate for 24 hours. The supernatant from these vials were measured on the GC using SPME in order to quantify the amount of TCE that desorbed from the zeolite once the TCE concentration in the surrounding water was reduced. It was found that if the original concentration of 500 ppb TCE were used, there was less than 20 ppb of TCE left in the water after sorption (see Figure 4-10). After desorption, an average of 11.5 ppb TCE reversibly desorbed off the zeolite. The amount of TCE on the zeolite was the amount on the zeolite after the first experiment (original mass – mass left in the water) minus the amount that desorbed from the zeolite.

Figure 4-15 shows q versus Ce for desorption, plotted with the adsorption isotherm found earlier. The error bars denote the 95% confidence interval. All experiments were done in triplicate.

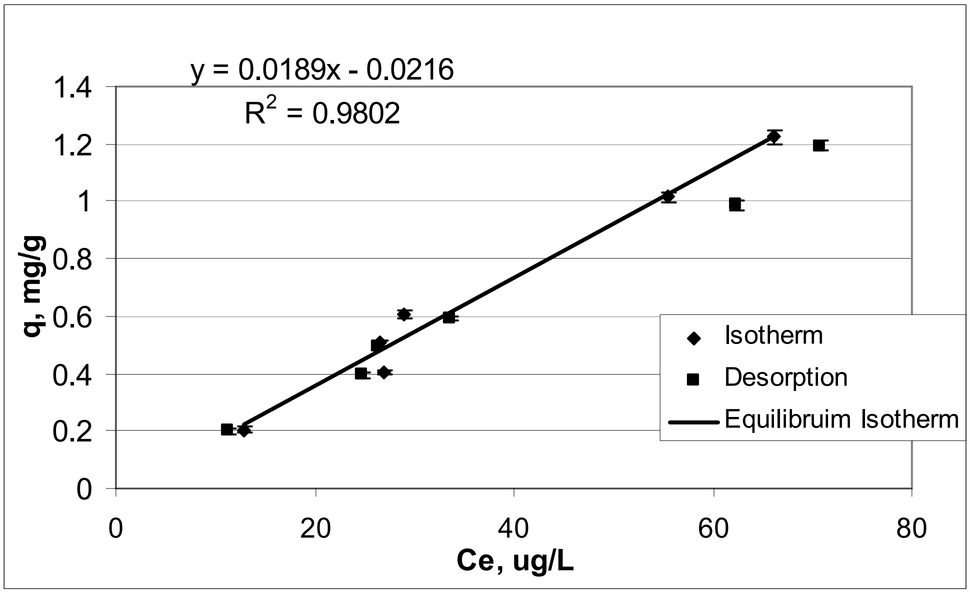

Figure 4-15: Equilibrium desorption of TCE from ZSM-5

This desorption data is significant for two reasons.

(1) The desorption data indicates good reproducibility of the adsorption isotherm. The greatest standard deviation for an individual desorption data point was 0.017 mg/g. This indicates that the desorption experiment is reproducible. As can be seen in the graph, the desorbed TCE agrees with the adsorption isotherm well. This suggests that the isotherm is a good representation of the adsorption and desorption of TCE by ZSM-5 at equilibruim.

(2) This data showed that TCE reversibly desorbed from the zeolite once the concentration of the water was reduced. Huling *et al*. (2000) stated that 2-chlorophenol reversibly desorbed from activated carbon. Our experiments showed that the TCE sorbed to ZSM-5 acted in a similar manner when the TCE concentration in the water was reduced. Besides providing a comparison of GAC and ZSM-5, this part of the research illustrated that TCE may be desorbed from ZSM-5. This is important because after sorbing the TCE and removing the supernatant (the isotherm step of this experiment), water containing iron and H_2O_2 are added to the TCE sorbed zeolite to conduct the Fenton's oxidation on the TCE sorbed zeolite. Any TCE that desorbs from the zeolite and into the water should be oxidized in an aqueous Fenton's oxidation manner, as discussed in section 4.1.

4.4 Oxidation of Zeolite-Bound TCE

4.4.1 TCE Extraction

Several methods of quantification of TCE on the zeolite were tried throughout this project: extraction by aqueous phase SPME, Thermogravimetric Analysis (TGA) and hexane extraction. Extraction with SPME was done in the same manner used throughout this research, except the fiber was left directly in contact with the zeolite for up to seven days (similar to work done by Mackenzie *et al.*, 2002). Each day for seven days the fiber was removed and analyzed by GC for TCE. This method resulted in low TCE recovery. The initial recovery after 24 hours was low (~46%). Thus, the experiment was extended to determine the recovery each day for 7 days. The results were inconclusive and therefore this technique was not pursued.

Quantification of contaminant on the zeolite by TGA was investigated during this project. A comparison of Figures 4-16 and 4-17, reveals that there is not much difference in the two plots. The original hypothesis was that the water and TCE should volatilize off at different temperatures and this difference would be revealed in the plots. After analysis of the amount of TCE that should have been sorbed on the zeolite, it was evident that the TGA was not sensitive enough to detect the small mass of TCE that would have been on the zeolite. This technique was therefore abandoned because in order for this technique to potentially work (not definitely work, more experiments would be needed to determine that) a higher mass of TCE would need to be sorbed to the zeolite. This was inapplicable to this project as this research was conducted at environmentally relevant concentrations. As stated in the introduction, the EPA (2001) reported the highest level of TCE at 440 μg/L, therefore it was not desired to start these experiments above a concentration of 500 μg/L.

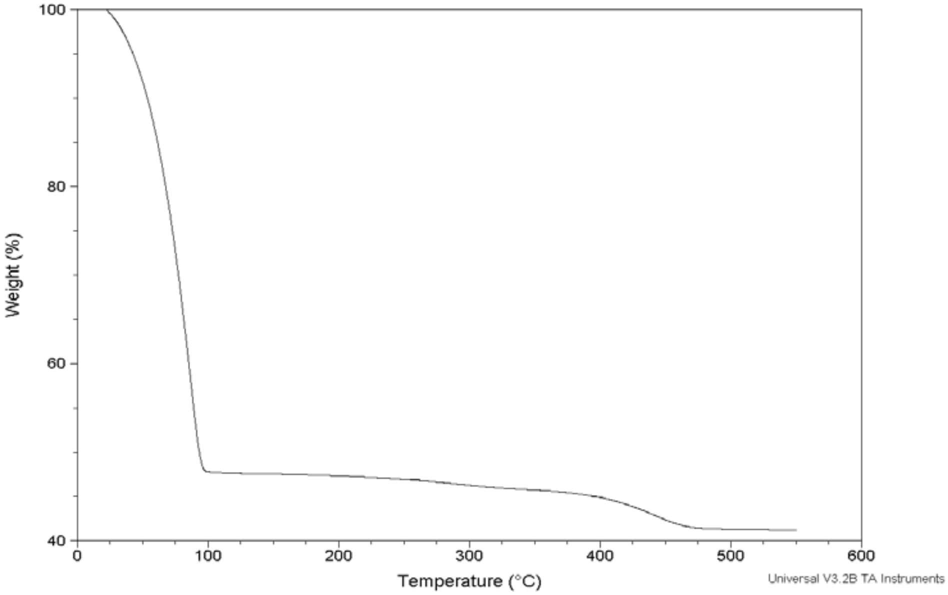

Figure 4-16: TGA of ZSM-5 equilibrated with water

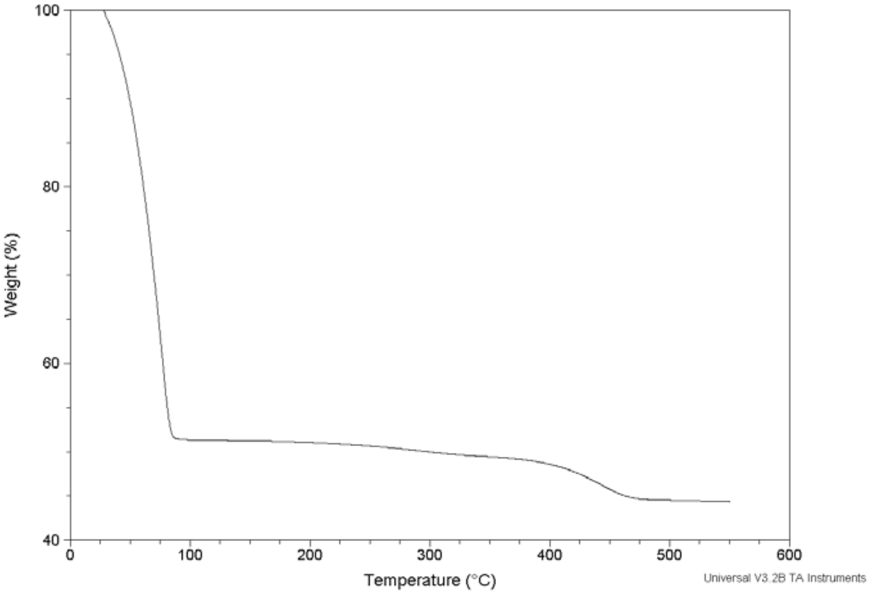

Figure 4-17: TGA of 0.021 mg TCE sorbed to ZSM-5

The final procedure for quantifying sorbed TCE on ZSM-5 was hexane extraction. The procedure was described in the Methods section. Originally, 2 mL of hexane was added to the zeolite (eventually 4 mL was used) and left on the shaker table for 4 hours as per Teel *et al*. (2001). An injection volume of 2 µL with a sampling depth of 5 mm was used which gave reproducible results and quantifiable peak areas. Control experiments were completed by sorbing a known mass of TCE on 0.1 gram of ZSM-5. The TCE sorbed zeolite was then subjected to hexane extraction. The percent recovery was found to be 7.6 % ± 1.7 % (95% confidence interval).

