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TREATMENT OF METHYL *TERT*-BUTYL ETHER IN METEA
SOIL USING FENTON'S REAGENT

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TREATMENT OF METHYL *TERT*-BUTYL ETHER IN METEA SOIL USING FENTON'S REAGENT

By

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ABSTRACT

TREATMENT OF METHYL *TERT*-BUTYL ETHER IN METEA SOIL USING FENTON'S REAGENT

By

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The degradation of methyl *tert*-butyl ether (MTBE) in Metea soil using hydrogen peroxide, with and without the addition of Fe^{2+}, was studied. Greater than 95% of MTBE was degraded when the concentration of hydrogen peroxide added was 30,000 mg/L or greater, under conditions where Fe^{2+} was not added to the reaction mixture. The average initial MTBE concentration in the soil was 15.9 mg/L, the initial pH was between 2 and 3, and the reaction time was two hours. When Fe^{2+} was added to the soil, greater than 99% removal of MTBE was obtained when the concentration of Fe^{2+} added was between 4 and 20 mM. The average initial concentration of MTBE in the soil in this case was 15.6 mg/L, the H_2O_2 concentration was 15 mM, the initial pH was between 2 and 3, and the reaction time was 120 minutes.

Although MTBE was almost completely degraded using this technology, the formation of higher and lower molecular weight byproducts was observed when no Fe^{2+} was added to the system. The presence of higher molecular weight compounds was possibly due to dimer formation. The lower molecular weight byproducts were tentatively identified as propionaldehyde and acetone. When Fe^{2+} was added to the system, only lower molecular weight byproducts were formed, which were tentatively identified as formaldehyde, propionaldehyde, and acetone.

To Ashok, Bharati, Sharmila, Sunil and Pradeep

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Background

Methyl *tert*-butyl ether (MTBE) is a synthetic compound, which is manufactured by the chemical reaction between methanol and isobutylene. MTBE is added to gasoline with the intent of lowering air pollution emissions by making the fuel burn cleaner. It has been used in the United States since 1979 as a replacement for lead as an octane enhancer in concentrations as high as 8% by volume in mid- and high-grade gasoline. It has also been used as a fuel oxygenate at higher concentrations (11 to 15% by volume) because it increases the combustion efficiency of gasoline by reducing the amount of harmful emissions, such as carbon monoxide and ozone, which are direct or indirect products of incomplete fuel combustion (USEPA MTBE Fact Sheet # 2, 1998; Jacobs et al., 2001).

However, the use of MTBE as a fuel additive has created one of the most widespread environmental problems of the late twentieth century. MTBE is highly soluble in water, and has been found in groundwater at over 250,000 contaminated sites throughout the US as of 2000 (Jacobs et al., 2001).

Sources of MTBE in soil and groundwater arise from leaking underground gasoline storage tanks, pipelines, gasoline spills, run-off, and precipitation. The major source of MTBE contamination originates from leaking underground storage tanks (USTs).

1.2 Oxygenate Requirements of the Clean Air Act

The Clean Air Act Amendments of 1990 (CAA) requires the use of oxygenated gasoline in areas with high levels of air pollution. Although the CAA does not specify MTBE, most refiners chose to use MTBE due to its blending properties and for economical reasons (USEPA, MTBE, Gasoline, 2003).

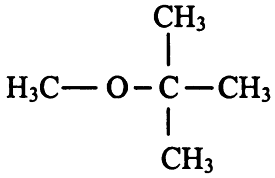
The two oxygenated gasoline programs are:

1. **Winter Oxyfuel Program:** This program was implemented in 1992, and requires that the gasoline sold in cities that have elevated levels of carbon monoxide during cold months contain 2.7% oxygen by weight. The primary oxygenate used in this program is ethanol (USEPA, MTBE, Gasoline, 2003).

2. **Year-round Reformulated Gasoline Program:** This program was implemented in 1995, and requires the use of reformulated gasoline (RFG) year-round in cities that have high levels of ground-level ozone. RFG is oxygenated gasoline that contains a minimum of 2% oxygen by weight and is specially blended to have fewer polluting compounds than conventional gasoline. As of 2003, 30% of the gasoline sold in the United States was RFG, out of which about 87% contained MTBE (USEPA, MTBE, Gasoline, 2003).

1.3 Physical and Chemical Properties of MTBE

MTBE is an -ether with a chemical formula of $C_5H_{12}O$ and the following structure (Howard, 1993):



$$H_3C{-}O{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}CH_3$$

The physical and chemical properties of MTBE are summarized in the following table:

Table 1-1. Physical and chemical properties of MTBE

CAS Registry Number [a]	634-04-4
Boiling Point (°C) [a]	55.2
Melting Point (°C) [a]	-109
Molecular Mass (g/mole) [a]	88.15
Water Solubility (mg/L) at 25 °C [a]	51,000
Vapor Pressure (mm Hg) at 25 °C [a]	249
Henry's Law Constant [b]	0.022
Log Octanol/Water Partition Coefficient [a]	1.24
Diffusivity in air (cm^2/s) [c]	0.0792
Diffusivity in water (cm^2/s) [c]	9.41×10^{-5}

[a] Howard, 1993; [b] Kinner, 2001; [c] MT DEQ, 2003

At standard temperature (25°C) and pressure (760 mm Hg), MTBE is a colorless and flammable liquid (Jacobs et al. 2001).

This aliphatic ether is highly soluble in water (51,000 mg/l) due to its hydrophilic nature. MTBE also has a low octanol-water partition coefficient (log $K_{OW} = 1.24$).

1.4 Fate and Transport of MTBE in Soil

The physical and chemical characteristics of MTBE determine its fate and transport in the environment. When MTBE is spilled on the surface of the soil, it volatilizes readily. Due to it high water solubility, MTBE does not readily sorb to soil or rocks. In the case of a petroleum release in soil, MTBE and BTEX are co-dissolved at first. However, since MTBE does not sorb to soil in aquifer systems, it moves readily with the groundwater, which results in considerable separation of these hydrocarbons (Douglas et al., 2002). The mobility of a contaminant in groundwater is expressed as a ratio of groundwater velocity to the contaminant's velocity and is termed as Retardation Factor. For MTBE, the retardation factor is approximately equal to 1, indicating that MTBE would move at approximately the same velocity as the groundwater in which it is dissolved (USEPA MTBE Fact Sheet # 2, 1998; Kinner, 2001).

Once MTBE volatilizes into the air, it may undergo degradation in the presence of UV light (Kinner, 2001). It has been found that MTBE is unstable in the atmosphere. Atmospheric water droplets (rain, clouds, and fog) contain hydrogen peroxide and iron ions, which, in the presence of UV radiation, react to form ·OH, a strong oxidizing agent (Guillard et al, 2003). MTBE can also be removed from the atmosphere by its dissolution into rainwater. After the rainwater falls to the ground surface, MTBE will infiltrate into the ground or flow over impervious surfaces such as roadways, potentially contaminating the ground water or being discharged into surface water (Kinner, 2001).

1.5 Regulatory Standards

The United States Environmental Protection Agency (USEPA) has not set a national drinking water standard for MTBE, although some states have defined their own limits. MTBE is on the Candidate Contaminant List and USEPA is considering setting regulatory standards for it. The potential health effects and occurrence of MTBE are under study by the USEPA, other government organizations, and academic institutions (USEPA, MTBE, Drinking Water, 2003).

The U.S. Environmental Protection Agency (EPA) Office of Water has issued an Advisory on methyl *tert*-butyl ether in drinking water. This advisory states that keeping MTBE concentrations in the range of 20 to 40 μg/L of water or below will avert unpleasant taste and odor effects in drinking water. Since these concentrations are approximately 20,000 to 100,000 times lower than the range of exposure levels that caused cancer and non-cancer effects in rodents, this taste and odor threshold would also protect consumers from potential health effects (USEPA, Drinking Water Advisory, 1997).

MTBE is regulated drinking water contaminant in California with a primary maximum contaminant level (MCL) of 13 μg/L, effective May 2000. The public health goal for

MTBE in California is also 13 μg/L. It also has a secondary MCL of 5 μg/L, which addresses taste and odor thresholds.

Several other states have set guidelines for MTBE in drinking water supplies. These guidelines have been summarized Table 1-2.

Table 1-2. Guidelines for MTBE in drinking water in various states

State	Guidelines (μg/L)	Basis
Arizona [a]	35	Health-based guideline
California [a]	5 13	Secondary MCL Proposed Primary MCL
Connecticut [a]	100	Guideline
Florida [a]	50	Drinking water standard
Massachusetts [a]	70	Proposed guideline
Michigan [b]	240 40	Health-based guideline Drinking water guideline
New Hampshire [a]	100	Guideline
New Jersey [a]	70	Health-based MCL
New York [a]	50	MCL
Rhode Island [a]	50	Guideline
Vermont [a]	40	Drinking Water Standard

[a] Douglas et al, 2002; [b] MDA, 2002

1.6 Toxicity Effects

Since the introduction of MTBE to oxygenated fuel in the United States, acute health system complaints such as headaches, nausea, dizziness, and breathing difficulties, have been reported nationwide. However, existing studies of acute health risks of MTBE do not support these claims (Jacobs et al., 2001).

No studies have been conducted on MTBE's carcinogenic effects on humans, but studies indicate that MTBE is carcinogenic to rats and mice. Research animals exposed by inhalation to high concentrations of MTBE developed cancerous or non-cancerous effects. USEPA's Office of Water has concluded that there does not exist sufficient available data to estimate the potential health risks of MTBE at low exposure levels in drinking water. However, the current data supports the conclusion that MTBE is a potential human carcinogen at high doses (USEPA, MTBE, Drinking Water, 2003).

However, little or no data exists for the reproductive, developmental, genotoxic, and carcinogenic effects of MTBE on humans. More studies are needed to determine the cancer and non-cancerous effects of MTBE on humans (Jacobs et al, 2001).

1.7 MTBE in the Michigan Environment

The presence of fuel oxygenates is tested in each official sample obtained under the State's Motor Fuels Quality Program. The Michigan Department of Agriculture obtains approximately 1800 samples in response to complaints and routine investigation and monitoring. Oxygenates, such as MTBE, that are present in excess of 1% in fuel are recorded on the test report of the sample (MDA, 2002).

In Fiscal Years 1994 and 1995, 1% or higher concentrations of MTBE were present in 40% of all samples. This percentage dropped through subsequent years until it reached 13% in Fiscal Year 1998. This drop was attributed to economic factors, cost and availability of MTBE. In 2000, 13% of all samples contained MTBE, with an average concentration of 3%. Based on Michigan's 4.8 billion-gallon consumption of gasoline, this amounted to 4,320,000 gallons of MTBE. In 2001, 17% of all samples tested contained MTBE, with an average concentration of 4.75% (MDA, 2002).