4.4.2 Oxidation of TCE on Zeolite

Two sets of experiments were conducted on the oxidation of TCE sorbed to the zeolite. The first experiment used an H_2O_2:TCE molar ratio of 100:1 and an iron:TCE ratio of 1.2:1. The second experiment used an H_2O_2:TCE molar ratio of 500:1 and an iron:TCE ratio of 6:1. Both experiments were left to equilibrate for 24 hours and were run at a pH of 3.5. The aqueous supernatant was analyzed for TCE and by-products. The zeolite was subjected to hexane extraction.

The concentration of TCE decreased, in the aqueous phase, with greater hydrogen peroxide and iron doses. By-products were seen in the liquid which indicates an oxidation process. The results are similar to those found in the aqueous Fenton's oxidation experiments, where the by-products formed. The two prominent by products were cis-DCE and trans-DCE. With the higher hydrogen peroxide and iron dose, only trans-DCE was at a noticeable concentration. The 1,1-DCE and vinyl chloride were below the detection limits in these experiments as they were in the aqueous Fenton's oxidation experiments as shown in Figure 4-18, which represents the constituents in the aqueous phase only.

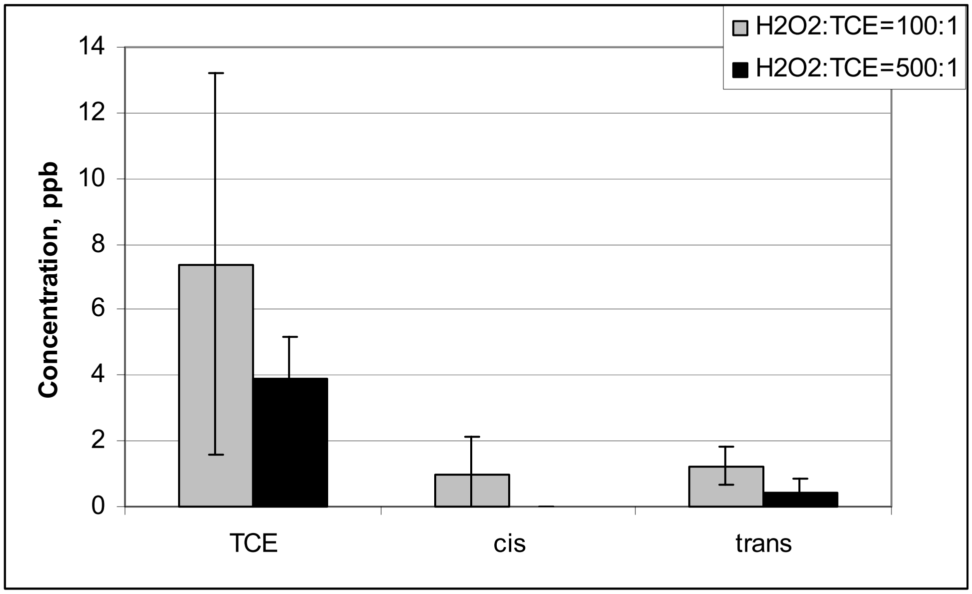

Figure 4-18: Aqueous concentrations of TCE and by-products at a pH = 3.5 following sorption and oxidation, H_2O_2:TCE molar ratios of 100:1 and 500:1 and iron:TCE molar ratios of 1.2:1 and 6:1 were used.

The hexane extraction of TCE from the ZSM-5 was determined to be inconclusive. The recovery rate for the hexane extraction was low, 7.6% ± 1.7 % (95% confidence interval).

By-product formation would be an indication as to whether or not oxidation was occurring on the zeolite bound TCE. The by-products, cis-DCE and trans-DCE, would be expected to show up on the chromatogram around 9 minutes and 7.5 minutes, respectively. As can be seen in Figure 4-19 the hexane peak on the chromatogram spans these times so cis-DCE and trans-DCE were not quantifiable. If the other by-products were formed, they should have volatilized earlier than TCE, cis-DCE or trans-DCE. These by-products were not seen. This could be for two reasons. (1) The 1,1-DCE and VC did not form. They were not expected to form because they were below the method detection limit throughout the aqueous Fenton's oxidation experiments. (2) They were formed in concentrations that were below the method detection limit for the hexane extraction procedure (autosampler) which had a higher method detection limit than the experiments run with SPME.

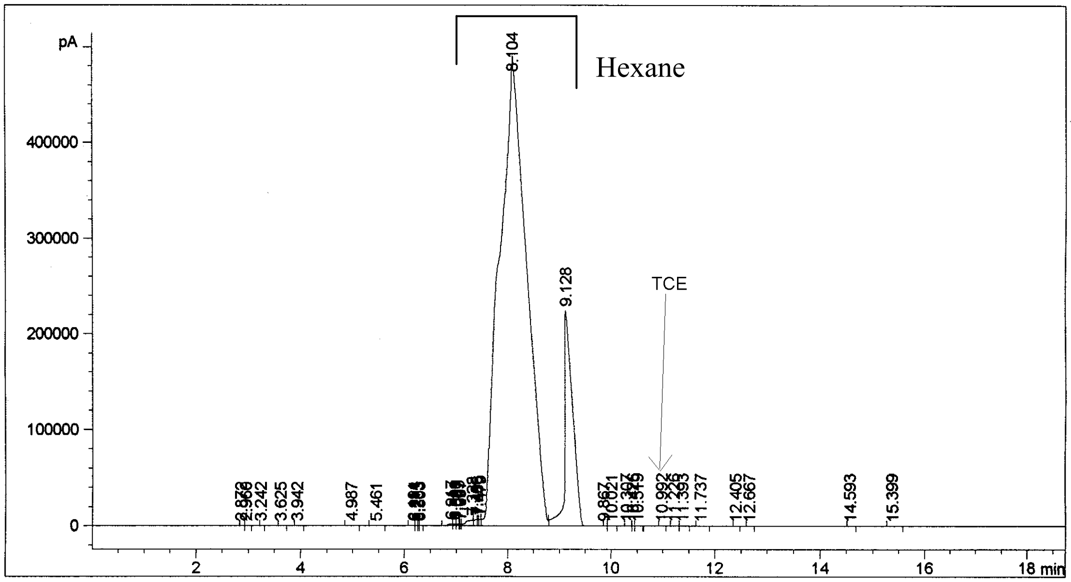

Figure 4-19: Chromatogram of TCE and by-product formation following oxidation of zeolite-bound TCE

The pH was taken after the sorption/oxidation experiments. The pH data increased in the experiments with hydrogen peroxide to TCE ratios of 100:1 and 500:1. For the experiments run with a H_2O_2:TCE molar ratio of 100:1 the pH increased from 3.5 to 4.57 ± 0.06 (95% confidence interval). For the experiments run with a H_2O_2:TCE molar ratio of 500:1 the pH increased from 3.5 to 4.09 ± 0.01 (95% confidence interval).

The average value of the pH after aqueous Fenton's oxidation was 3.6, thus these experiments showed a larger increase in the pH. In comparison, the experiment with less hydrogen peroxide recorded a higher pH value than the experiment with more hydrogen peroxide.

4.5 Zeolite Synthesis

Silicalite is an aluminum-free ZSM-5 (Gonthier and Thompson, 1994; Pope, 1987). Silicalite was synthesized and is shown in Figure 4-20. A significant quantity of amorphous silica was also seen in the SEM.

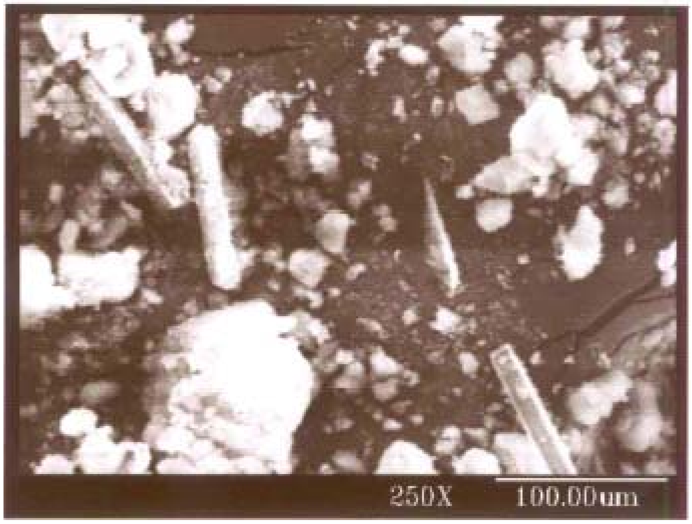

Figure 4-20: SEM of silicalite after a 7 day incubation time

The following figure is crystalline silicalite. This figure portrays the "coffin shaped" silicalite crystals with a characteristic length around 300 μm. These crystals were formed at 7 days under the same conditions as this research (Gonthier and Thompson, 1994).