In Michigan, the health-based clean up level for MTBE for residential use is 240 ppb (MDA, 2002). Water sources contaminated with MTBE become unsuitable for human consumption due to its turpentine-like taste and odor (Jacobs, 2001). The Michigan Department of Environmental Quality (MDEQ) has established an aesthetic drinking water concentration, protective of taste and odor thresholds, of 40 ppb for MTBE. Since the health-based criterion is much higher than the aesthetic-criteria, a person should thus taste or smell MTBE before it poses a health risk. Several of Michigan's lakes and rivers have been analyzed for the presence of MTBE by the MDEQ Surface Water Quality Division. MTBE has not been detected in any of these samples (MDA, 2002).

The total number of Underground Storage Tanks reported by the Waste and Hazardous Materials Division, MDEQ, as of December 31, 2003 was equal to 86,525. The number of facilities out of these was reported to be equal to 25,705. The number of confirmed releases with MTBE groundwater impacts greater than or equal to 40 ppb, have been reported to be 678 as of April 2003 (Storage Tank Information Database, 2004, MDEQ).

1.8 Remediation Strategies for MTBE

Treatment technologies for MTBE remediation in soil include excavating the soil, soil vapor extraction, Fenton's reagent and Advanced Oxidation Processes (AOPs).

Excavation is reasonably successful to depths of about 20 to 30 feet, the practical limit equipment such as backhoes and excavators can reach. After the soil is excavated, on-site treatment may be achieved using low temperature thermal desorption. The drawbacks of this technique are high transportation costs if the MTBE contaminated soil has to be transported off-site for treatment and major site disruption (Jacobs et al., 2001).

Soil vapor extraction, an in-situ technology, removes volatile contaminants from the soil in the unsaturated zone above the groundwater by drawing out the contaminant vapors with a vacuum applied to the subsurface (USEPA MTBE Fact Sheet #2, 1998; Jacobs et al., 2001). When excavation together with soil vapor extraction was applied to a contaminated site located at North Tahoe P.U.D. Maintenance (National Avenue), Lake Tahoe, CA, it was observed that the MTBE concentration dropped form 40 μg/L to non-detectable (MTBE Treatment Profiles, 2003).

Biodegradation methods for soil treatment are not recommended for treating MTBE because it is considered recalcitrant to biodegradation USEPA MTBE Fact Sheet #2, 1998; Jacobs et al., 2001). In experiments conducted by Yeh and Novak (1995), it was observed that MTBE was not biodegraded in over 100 days. Due to the high solubility and mobility of MTBE in groundwater, it is recommended to treat MTBE at the source, i.e., while it is still in the soil.

Using activated carbon is not considered a good alternative for the treatment of MTBE since its high solubility in water limits adsorption onto activated carbon (Anderson, 2000). In studies conducted by Anderson (2000), he observed that only 52% removal of MTBE was obtained for an initial solution concentration of 100 μg/L. The low affinity of MTBE towards granular activated carbon makes this process undesirable and expensive. Advanced Oxidation Processes (AOPs) provide a promising alternative technique for the treatment of MTBE. These processes depend on the generation of the highly reactive hydroxyl radical that reacts with most organic compounds (Jacobs et al., 2001). The relative oxidizing power of the hydroxyl radical from Fenton's Reagent, which is a combination of H_2O_2 and Fe^{2+}, is 2.06, with Cl_2 being assigned a value of 1.0. The oxidizing power of $\cdot OH$ is only second to fluorine, which has a value of 2.23 (Jacobs et al., 2001).

Fenton's Reagent is one such Advanced Oxidation Process, where the $\cdot OH$ radical is produced as a result of reaction between H_2O_2 and Fe^{2+}. Fenton's Reagent has been documented as an effective treatment technology for the oxidation of MTBE (Ray and Selvakumar, 2000; Kealey et al, 2001; Burbano et al., 2003; Xu et al. 2004).

Ray and Selvakumar (2000) studied the removal of MTBE from water using Fenton's Reagent. They observed that although complete mineralization of MTBE was not achieved, greater than 99% degradation of MTBE was accomplished after one hour contact time using a H_2O_2: Fe^{2+} ratio of 1:1. The major byproducts obtained in their study were *tert*-butyl alcohol, *tert*-butyl formate, and acetone. Small quantities of isobutene were also detected. The pH of the mixture dropped form about 5 to 3 after one-hour contact time, which may have occurred due to the formation of organic acids. Mass balances for two tests, which gave MTBE removal percentages of approximately 99% each at H_2O_2: Fe^{2+} ratios of 1:1 and 6:1 respectively, were conducted as input of MTBE and output of products (calculated as carbon). Approximately 80% and 60% of the product could not be accounted for with H_2O_2: Fe^{2+} ratios of 1:1 and 6:1 respectively, which was attributed to the formation of some volatile products that escaped the reaction system, or the generation of certain non-volatile organics.

Xu et al. (2004) investigated the remediation of MTBE using Fenton's Reagent in aqueous solution. They observed that, under optimum conditions of 15 mM H_2O_2, 2 mM Fe^{2+}, pH 2.8, and at room temperature, 99% degradation of 1mM MTBE solution was achieved in 120 minutes. They hypothesize that the degradation of MTBE followed a two-stage reaction. In the first stage, MTBE degrades swiftly based on a Fe^{2+}/H_2O_2 reaction. During the second stage, which was the Fe^{3+}/H_2O_2 stage, the degradation of MTBE is less rapid. The primary intermediates and byproducts identified in their study were *tert*-butyl formate, *tert*-butyl alcohol, methyl acetate, and acetone.