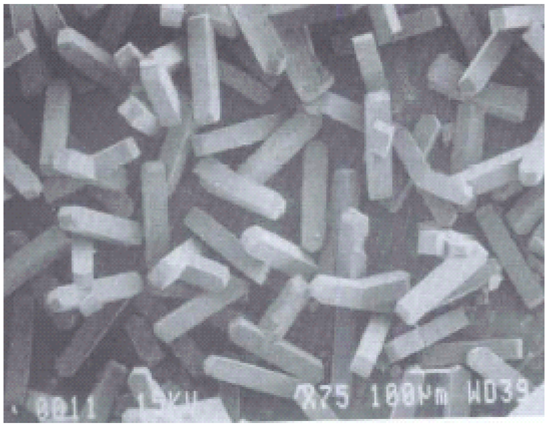

Figure 4-21: SEM of pure Silicalite (Gonthier and Thompson, 1994)

Incubation times of seven and eight days were used in the synthesis procedure. By comparing the SEM diagrams, it can be seen that there are differences in the two samples of silicalite. The second figure shows all crystals. The first figure shows several crystals, and significant amorphous silica.

The zeolites were also characterized by XRD, and is shown in Figure 4-22. An XRD of a pure silicalite sample is shown in Figure 4-23 (http://iza-online.org). The peaks between the two graphs are different which shows that this sample of silicalite is not entirely pure.

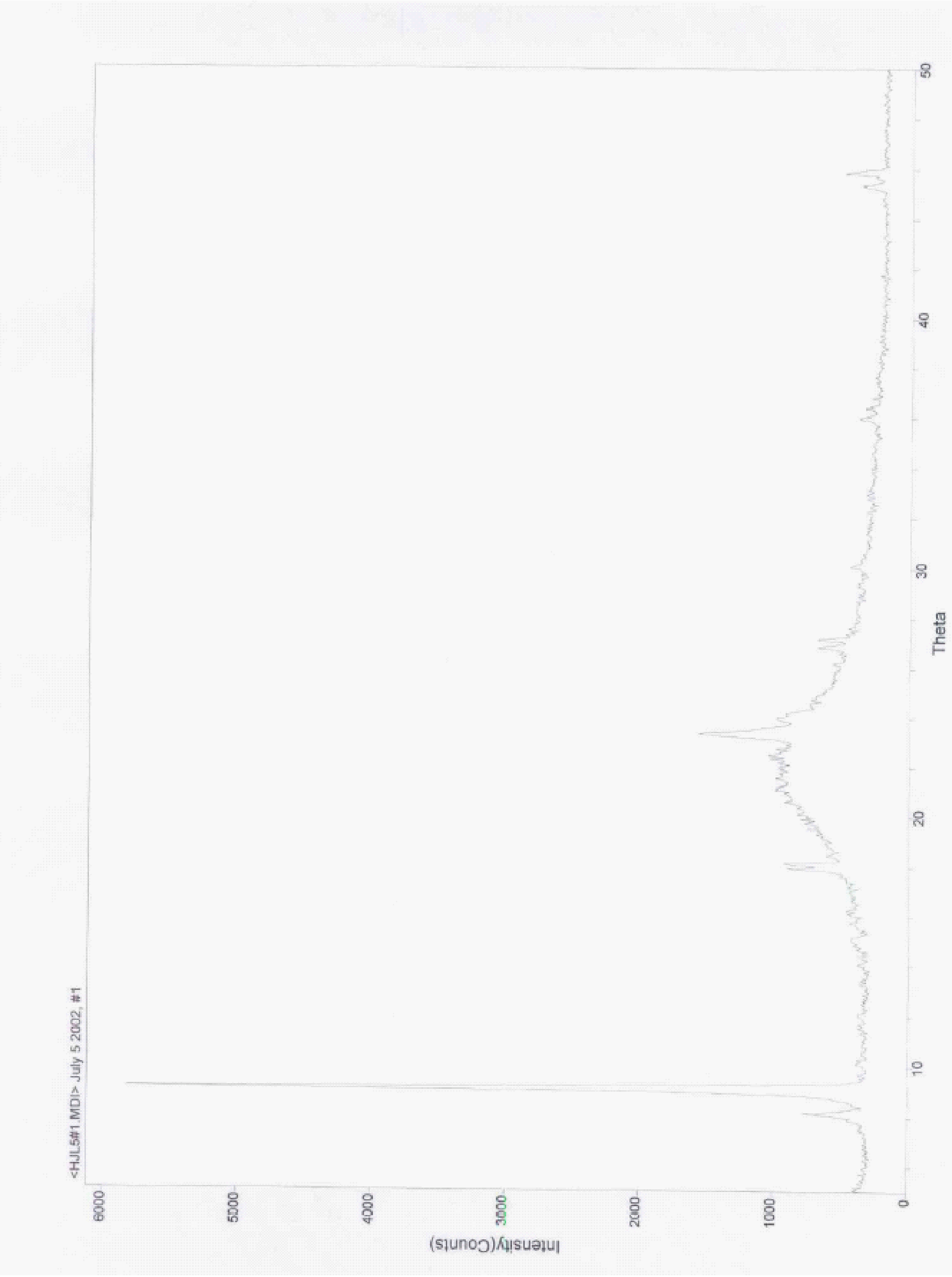

Figure 4-22: XRD analysis of the silicalite sample

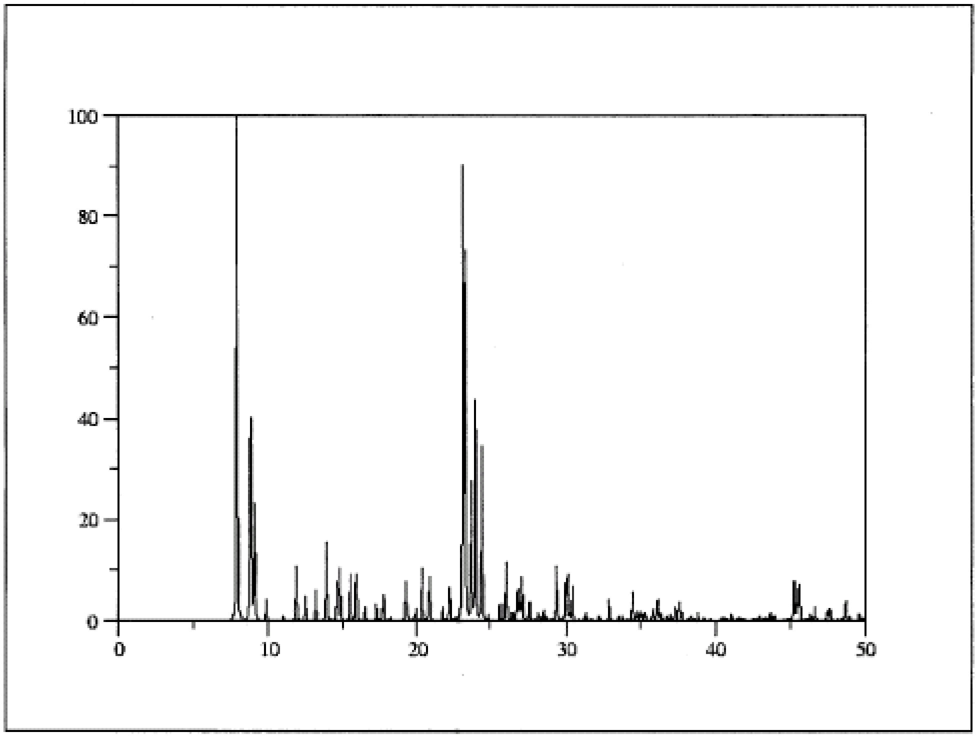

Figure 4-23: XRD of pure silicalite (http://www.iza-online.org)

Chapter 5 Future Work

The experiments with aqueous Fenton's oxidation should be run with higher amounts of iron and hydrogen peroxide to see if the byproducts would degrade further. The results from this research show that at pH = 3.5, the concentrations of cis-DCE and trans-DCE increased and then started to decrease. The other potential by products did not appear in any of the experiments. If higher concentrations of H_2O_2 were used, they could possibly appear. Thus, experiments should be conducted with greater amounts of H_2O_2. Another relevant experiment would be to use the same conditions as this research (i.e. do not add more H_2O_2 or iron) but let the experiments run for a longer reaction time to see if the DCE isomers would continue to degrade.

Silicalite synthesis should be attempted using the procedure outlined here but with a longer incubation time. Crystals did form during the synthesis experiments, however substantial amorphous silica was produced.

Future work on quantifying the amount of TCE on the zeolite is necessary for continued work on oxidation of sorbed contaminants. It is recommended that experiments be conducted to find a successful solvent extraction procedure. Other solvents could be tried in lieu of hexane. For example extraction with methylene chloride or methanol could be tried. Once a method for quantifying the amount of TCE on the zeolite is determined, experiments should be conducted on the feasibility of regenerating the zeolite by Fenton's oxidation. Higher concentrations of hydrogen peroxide and iron should be examined as well as similar pH values that were used during this project. Preliminary data showed that oxidation is occurring (the formation of the same by-products as aqueous Fenton's oxidation) and therefore there is reason for further exploration into this topic.