In experiments conducted by Burbano et al. (2003), the effect of H_2O_2: Fe^{2+} molar ratio on the extent of degradation of MTBE was studied in water at a pH of 3. They discovered that 99% degradation of MTBE was observed when the Fe^{2+}: H_2O_2 ratio was 1:1. The degradation of MTBE decreased when the Fe^{2+}: H_2O_2 ratio was changed to values greater than or smaller than 1.0. Their results showed that for ratios of 1.0, 2.0, 5.0, and 10.0, the maximum difference in percent MTBE transformation was approximately 8%. However, experiments with lower ratios of 0.5:1 and 0.75:1 showed significant differences. The

MTBE transformation was only 63.6% when a molar ratio of 0.5:1 was used. The MTBE degradation increased to 84.9% when the ratio of Fe^{2+}: H_2O_2 was 0.75:1. They deduced that an excess of H_2O_2 would promote the formation of hydroperoxyl radicals ($HO_2\cdot$), which would favor the consumption of $OH\cdot$ (refer reaction 2-6), whereas a lower concentration of H_2O_2 would limit the Fenton's reaction.

The Terra Vac Corporation, (2002) utilized the OxyVac Technology on a site contaminated with BTEX (Benzene, Toluene, Ethyl benzene, and Xylene) and MTBE from a gasoline spill in Concord, Massachusetts. This technology is patented by the Terra Vac Corporation, which utilizes in-situ chemical oxidation combined with soil vapor extraction for the remediation of volatile and semi-volatile compounds. Fenton's Reagent was used to remediate the contamination at this site. The site dimensions were approximately 200 ft x 200 ft. The soil and groundwater were treated using Fenton's reagent based on results from a bench-scale study. The system consisted of 20 injection points and 5 soil vapor extraction wells. 10% H_2O_2 and 5% $FeSO_4$ solutions were periodically injected. Eight applications, amounting to approximately 1600 gallons of H_2O_2 solution, were made over a one-year period. Groundwater monitoring results from two wells showed reductions in MTBE concentrations from 964 μg/L to 64 μg/L (93% reduction), and from 3400 μg/L to 61 μg/L (98% reduction), respectively. As of January 2002, only one monitoring well remained with an MTBE concentration greater than the clean up criteria of 70 μg/L (MTBE Treatment Profiles, 2002)

The goal of the current study is to study the feasibility of the oxidation of MTBE in soil using Fenton's reagent with an attempt to understand how pH, concentrations of H_2O_2 and Fe^{2+}, and the ratio of H_2O_2: Fe^{2+} would effect the degradation of MTBE. The experiments conducted in this study have been designed specifically to control volatilization losses that may occur from the MTBE or its byproducts that are formed during the reactions, thus giving accurate information about treatment efficiencies. These experiments would also prove valuable for the detection and quantification of the byproducts formed, since volatilization losses were minimized. The experiments were also planned in a manner such that they were completely safe to conduct in the lab. We have also made an effort to characterize the possible byproducts of MTBE using hydrogen peroxide and Fenton's Reagent.

CHAPTER 2

REACTION MECHANISM AND BYPRODUCTS

2.1 Chemistry of Hydrogen Peroxide Reactions

Hydrogen peroxide reacts with both Fe^{2+} and Fe^{3+}. Fenton's reaction, which takes place between Fe (II) and H_2O_2 (Barb et al., 1951; Walling, 1975), generates •OH, a very reactive oxidant (Reaction 2-1) (Pignatello, 1992). This •OH may be scavenged by reacting with another Fe^{2+} (Reaction 2-2) or may react with an organic compound (Pignatello, 1992; Xu et al., 2004).

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + HO^- + \cdot OH \qquad (2\text{-}1)$$

$$\cdot OH + Fe^{2+} \longrightarrow Fe^{3+} + HO^- \qquad (2\text{-}2)$$

$$\cdot OH + \text{Organic} \longrightarrow \text{Products} \qquad (2\text{-}3)$$

The chain radical mechanism for the reaction of Fe^{3+} (aq) systems is as follows (Barb, 1951; Walling, 1975):

$$H_2O_2 + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + HO_2\cdot \qquad (2\text{-}4)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^- + HO\cdot \qquad (2\text{-}5)$$

$$\cdot OH + H_2O_2 \longrightarrow H_2O + HO_2\cdot \qquad (2\text{-}6)$$

$$HO_2\cdot + Fe^{3+} \longrightarrow H^+ + O_2 + Fe^{2+} \qquad (2\text{-}7)$$

$$HO_2\cdot + Fe^{2+} \longrightarrow HO_2^- + Fe^{3+} \qquad (2\text{-}8)$$

Reactions (2-4) and (2-7) are complex and pH dependent, due to the following equilibria:

$$Fe^{3+} + H_2O_2 \longleftrightarrow H^+ + FeOOH^{2+} \longrightarrow Fe^{2+} + HO_2\cdot \qquad (2\text{-}9)$$

In the presence of excess peroxide, the concentration of Fe^{2+} is much less than that of Fe^{3+} since the rate of decomposition of hydrogen peroxide by ferric ion is slower than that by ferrous ion (Barb, 1951). Reaction (2-6) is another mechanism for hydroxyl radical scavenging (Pignatello, 1992).