Chapter 6 Conclusions

The EPA estimated the TCE may be found in 9%-34% of drinking water sources in the United States. The EPA set a maximum contaminant level of TCE of 5 μg/L for drinking water. This project presents a possible alternative to the current remediation technologies which consist of air stripping and GAC. There were three hypotheses formed at the beginning of this project. The first one was that TCE could be destroyed by Fenton's oxidation. The second hypothesis was that TCE could be removed from water by zeolites, specifically ZSM-5. The third hypothesis was that the TCE on the zeolite could be destroyed by Fenton's oxidation.

TCE was degraded by Fenton's oxidation rapidly in these experiments. Chlorinated by products were measured after aqueous Fenton's oxidation of TCE. Cis-DCE and trans-DCE were found in the greatest concentrations. 1,1-DCE and VC were not found in concentrations above the method detection limits.

ZSM-5 was able to rapidly remove TCE from water. The uptake of TCE by ZSM-5 was found to follow a Freundlich model, which was the same model that other researchers found using silicalite (the aluminum free analog of ZSM-5). The 1/n values were very similar to work done by Giaya *et al*. (2000); however the K value differed for ZSM-5 than for their silicalite sample. This difference could be due to differences in the compositions of the ZSM-5 and the silicalite samples.

Preliminary experiments showed that Fenton's oxidation could destroy some TCE that was sorbed to ZSM-5. More research needs to be done in this area as only preliminary experiments were conducted in this project. It is also recommended that research be conducted on extraction methods to quantify the amount of contaminant on the ZSM-5.

In conclusion, the removal of TCE from water by coupled sorption to zeolite and Fenton's oxidation is a promising technology. The applicability of this topic to modern day environmental problems is clear. However it is still in its preliminary stages.

Chapter 7 Works Cited

Anderson, Michael A. Removal of MTBE and Other Organic Contaminant from Water by Sorption to High Silica Zeolites. *Environmental Science & Technology*. 34 (4), **2000**, 725-727.

Black. Lisa; Fine, Dennis. High Levels of Monoaromatic Compounds Limit the Use of Solid-Phase Microextraction of Methyl *tert*-Butyl Ether and *tert*-Butyl Alcohol. *Environmental Science and Technology*. **2001**, 35 (15), 3190-3192.

Chen, Ge; Hoag, George, E.; Chedda, Pradeep; Nadim, Farhad, Woody, Bernard A.; Dobbs, Gregory M. The Mechanism and Applicability of In Situ Oxidation of Trichloroethylene with Fenton's Reagent. *Journal of Hazardous Materials*. **2001**, 87 (1), 171-186.

Crab, Charlene. No zzzzz's for Zeolites. *Chemical Engineering*. May **2001**, 59-61.

Dyer, Alan. An Introduction to Zeolite Molecular Sieves. J. Wiley & Sons, Chichester, New York. 1988, 149 pages.

Engwall, Margaret A.; Pignatello, Joseph J.; Grasso, Domenico. Degradation and Detoxification of the Wood Preservatives Creosote and Pentachlorophenol in Water by the Photo-Fenton Reaction. *Water Research*. **1999**, 33 (5), 1151-1158.

Environmental Protection Agency (EPA). 2001. Sources, Emission and Exposure for Trichloroethylene (TCE) and Related Chemicals. EPA/600/R-00/099. March, 2001. National Center for Environmental Assessment-Washington Office.

Gates, Dianne D.; Siegrist, Robert L. In-Situ Chemical Oxidation of Trichloroethylene Using Hydrogen Peroxide. *Journal of Environmental Engineering*. **1995**, 121 (9), 639-644.

Giaya, Arjan; Thompson, Robert W.; Denkewicz, Raymond Jr. Liquid and Vapor Phase Adsorption of Chlorinated Volatile Organic Compounds on Hydrophobic Molecular Sieves. *Microporous and Mesoporous Materials*. **2000**, 40, 205-218.

Gonthier, Sylvie; Thompson, Robert W. Effects of Seeding on Zeolite Crystallisation, and the Growth Behavior of Seeds. In *Advanced Zeolite Science and Applications*; Jansen, J.C., Stocker, M., Karge, H.G., Weitkamp, J., Eds.; Elsevier: New York, 1994; Volume 85, 43-73.

Greene, Howard L.; Prakash, Deepak S.; Athota, Kiran, V. Combined sorbent/catalyst media for destruction of halogenated VOCs. *Applied Catalysis B: Environmental*. **1996**, 7, 213-224.

Hugh, Russell, H.; Matthews, John, E.; Sewell, Guy, W. EPA Ground Water Issue: TCE Removal from Contaminated Soil and Ground Water. EPA/540/S-92/002. 1992.

Huling, Scott G.; Arnold, Robert G.; Sierka, Raymond A.; Jones, Patrick K.; Fine, Dennis D. Contaminant Adsorption and Oxidation via Fenton Reaction. *Journal of Environmental Engineering*. **2000**, 126 (7), 595-600.

Lorah, Michelle M.; Olsen, Lisa D.; Capone, Douglas, G.; Baker, Joel E. Biodegradation of Trichloroethylene and Its Anaerobic Daughter Products in Freshwater Wetland Sediments. *Bioremediation Journal.* **2001**, 5 (2), 101-118.

Mackenzie, Katrin; Georgi, Anett; Kumke, Michael; Kopinke, Frank-Dieter. Sorption of Pyrene to Dissolved Humic Substances and Related Model Polymers. 2. Solid-Phase Microextraction (SPME) and Fluorescence Quenching Technique (FQT) as Analytical Methods. *Environmental Science & Technology*. **2002**, 36 (20), 4403-4409.

O'Brien, Daniel. Tremblay, Bryan. 2002. Major Qualifying Project, WPI. Fenton's Oxidation of TCE Contaminated Water.

Pope, Christopher George. Water Adsorption on ZSM-5 and Its Aluminum Free Analog, Silicalite. *Journal of Colloid and Interface Science*. **1987**, 116 (1), 221-223.

Russell, Hugh H.; Matthews, John E.; Sewell, Guy W. TCE Removal from Contaminated Soil and Ground Water. EPA Ground Water Issue. January 1992.

Santos, F.J.; Galceran, M.T.; Fraisse, D. Application of solid-phase microextraction to the analysis of volatile organic compounds in water. *Journal of Chromatography A*. **1996**, 742, 181-189.

Snoeyink, Vernon L.; Summers, R. Scott. Adsorption of Organic Compounds. In *Water Quality and Treatment: A Handbook of Community Water Supplies*, Fifth Edition; Letter, Raymond D. Ed.; McGraw-Hill, Inc.: New York, 1999; pp 13.1-13.3.

Teel, Amy L.; Warberg, Christopher R.; Atkinson, David A.; Watts, Richard J. Comparison of Mineral and Soluble Iron Fenton's Catalysts for the Treatment of Trichloroethylene. *Water Research*. **2001**, 35 (4), 977-984.

Theis, Timothy. M.S. thesis, 2002, Environmental Engineering, WPI. Advanced Oxidation of MTBE in the Presence of Zero-Valent Iron.

Tiscareno-Lechuga, F; Tellez, C.; Menendez, M.; Santamaria, J. A Novel Device for Preparing Zeolite—A Membranes Under a Centrifugal Force Field. *Journal of Membrane Science*. **2003**, 212, 135-146.

Weber, Walter J., Jr. Environmental Systems and Processes: Principles, Modeling, and Design. John Wiley & Sons, Inc., New York, 2001, pp 396-399

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

Yamamoto, Kohji; Fukushima, Minoru; Kakutani, Naoya; Tsuruho, Kenshiro. Research Note: Contamination of Vinyl Chloride in Shallow Urban Rivers in Osaka, Japan. *Water Research*. **2001**, 35 (2), 561-566.