2.2 Degradation Products of MTBE by Fenton's Reagent

The two characteristic features of MTBE are its ether linkage and the tertiary carbon atom. The initial attack by the ·OH radical can take place either at the methoxy group or any of the three equivalent methyl groups leading to carbon-centered radicals (Stefan et al, 2000; Xu et al., 2004).

This has been illustrated in the following reactions (Stefan et al, 2000; Xu et al., 2004):

$$(CH_3)_3C\text{-}OCH_3 + \cdot OH \longrightarrow (CH_3)_3C\text{-}OCH_2\cdot + H_2O \qquad (2\text{-}10)$$

$$CH_3OC(CH_3)_2CH_3 + \cdot OH \longrightarrow CH_3OC(CH_3)_2CH_2\cdot + H_2O \qquad (2\text{-}11)$$

The ·OH radical is an electrophile, and the C-H bonds adjacent to the oxygen are responsible for a pronounced stereoelectronic effect that produces high rates of H-atom abstraction. As a result, the H atoms of the methoxy group are more likely to be attacked by the ·OH radical (Stefan et al, 2000; Xu et al., 2004). This has been depicted in Figure 2-1 as Route A.

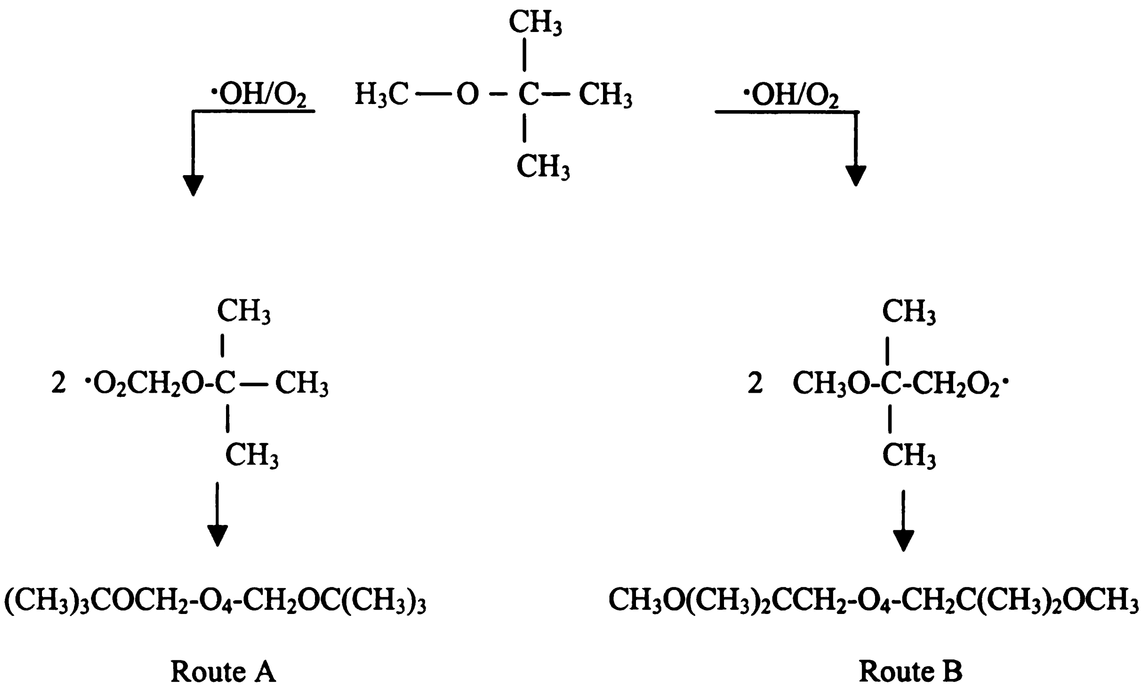


Figure 2-1. Mechanism of MTBE degradation by ·OH radical (Stefan et al., 2000; Xu et al., 2004)

The tetraoxides formed in Routes A and B are generated due to self-termination reactions of the corresponding peroxyl radicals (Stefan et al., 2000; Xu et al., 2004). These tetraoxides undergo further reactions to give several products as shown in figures 2-2 and 2-3.

$$(CH_3)_3COCH_2\text{-}O_4\text{-}CH_2OC(CH_3)_3$$

$$\downarrow$$

$$HCHO$$

$$CH_3COCH_3$$

$$(H_3C)_3COCHO$$

$$(H_3C)_3COH$$

$$(H_3C)_3CO_2C(CH_3)_3$$

$$(CH_3)_3COCH_2OH$$

Figure 2-2. MTBE degradation products obtained from Route A (Stefan et al., 2000)

$$CH_3O(CH_3)_2CCH_2\text{-}O_4\text{-}CH_2C(CH_3)_2OCH_3$$

$$\Big\downarrow$$

$$CH_3O(CH_3)_2CCHO$$

$$CH_3O(CH3)_2CCH_2OH$$

$$HCHO$$

$$CH_3COOCH_3$$

$$CH_3COCH_3$$

$$(H_3C)_3COH$$

$$CH_3O(CH_3)_2COH$$

Figure 2-3. MTBE degradation products obtained from Route B (Stefan et al., 2000)

In earlier studies conducted on MTBE, several different products and intermediates have been identified. Experiments were conducted by Xu et al., (2004), for an initial MTBE concentration of 1 mM, Fe^{2+} concentration of 2 mM, hydrogen peroxide concentration of 15 mM at a pH of 2.8 for a reaction time of 420 minutes. The intermediates and by-products of MTBE using Fenton's Reagent were identified as *tert*-butyl formate (TBF), *tert*-butyl alcohol (TBA), methyl acetate (MA), and acetone. The reactions were carried out in graduated and plugged test tubes at room temperature of 21 ± 1 °C. No carbon balance for the initial and final organic compounds was conducted. The addition of Fe^{2+} and pH adjustment of the reaction mixture was performed after MTBE was already added to the test tubes. Additionally, the reaction mixture was not chilled before analysis was made. The experiments were not controlled to prevent volatilization of MTBE or it s byproducts due to the reasons listed above. It is thus possible that some byproducts may have escaped due to volatilization losses since no other byproducts were detected during the course of the experiment.