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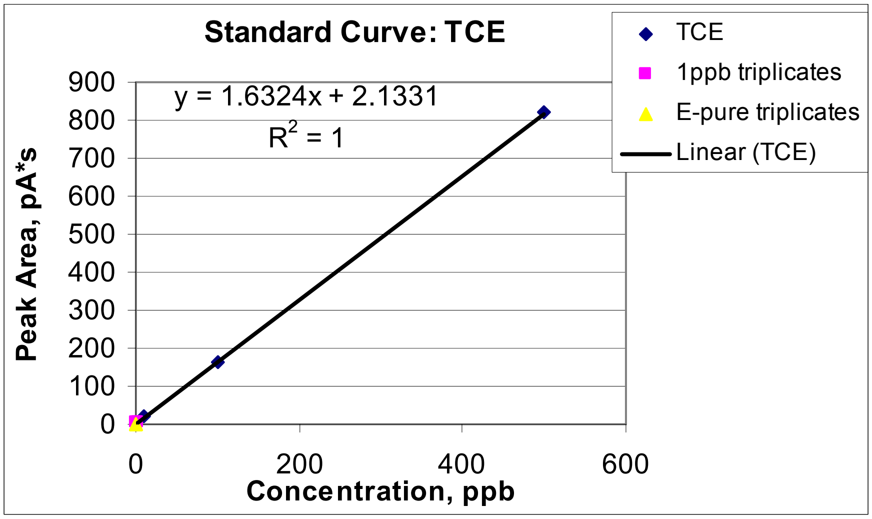
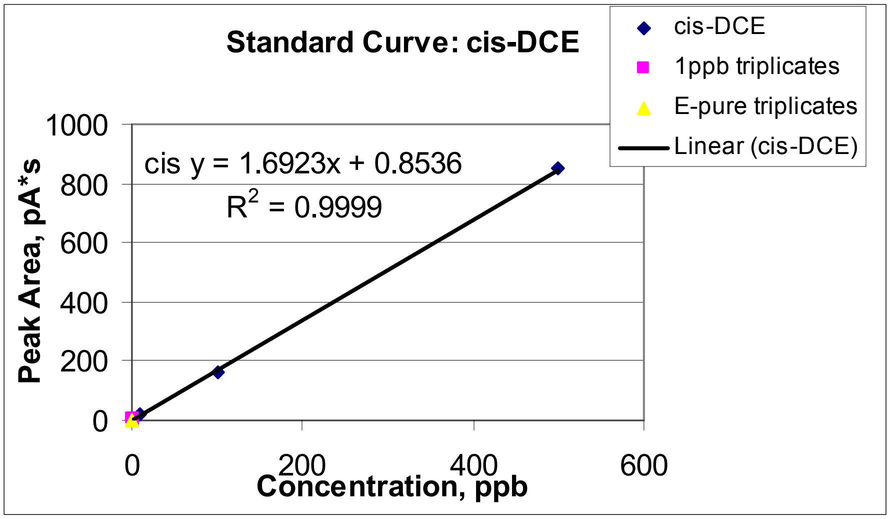
Appendix A: Standard Curves and Method Detection Limit Data

Standard Curves

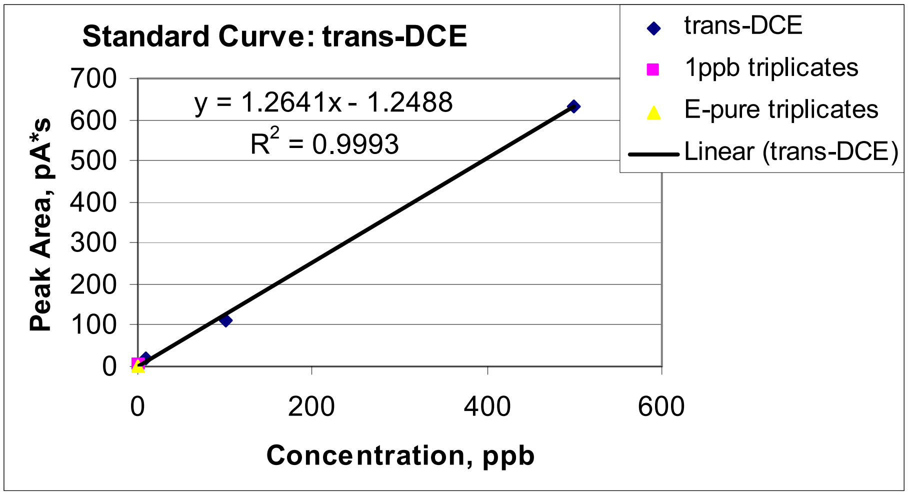
The equation and R^2 values for the five constituents were determined and presented in the following five graphs.



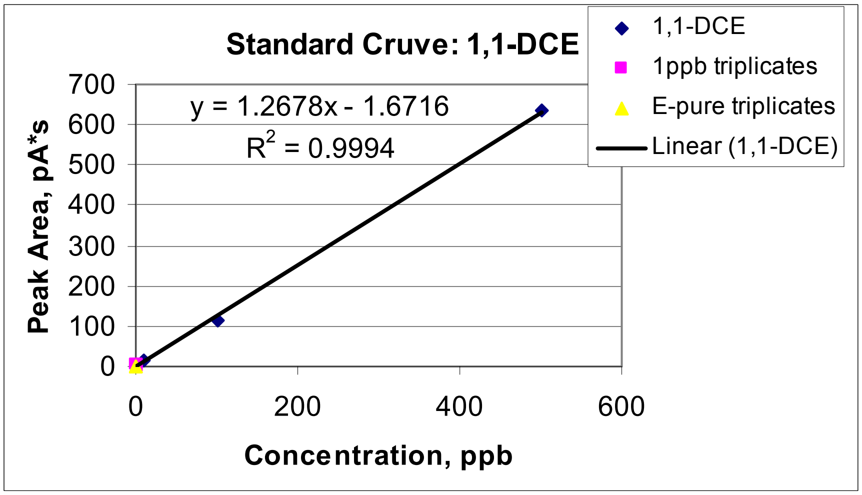
Standard Curve for TCE



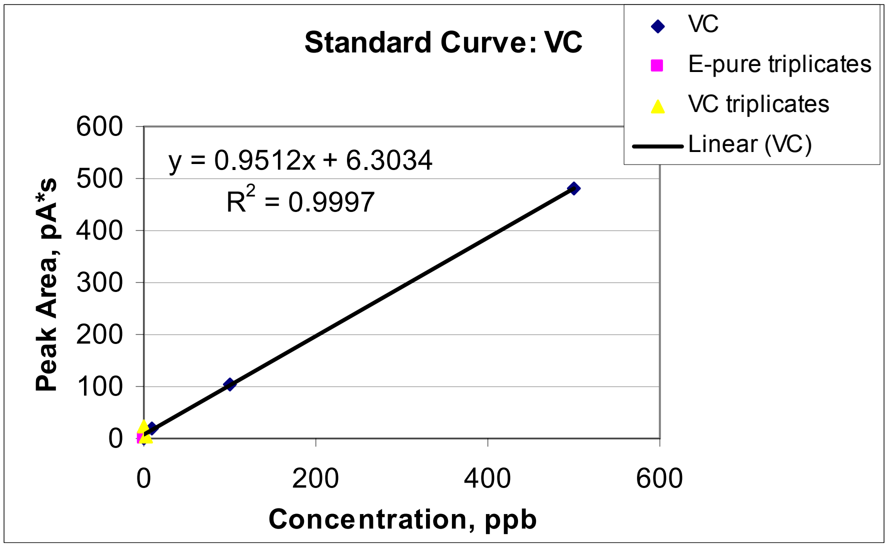
Standard Curve for cis-DCE



Standard Curve for trans-DCE



Standard Curve for 1,1-DCE



Standard Curve for VC

Method Detection Limits

Hypothesis testing was done to compare triplicates at 1 ppb and 5 ppb to E-pure blanks (concentatration = 0 ppb). These are: t-test: two samples assuming equal variances done in Microsoft Excel.

	Peak Area				
Conc. ppb	**TCE**	**cis-DCE**	**trans-DCE**	**1,1-DCE**	**VC**
0	0	0	2.66	0	0
0	0	0	0	0	0
0	0	0	0	0	0
1	3.06624	2.04636	1.95484	0.17045	1.26001
1	2.88444	2.27103	1.95899	1.68797	5.47221
1	3.07291	5.26924	0.803924	1.52291	2.22451
5	15.3814	15.32467	10.62632	10.6189	46.09336
5	11.42904	11.89495	7.62622	6.71427	16.94348
5	6.47338	6.57037	3.95701	4.79606	0

TCE 1ppb

	Variable 1	*Variable 2*
Mean	0	3.007863
Variance	0	0.011436
Observations	3	3
Pooled Variance	0.005718	
Hypothesized Mean Difference	0	
df	4	
t Stat	-48.7169	
P(T<=t) one-tail	5.31E-07	
t Critical one-tail	2.131846	
P(T<=t) two-tail	1.06E-06	
t Critical two-tail	2.776451	

TCE: 5 ppb

	Variable 1	*Variable 2*
Mean	0	11.09461
Variance	0	19.92209
Observations	3	3
Pooled Variance	9.961045	
Hypothesized Mean Difference	0	
df	4	
t Stat	-4.30532	
P(T<=t) one-tail	0.006296	
t Critical one-tail	2.131846	
P(T<=t) two-tail	0.012593	
t Critical two-tail	2.776451	

cis-DCE: 1 ppb

	Variable 1	*Variable 2*
Mean	0	3.195543
Variance	0	3.237783
Observations	3	3
Pooled Variance	1.618891	
Hypothesized Mean Difference	0	
df	4	
t Stat	-3.07597	
P(T<=t) one-tail	0.018538	
t Critical one-tail	2.131846	
P(T<=t) two-tail	0.037077	
t Critical two-tail	2.776451	

cis-DCE: 5 ppb

	Variable 1	*Variable 2*
Mean	0	11.26333
Variance	0	19.45865
Observations	3	3
Pooled Variance	9.729325	
Hypothesized Mean Difference	0	
df	4	
t Stat	-4.42253	
P(T<=t) one-tail	0.005744	
t Critical one-tail	2.131846	
P(T<=t) two-tail	0.011488	
t Critical two-tail	2.776451	

trans-DCE: 1 ppb

	Variable 1	*Variable 2*
Mean	0.886667	1.572585
Variance	2.358533	0.443134
Observations	3	3
Pooled Variance	1.400834	
Hypothesized Mean Difference	0	
df	4	
t Stat	-0.70978	
P(T<=t) one-tail	0.258513	
t Critical one-tail	2.131846	
P(T<=t) two-tail	0.517026	
t Critical two-tail	2.776451	

trans-DCE: 5 ppb

	Variable 1	*Variable 2*
Mean	0.886667	7.403183
Variance	2.358533	11.15723
Observations	3	3
Pooled Variance	6.757883	
Hypothesized Mean Difference	0	
df	4	
t Stat	-3.07012	
P(T<=t) one-tail	0.018644	
t Critical one-tail	2.131846	
P(T<=t) two-tail	0.037288	
t Critical two-tail	2.776451	

1,1-DCE: 1 ppb

	Variable 1	*Variable 2*
Mean	0	1.12711
Variance	0	0.69321
Observations	3	3
Pooled Variance	0.346605	
Hypothesized Mean Difference	0	
df	4	
t Stat	-2.34474	
P(T<=t) one-tail	0.039484	
t Critical one-tail	2.131846	
P(T<=t) two-tail	0.078968	
t Critical two-tail	2.776451	

1,1-DCE: 5 ppb

	Variable 1	*Variable 2*
Mean	0	7.37642
Variance	0	8.805286
Observations	3	3
Pooled Variance	4.402643	
Hypothesized Mean Difference	0	
df	4	
t Stat	-4.30561	
P(T<=t) one-tail	0.006295	
t Critical one-tail	2.131846	
P(T<=t) two-tail	0.01259	
t Critical two-tail	2.776451	

VC: 1 ppb

	Variable 1	*Variable 2*
Mean	0	2.985577
Variance	0	4.870074
Observations	3	3
Pooled Variance	2.435037	
Hypothesized Mean Difference	0	
df	4	
t Stat	-2.34326	
P(T<=t) one-tail	0.039548	
t Critical one-tail	2.131846	
P(T<=t) two-tail	0.079096	
t Critical two-tail	2.776451	

VC: 5 ppb

	Variable 1	*Variable 2*
Mean	0	21.01228
Variance	0	543.5658
Observations	3	3
Pooled Variance	271.7829	
Hypothesized Mean Difference	0	
df	4	
t Stat	-1.56102	
P(T<=t) one-tail	0.096771	
t Critical one-tail	2.131846	
P(T<=t) two-tail	0.193542	
t Critical two-tail	2.776451	

Appendix B: Charts in Methodology

Centrifuge times

Wavelength = 500 nm

Time, min	absorbance
0	2.7969
10	0.0852
13	0.1132
15	0.1437
20	0.0748
25	0.1318

Preliminary Sorption experiments with 1.0 g ZSM-5 for 24 hours

time, min	TCE concentration in effluent, ppb
0	500
30	2.684215871
60	2.657783258
120	2.916538517
240	3.340954592
480	1.845713042
960	2.735891484
1440	2.945509938

Appendix C: Aqueous Fenton's Oxidation

pH=3.5 run 3 times

	TCE Concentration, ppb					
Time	Run1	Run2	Run3	Average	St dev	95% ci
0	500	500	500	500	0	0
5	85.22732	106.4085	162.0707	117.9022	39.6901	44.91273
10	100.4519	92.02981	136.7689	109.7502	23.77478	26.90319
20	76.54917	93.66945	113.3694	94.52935	18.42519	20.84967
40	100.6024	98.98656	111.1365	103.5751	6.59796	7.466152
90	100	71.25576	115.2156	95.49046	22.32418	25.26171
180	78.53588	61.64677	113.3578	84.51347	26.36865	29.83837
360	0	87.06063	81.86233	56.30765	48.83308	55.25878

	cis-DCE Concentration, ppb					
Time	Run1	Run2	Run3	Average	st dev	95% ci
0	0	0	0	0	0	#NUM!
5	46.51402	42.46452	49.34935	46.1093	3.460213	3.915526
10	50.55123	44.89706	42.31884	45.92238	4.210879	4.764968
20	47.5088	39.81399	35.86646	41.06309	5.920828	6.69992
40	56.19958	13.85031	41.83792	37.29594	21.53689	24.37082
90	97.77869	33.96146	52.8808	61.54032	32.77804	37.09115
180	56.19987	37.2224	36.2344	43.21889	11.25271	12.73339
360	16.44949	41.14038	40.70856	32.76614	14.13229	15.99188

	trans-DCE Concentration, ppb					
Time	Run1	Run2	Run3	Average	st dev	95%ci
0	0	0	0	0	0	0
5	81.28972	47.68127	75.42513	68.13204	17.95199	20.3142
10	98.48259	52.45126	55.7325	68.88878	25.68145	29.06074
20	48.69018	35.42299	54.01067	46.04128	9.572773	10.83241
40	63.10443	31.46668	63.85625	52.80912	18.48692	20.91952
90	133.6395	28.17	81.35396	81.0545	52.7354	59.67459
180	64.11654	31.83634	53.41002	49.78763	16.44214	18.60568
360	8.425863	37.72149	59.69238	35.27991	25.72032	29.10473

	1,1-DCE Concentration, ppb					
Time	Run1	Run2	Run3	average	st dev	95%ci
0	0	0	0	0	0	0
5	0	0.894339	0	0.298113	0.516347	0.584291
10	5.827674	0	0.537907	2.12186	3.220579	3.644359
20	7.167576	2.024841	0.887412	3.359943	3.34619	3.786499
40	7.934681	0	0.959256	2.964645	4.330818	4.900688
90	7.481624	2.557587	0.528797	3.522669	3.57547	4.045949
180	9.002038	1.96998	1.211213	4.061077	4.295783	4.861044
360	0	1.896747	0	0.632249	1.095088	1.239185

	VC Concentration, ppb					
Time	Run1	Run2	Run3	average	st dev	95% ci
0	0	0	0	0	0	0
5	0	0	0	0	0	0
10	0	0	0	0	0	0
20	0	0	0	0	0	0
40	0	0	0	0	0	0
90	4.555644	0	0	1.518548	2.630202	2.976297
180	0	0	0	0	0	0
360	0	0	0	0	0	0

pH = 2.5 1 run

	Concentration, ppb				
Time	TCE	cis	trans	1,1	VC
0	500	0	0	0	0
5	229.5396	62.35339	267.3303	0	0
10	204.0377	74.96887	300.753	0	0
20	181.1932	62.30497	227.4166	0	0
40	254.5833	74.18958	298.1656	0	0
90	218.9429	46.76359	178.0083	0	0
180	182.2246	67.51278	278.1282	2.218333	0
360	260.6982	84.25331	351.1814	0	0

pH=4.5 1 run

	Concentration, ppb				
Time	TCE	cis	trans	1,1	VC
0	500	0	0	0	0
5	207.3194	65.45409	32.88652	1.8834	0
10	175.4257	70.76921	41.27203	0	0
20	146.3974	72.30327	40.66342	0	0
40	109.5112	71.6807	38.91397	0	0
90	109.3659	94.72112	57.92094	0	0
180	162.3051	81.86502	56.27714	4.194842	0
360	86.03759	75.38734	49.56136	0	0

Appendix D: TCE Sorption Kinetics

0.1 g ZSM-5, C_0 = 500 ppb TCE, 3 runs

	TCE Concentration remaining in supernatant, ppb					
Time, min	run1	run 2	run3	Average	Std Deviation	95% ci
0	500	500	500	422.2907	34.83797047	39.42213
15	59.62175	62.49444	28.5646	50.22693	18.81503097	21.29081
20	75.33345	41.95663	23.85218	47.04742	26.1154606	29.55186
30	83.08727	42.62816	17.33691	47.68411	33.16548854	37.52957
60	28.42463	17.96746	19.62721	22.00643	5.619928142	6.359427
90	40.83477	43.7808	30.74841	38.45466	6.834432051	7.733741
120	29.14249	41.61727	9.279958	26.67991	16.30869866	18.45468
180	18.95136	21.18957	16.95108	19.03067	2.120355168	2.399362

Appendix E: pH from Aqueous Fenton's Oxidation

Initial pH = 3.5

	pH					
Time	**8/7/2002**	**8/8/2002**	**8/9/2002**	**Average**	**St. Dev**	**95%ci**
0	3.77	3.49	3.58	3.61	0.142945	0.161755
5	3.79	3.41	3.5	3.57	0.198578	0.224708
10	3.76	3.41	3.5	3.56	0.181751	0.205666
20	3.9	3.42	3.53	3.62	0.251462	0.284551
40	3.89	3.43	3.56	3.63	0.237136	0.268339
90	3.87	3.46	3.58	3.64	0.210792	0.238529
180	3.95	3.38	3.63	3.65	0.285715	0.323311
360	3.89	3.42	3.53	3.61	0.245832	0.27818

Initial pH = 2.5

Time	**pH**
0	2.21
5	2.38
10	2.38
20	2.27
40	1.99
90	1.97
180	2
360	2.06
Average	2.1575

Initial pH = 4.5

Time	**pH**
0	5.13
5	5.26
10	5.07
20	4.98
40	4.83
90	4.8
180	4.76
360	4.87
Average	4.9625

Appendix F: Adsorption Isotherms

Sorb TCE to 0.1 g ZSM-5 for 24 hours. 3 runs.