In experiments conducted by Stefan et al. (2000), the initial concentration of MTBE and H_2O_2 were 0.92 and 18.26 mM, respectively. It was observed that the some of the primary reaction products during treatment of MTBE using UV/ H_2O_2 process were *tert*-butyl formate (TBF), *tert*-butyl alcohol (TBA), acetone, methyl acetate, 2-methoxy-2-methyl propionaldehyde (MMP), and formaldehyde, which were obtained during the reaction time of 80 minutes. These may be further oxidized to the corresponding aldehydes and acids. A good carbon balance obtained during the treatment indicated that most of the byproducts had been accurately detected and quantified. They also observed that acetone reaches the highest concentration compared to other early intermediates, suggesting that acetone is comparatively less reactive than other organic compounds towards ·OH radicals and it may be generated from some MTBE byproducts. Formaldehyde reacted very rapidly with the hydroxyl radicals, however, its time profile suggested that it was possibly generated from some of the MTBE byproducts. Other intermediates, such as hydroxy-iso-butyraldehyde, hydroxyacetone, pyruvaldehyde, and some organic acids such as hydroxy-iso-butyric, formic, pyruvic, acetic, and oxalic acid were also detected during the reaction time of 80 minutes. Acetaldehyde, iso-butyraldehyde, glycolic, and glyoxylic acids were detected at concentrations lower than 0.02 mM (Stefan et al., 2002). All organic compounds were eventually mineralized after 80 minutes in this study. As part of this study, the byproducts TBF and TBA were also subjected to treatment using H_2O_2/UV. It was observed that when a 0.92 mM TBF solution was treated with 10 mM H_2O_2, the major primary byproducts obtained were acetone and formaldehyde. Other primary intermediates obtained were formic acid, hydroxy-iso-butyraldehyde, and low levels of TBA. Further byproducts obtained were hydroxyacetone, pyruvaldehyde, hydroxy-iso-butyric, pyruvic, acetic, and oxalic acids. a good carbon balance was obtained during the reaction time of 80 minutes. 0.55 mM TBA solution was treated with 10 mM H_2O_2 solution for 60 minutes, which resulted in complete mineralization. The primary intermediates formed were acetone, formaldehyde, and hydroxy-*iso*-butyraldehyde. Pyruvaldehyde, formic, hydroxy-iso-butyric, pyruvic, acetic, and oxalic acids were formed as a result of further oxidation processes. It should be noted that the pH of the reaction mixture was not adjusted to a value between 2 and 3, as it had been in all other studies considered. This may have lead to different products being formed or effected the rate of the reaction.

Yeh and Novak (1995) studied the effect of hydrogen peroxide on the degradation of MTBE in soils and observed that MTBE was chemically oxidized to tertiary butyl alcohol (TBA) and acetone when hydrogen peroxide was added to soil microcosms that contained aquifer material from an organic rich site. The soil utilized for this study was mainly silty loam and rich in organics. The concentrations of total iron and dissolved oxygen in the groundwater at this site were 7.0 mg/L and 0.4 mg/L, respectively. The aquifer material was obtained from depths of 0, 0.6, 1.2, 2.1, and 3 m. 2 μL of a 30% H_2O_2 solution was added to the soil microcosms every 7 to 10 days.

The approximate values obtained for the initial and final concentrations of MTBE in soil microcosms receiving 2μL of 30% H_2O_2 each week have been summarized in table 2-1.

Table 2-1. Degradation of MTBE in soil microcosms receiving 2 μl of H_2O_2 (Yeh and Novak, 1995)

Experimental Conditions	Initial MTBE Concentration (mg/l)	Final MTBE Concentration (mg/l)
H_2O_2 Added	100	85
H_2O_2 + Nutrients Added	105	55

The degradation of MTBE increased when nutrients were added to the system has been attributed to the impact of a biological phenomenon, rather than a chemical reaction (Yeh and Novak, 1995).

In the work done by Yeh and Novak, 1995, it was observed that soils from 1.2 m and 2.1 m depths exhibited the highest rates of MTBE loss. The approximate values of MTBE degradation rates obtained by Yeh and Novak (1995) at depths of 1.2 m and 2.1 m have been presented in Table 2-2.

Table 2-2. MTBE degradation rates in soil microcosms at depths of 1.2 m and 2.1 m (Yeh and Novak, 1995)

Experimental Conditions	Degradation Rate (mg/l/day·g) Depth = 1.2 m	Degradation Rate (mg/l/day·g) Depth = 2.1 m
H_2O_2 Added	0.025	0.07
H_2O_2 + Nutrients Added	0.08	0.08

The variation in the degradation of MTBE with depth may depend on the depth of the groundwater table, which was approximately 1 m below the surface at this site. This might have enhanced the movement of the hydroxyl radicals and increased the efficiency of the process.

Yeh and Novak, 1995, conducted another set of experiments where the oxidation of MTBE was carried out in aqueous solution without the addition of soil. The experiment was conducted using an initial concentration of MTBE of approximately 80 mg/L, Fe^{2+} concentration of 1 mM, H_2O_2 volume of 2 μL and a pH value of 4.0. The concentration of MTBE was reduced to approximately 30 mg/L. TBA, acetone, and several other unidentified reaction products were obtained (Yeh and Novak, 1995). It is thus possible that when the oxidation of MTBE was carried out in soil, no other byproducts were obtained due to the oxidation of those byproducts by soil microorganisms.

It was also observed that when the initial concentration of Fe^{2+} was 1 mM, the volume of 30% hydrogen peroxide used was 2 μL, and the pH was 4.0, the MTBE oxidized was

0.45 mg and 0.5 mg without and with the addition of nutrients, respectively. Thus, the oxidation of MTBE was not inhibited by the phosphate was present in solution. It was hypothesized that phosphate undergoes reactions in solution such as precipitation, complexation, and adsorption, which reduces the impact of phosphorous on H_2O_2 (Yeh and Novak, 1995).

It was also hypothesized that biological degradation of TBA and acetone, generated during the degradation of MTBE, may deplete the oxygen in the soil, thus creating an environment that would cause iron reduction. The reduced iron would thus catalyze the added hydrogen peroxide to generate hydroxyl radicals. This would lead to an aerobic-anaerobic cycle (Yeh and Novak, 1995). Since MTBE is recalcitrant to biodegradation, this mechanism could be used for remediation of MTBE in groundwater containing iron (Yeh and Novak, 1995).

Ray and Selvakumar, (2000), studied the removal of MTBE from water using Fenton's Reagent. The major byproducts obtained in their study were *tert*-butyl alcohol, *tert*-butyl formate, and acetone. Small quantities of isobutene, and a gas of molecular weight 56, not soluble in water, were also detected but not quantified. The volume of gas produced during this experiment was not quantified. Mass balances for two tests, which gave MTBE removal percentages of approximately 99% each at H_2O_2: Fe^{2+} ratios of 1:1 and 6:1 respectively, were conducted as input of MTBE and output of products (calculated as carbon). The initial MTBE concentrations in these tests were approximately 21.0 mg/L and 17.4 mg/L, respectively, and the initial concentration of a 5% H_2O_2 solution used was

236 mg/L for both these tests. Approximately 80% and 60% of the product was unaccounted for H_2O_2: Fe^{2+} ratios of 1:1 and 6:1 respectively, which was attributed to the formation of some volatile products that escaped the reaction system, or the generation of certain non-volatile organics. These experiments show that certain byproducts that were formed were not identified and quantified during the experiments.

From the above review of several studies conducted on the treatment of MTBE using Fenton's reagent, it is obvious that better techniques and experimental designs are required to ensure that volatilization losses of the parent compound and its byproducts are minimized to efficiently identify and quantify the byproducts formed. This is very essential if this technology is to be adopted for use in the field. It is also possible that the byproducts depend on the ratio of concentration of MTBE and H_2O_2 used, the time of the reaction, and the presence of other organic compounds, such as other contaminants or soil organic matter, that may be present in the system. These conditions should be evaluated and optimum conditions must be developed using bench-scale studies before Fenton's reagent or similar Advanced Oxidation processes are applied in the field.

In the current study, some of the byproducts obtained with and without the addition of soluble Fe^{2+} to the soil system have been discussed in later chapters. However, additional work is recommended for complete identification and quantification of all the byproducts and intermediates formed during the reaction of MTBE with Fenton's Reagent.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Chemicals. Methyl-tert butyl ether (99%) was obtained from Acros Organics. Methanol, Baker analyzed ® HPLC solvent, was used for the preparation of the MTBE stock solution. All dilutions were prepared using distilled deionized water (Ultra Pure Water System, Technic Central Systems). MTBE stock solution (40,000 mg/L) was stored at 4°C for not more than a week.

Soil. Metea soil, which is a low organic content soil, was cleaned of debris, and the soil was screened using a 20-mesh sieve. The sieved soil was then contaminated with MTBE in the lab to achieve a concentration of 50 g MTBE/kg of soil. This soil was placed in a bell jar, which was wrapped with aluminum foil to prevent the photolysis of MTBE, and stored at 4 °C to slow down bacterial degradation and avoid volatilization of MTBE.

The soil characteristics of Metea soil are summarized in Table3-1.

Table 3-1. Soil characteristics of Metea soil [a]

Category	Result	Method [b]
pH	5.43 ± 0.87	Water pH Measurement
Organic Matter (%)	0.4 ± 0.1	Loss on Ignition
Iron (ppm)	2	0.1 N HCl Extraction
Lime Index	71	SMP Buffer Method
Neutralizing Value (%)	13.1	Indicator Titrimetric Method
% Sand	78.9	Bouyoucos Hydrometer
% Silt	12.5	Bouyoucos Hydrometer
% Clay	8.6 ± 0.71	Bouyoucos Hydrometer

[a] Soil tests conducted at Soil and Plant Nutrient Laboratory, Michigan State University

[b] Recommended Chemical Soil Test Procedures for the North Central Region, SB 1001, Revised January, 1998

3.2 Analytical Methods

MTBE was quantified using a Perkin Elmer Headspace Sampler HS 40 equipped with a Perkin Elmer Auto System Gas Chromatograph (GC) and a photo ionization detector (PID). The GC was equipped with a fused silica PE 624 glass capillary column (30 m x 0.53 mm). The oven temperature was programmed at 45 °C for the entire run. The injector and detector temperatures were 200 °C each. The carrier gas flow rate was 19.0 mL/min. The sample temperature for the autosampler was 80 °C. The needle temperature and transfer temperature were both 100 °C. The thermostat time was 25.0 minutes. The pressure was maintained at approximately 25 psi.