Run1

concentration TCE, ppm	TCE concentration in supernatant, ppb (Ce)
0.5	0.315840771
1	9.590511991
1.25	11.80984012
1.5	16.67943472
2.5	23.75447278
3	23.38459269
12000	461.4582
20000	731.3817

Converts to

g, zeolite	Co, mg	Ce, mg	q, mg/g
0.1	0.021815	1.3543E-05	0.218019
0.1	0.041636	0.0003952	0.412409
0.1	0.051969	0.00048811	0.514804
0.1	0.062284	0.00068786	0.615963
0.1	0.103774	0.00098121	1.027929
0.1	0.125332	0.00096668	1.243656
0.1	0.482712	0.019842704	4.62869
0.1	0.819141	0.031449411	7.87692

Run 2

TCE concentration ppb	concentration in supernatant, ppb
500	20.68043
1000	34.31288
1250	34.6993
1500	35.01922
2500	81.9965
3000	79.36628
12000	389.3376
20000	549.899

Converts to

g, zeolite	**Co, mg**	**Ce, mg**	**q, mg/g**
0.1	0.020821	0.000857	0.199649
0.1	0.04162	0.001422	0.401977
0.1	0.051187	0.001413	0.497734
0.1	0.062541	0.001452	0.610885
0.1	0.103654	0.003381	1.002731
0.1	0.125254	0.003295	1.219596
0.1	0.481981	0.016741519	4.652396
0.1	0.810824	0.023645658	7.871788

Run 3

TCE concentration, ppb	**Concentration in supernatant, ppb**
500	17.75527
1000	36.71801
1250	32.92857
1500	68.86947
2500	60.76852
3000	95.44946
12000	385.694
20000	938.11

Converts to

g, zeolite	**Co, mg**	**Ce, mg**	**q, mg/g**
0.1	0.020568	0.000763	0.198042
0.1	0.041308	0.001509	0.397985
0.1	0.051932	0.001359	0.505731
0.1	0.062027	0.002833	0.591944
0.1	0.10356	0.002499	1.010616
0.1	0.124496	0.003935	1.205611
0.1	0.488513	0.016584844	4.719283
0.1	0.826895	0.040338732	7.86556

Linear Isotherm

Ce, ug/L	**q (run1)**	**q (run2)**	**q (run 3)**	**Average q, mg/g**	**St Dev**	**95%ci**
12.91717	0.218019	0.199649421	0.1980418	0.205236739	0.011099	0.012559
26.8738	0.412409	0.401976637	0.3979853	0.404123674	0.007448	0.008428
26.47923	0.514804	0.497733587	0.5057306	0.506089484	0.008541	0.009665
28.90595	0.615963	0.610885463	0.5919436	0.60626397	0.012659	0.014325
55.50649	1.027929	1.002730578	1.0106162	1.013758484	0.01289	0.014586
66.06677	1.243656	1.219595578	1.2056109	1.222954205	0.019244	0.021776
412.1633	4.62869	4.652396248	4.719283	4.666789838	0.04698	0.053162
739.7969	7.87692	7.871788152	7.8655595	7.871422602	0.005689	0.006438

Freundlich Model

Ce, ug/L	**log Ce**	**q, avg, mg/g**	**log q**
12.917179	1.111168	0.205236739	-0.6877449
26.8738	1.429329	0.404123674	-0.3934857
26.479236	1.422905	0.506089484	-0.2957727
28.905959	1.460987	0.60626397	-0.2173382
55.506495	1.744344	1.013758484	0.0059345
66.066775	1.819983	1.222954205	0.0874102
412.16331	2.615069	4.666789838	0.6690182
739.79691	2.869113	7.871422602	0.8960532

Langmuir Model

Ce, ug/L	**q, average, mg/g**	**Ce/q**
12.91718	0.205236739	62.937945
26.8738	0.404123674	66.49895
26.47924	0.506089484	52.321252
28.90596	0.60626397	47.678834
55.5065	1.013758484	54.753174
66.06677	1.222954205	54.02228
412.1633	4.666789838	88.318378
739.7969	7.871422602	93.985159

Appendix G: Desorption Points

Sorb TCE to zeolite, fill vials with water, equilibrate for 24 hours, 3 runs

Run 1

Concentration TCE, ppm	**concentration in supernatant, ppb**
0.5	15.2608003
1	19.50459037
1.25	31.88925725
1.5	36.68407714
2.5	73.55302837
3	72.05898948

Converts to

g, zeolite	**Ce, mg**	**q = (Co-Ce-C-today)/g**
0.1	0.000658	0.21143714
0.1	0.000815	0.40425819
0.1	0.001326	0.50153987
0.1	0.001569	0.60026976
0.1	0.003052	0.99740409
0.1	0.003054	1.21311627

Run 2

concentration ppb, TCE	**concentration in supernatant, ppb**
500	11.63998
1000	32.05317
1250	31.01877
1500	44.77121
2500	77.05574
3000	83.86432

Converts to

Ce, mg	**q = (Co-Ce-C-today)/g**
0.000486	0.194791
0.001341	0.388568
0.001295	0.484788
0.001863	0.592252
0.003232	0.970411
0.003481	1.184789

Run 3

concentration ppb, TCE	**concentration in supernatant, ppb**
500	7.160324
1000	22.52065
1250	15.79493
1500	19.2932
2500	36.1191
3000	56.10606

Converts to

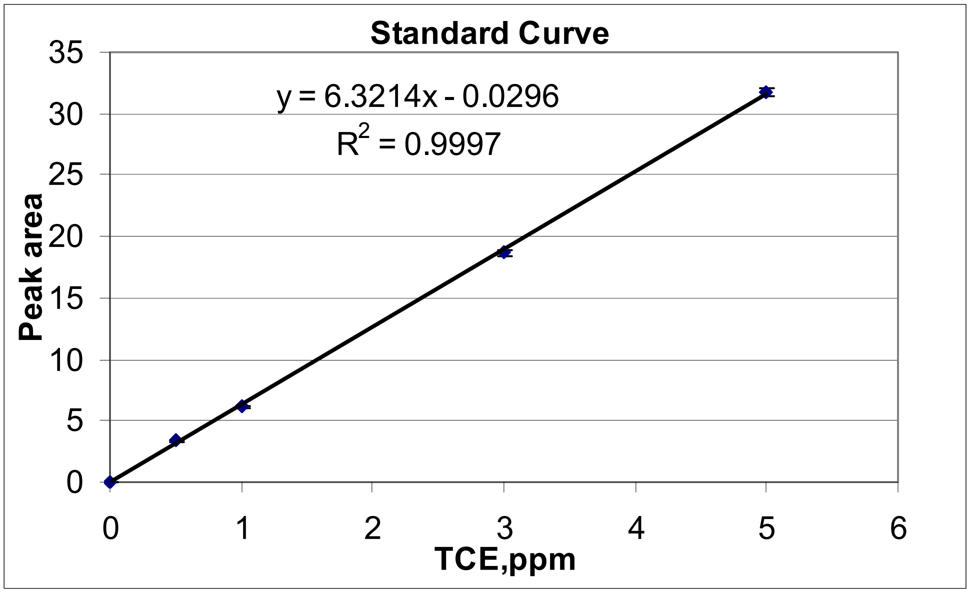
Ce, mg	**q = (Co-Ce-C-today)/g**
0.000304	0.195002
0.000937	0.388617
0.000664	0.499095
0.000813	0.583814
0.001511	0.995509
0.00235	1.182107

Averages

	q values						
Concentration TCE, ppm	Ce, ug/L	run1	run2	run3	Average, q	St Dev	95%ci
0.5	11.3537	0.211437143	0.1947909	0.195001657	0.20041	0.00955	0.010807
1	24.6928	0.404258186	0.3885678	0.38861682	0.393814	0.009045	0.010235
1.25	26.23432	0.501539865	0.4847881	0.499095057	0.495141	0.009049	0.01024
1.5	33.58283	0.600269757	0.5922517	0.583813593	0.592112	0.008229	0.009312
2.5	62.24262	0.997404091	0.9704106	0.99550889	0.987775	0.015067	0.01705
3	70.67645	1.213116268	1.1847886	1.182106863	1.193337	0.017182	0.019442

Appendix H: Hexane Extraction

Standard Curve



Hypothesis Test: Method Detection Limit = 0.5 mg/L

	Variable 1	*Variable 2*
Mean	0	3.35068
Variance	0	0.001308
Observations	3	3
Pooled Variance	0.000654	
Hypothesized Mean Difference	0	
df	4	
t Stat	-160.452	
P(T<=t) one-tail	4.53E-09	
t Critical one-tail	2.131846	
P(T<=t) two-tail	9.05E-09	
t Critical two-tail	2.776451	

Control Experiments

Let 500 ppb TCE solution equilibrate with 0.1 g ZSM-5 for 24 hours. Extract with 4 mL of hexane. 3 runs.

What should be on ZSM-5: 0.0208 g

Sample	**TCE on zeolite, ppm**	**ppm*.004L**	**% recovery = (recovered/total)*100**
1	0.36921	0.004	7.096099
2	0.422933	0.008	8.128638
3	0.263081	0.012	5.056326

Average	St dev	95%ci
6.760354	1.563432	1.769156

Appendix I: Sorption/Oxidation Experiments

pH = 3.5, samples 1-3 had H_2O_2:TCE of 100:1 and a iron:TCE of 1.2:1, samples 4-6 had H_2O_2:TCE of 500:1 and a iron:TCE of 6:1

In supernatant after oxidation

samples	**TCE, ppb**	**Cis-DCE, ppb**	**Trans-DCE, ppb**	**1,1-DCE, ppb**	**VC, ppb**
1	13.27629	2.049	1.827742	1.005167	0
2	4.999193	0	0.926492	1.267847	0
3	3.899725	0.79	0.980705	0.694418	1.451876
4	3.232782	0	0.718047	0.4861	0
5	3.345553	0	0.611955	0.507564	3.994597
6	5.195455	0	0	0	0

100:1	**TCE**	**Cis-DCE**	**Trans-DCE**	**1,1-DCE**	**VC**
Average, ppb	7.391736	0.946533	1.24498	0.989144	0.483959
St dev	5.125737	1.033598	0.505414	0.28705	0
95%ci	5.800208	1.169604	0.571919	0.324821	0
500:1	**TCE**	**cis**	**trans**	**1,1**	**VC**
Average, ppb	3.924597	0	0.443334	0	1.331532
St dev	1.102039	0	0.387586	0	2.306282
95%ci	1.24705	0	0.438586	0	2.609754

Hexane Extraction (2 vials = 1 sample; so vials 1-6 are H_2O_2:TCE 100:1 ratio and vials 7-12 are H_2O_2:TCE 500:1 ratio)

Vial	**TCE, ppm**	**TCE, mg**	**account for 7% recovery**	**% remaining**
1	0.587899	0.002	0.033594	167.9713
2	0.609523	0.002	0.03483	174.1493
3	0.508799	0.002	0.029074	145.3713
4	0.718093	0.003	0.041034	205.1693
5	0.558222	0.002	0.031898	159.4921
6	0.50433	0.002	0.028819	144.0943
7	0.522329	0.002	0.029847	149.2369
8	0.685403	0.003	0.039166	195.8295
9	0.839633	0.003	0.047979	239.895
10	0.676016	0.003	0.038629	193.1474
11	0.710275	0.003	0.040587	202.9358
12	0.515609	0.002	0.029463	147.3167

% remaining = (recovered, mg/ amount before oxidation, mg) * 100

pH data after sorption/oxidation

H_2O_2:TCE of 100:1 and a iron:TCE of 1.2:1

sample	**pH**
1	4.52
2	4.62
3	4.59

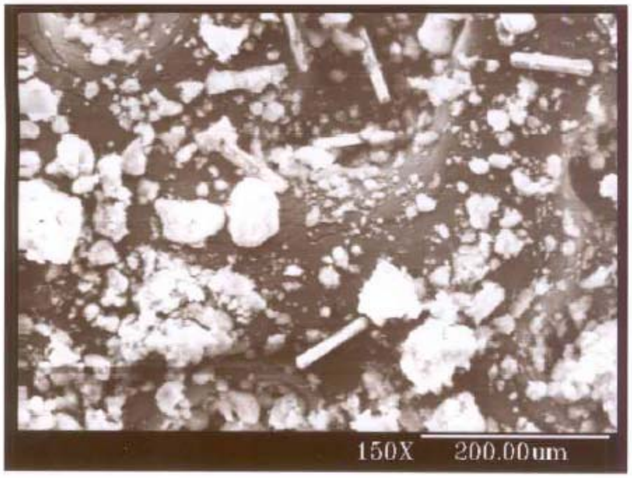
Average	St dev	95%ci
4.576667	0.051316	0.058068

H_2O_2:TCE of 500:1 and a iron:TCE of 6:1

sample	**pH**
4	4.11
5	4.09
6	4.09

Average	St dev	95%ci
4.096667	0.011547	0.013066

Appendix J: SEM Photographs of Silicalite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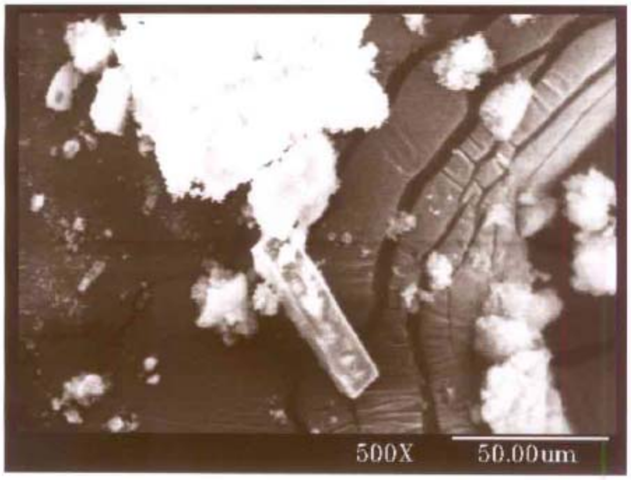
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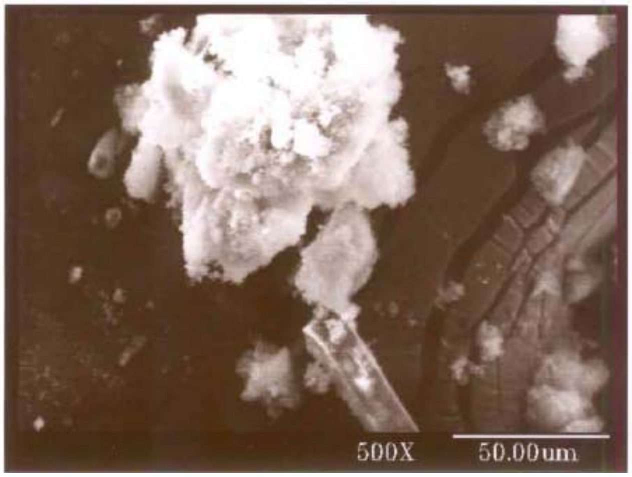
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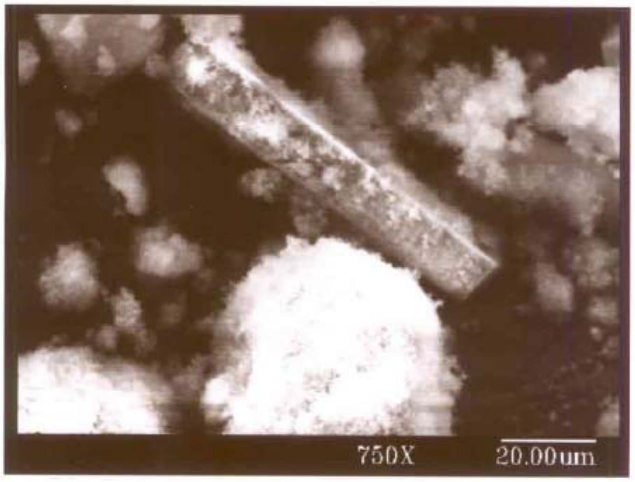
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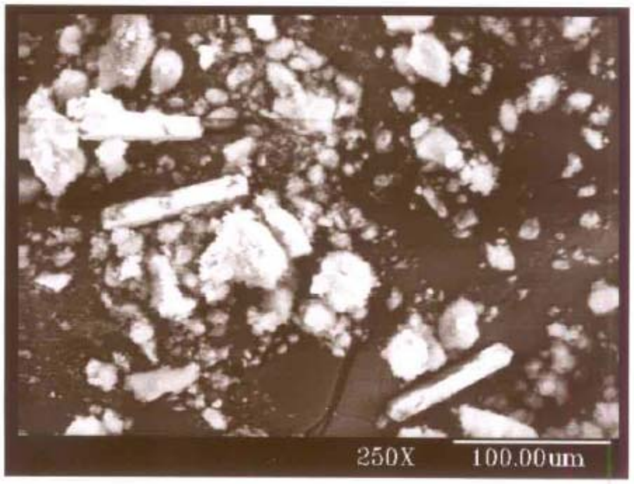
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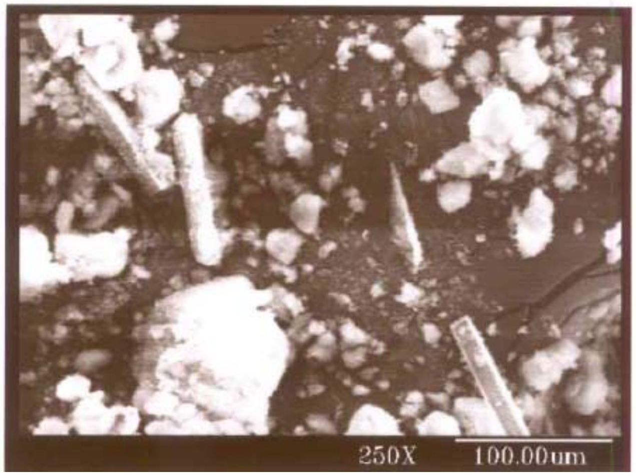
250X
100.00um