Assay and calibration samples were carried out in clear, flat bottom 20 ml headspace vials, which were sealed with 20 mm crimp seal with Teflon® lined rubber septa obtained from National Scientific Company, Duluth, GA. A calibration curve was obtained by diluting the stock solution in double deionized water. The samples vials each contained 5 ml aqueous solution. The calibration curve, which bracketed the concentrations of the test samples, was obtained by running triplicate samples of MTBE solutions at concentrations between 0 and 160 mg/L. The MTBE stock solution was kept chilled in an ice bath throughout the experiment to avoid the volatilization of MTBE. Chromatograms were recorded and the data was assessed using the Turbochrom Navigator software (Perkin Elmer Corp.).

The analysis of the byproducts was conducted using a Perkin Elmer Autosystem gas chromatogram equipped with an ECD, an autosampler, and a DB-5 column (J & W Scientific, Folsom, CA). The oven temperature was programmed to hold for 1 minute at 50°C. The temperature was then programmed to increase to 220°C at a rate of 4 °C/min, and finally increase to 250°C at a rate of 20 °C/min, where it was held for 5 minutes. The injector and detector temperatures were 180 °C and 300 °C, respectively. The carrier flow rate was 1.0 mL/min.

Formaldehyde, propionaldehyde, and acetone were analyzed using USEPA Method 556 with the modification of using MTBE instead of hexane for the extraction (USEPA, Method 556).

CHAPTER 4

TREATMENT OF MTBE USING FENTON'S REAGENT (I)

4.1 Introduction

The use of Fenton's Reagent has been documented as an effective technology for the oxidation of MTBE in contaminated soil and groundwater (Ray and Selvakumar, 2000; Kealey et al., 2001; Burbano et al., 2003; Xu et al., 2004). This current study is an attempt to investigate the oxidation of MTBE using Fenton's Reagent. Fenton's reagent utilizes the oxidation power of the hydroxyl radical, ·OH, which is generated as a result of the reaction between Fe^{2+} and H_2O_2, to degrade organic contaminants. These radicals are very unstable and have a high oxidation potential of 1.9 eV (Burbano et al., 2003). They non-selectively attack organic compounds and initialize oxidation pathways to eventually yield complete degradation pathways of the parent organics (Burbano et al., 2003). The present work considers the degradation of MTBE with and without the addition of soluble iron.

4.2 Materials and Methods

4.2.1 Materials

Hydrogen peroxide (purity, 30%) Baker analyzed ® ACS reagent (Stabilized) was used after dilution. An aqueous solution of 5N solution of sodium thiosulfate (obtained from Sigma) was prepared using distilled deionized water (Ultra Pure Water System, Technic

Central Systems). Reagent water, sterile filtered, was obtained from Sigma-Aldrich Co., and was used for preparing 15% and 3% hydrogen peroxide. Sulfuric acid (with more than 51% acid, Baker Analyzed ® ACS reagent) was used to acidify water and hydrogen peroxide solutions to obtain an initial pH of 1.8 for the reactions. When 4.65 mL of the pH 1.8 solutions was added to 0.2 grams of soil, the final pH was between 2 and 3. The 15% and 3% solutions of hydrogen peroxide were prepared before each reaction. The solution pH was measured using Orion Model SA 720A pH meter. The initial and final pH of the reaction mixture was measured using pH paper.

4.2.2 Experimental Method

To evaluate if the degradation of MTBE occurred in the presence of mineral iron, this set of experiments was conducted without the addition of soluble iron. The oxidation reaction of hydrogen peroxide was carried out in clear, flat bottom 20 mL headspace vials. The pH of the initial reaction mixture was maintained between 2 and 3 for optimum reaction conditions (Pignatello, 1992; Burbano et al., 2003; Xu et al., 2004) by using acidified water and hydrogen peroxide. These headspace vials, containing appropriate volumes of acidified water, were weighed on an analytical balance. An aliquot (0.2 grams) of the contaminated soil, which had been stored at 4 °C, was added to these vials using a spatula. The soil was introduced into the vials gently to reduce agitation, which might drive off volatile compounds, and the vials were then sealed immediately using a Mininert 2-way valve. Only 0.2 g of soil was chosen due to the exothermic nature of the reaction.

The reaction was initiated by adding acidified hydrogen peroxide, which was introduced into these vials via a syringe that could pass through the auxiliary septum of the valve. The final H_2O_2 concentrations in the reaction mixtures were between 60 and 40,000 mg/L (i.e. 1500 mg/kg soil and 1,000,000 mg/kg soil, respectively). 15% H_2O_2 was used for concentrations from 40,000 mg/L (1,000,000 mg/kg) to 15,000 mg/L (375,000 mg/kg). 3% H_2O_2 was used for concentrations from 10,000 mg/L (250,000 mg/kg) to 60 mg/L (1500 mg/kg). Two solutions with different concentrations of hydrogen peroxide were used so that the volume of H_2O_2 added was easily measurable. The volumes of acidified water and the hydrogen peroxide were adjusted so that the final volume of the reaction mixture in the headspace vials was 5 mL. The auxiliary septum of the 2-way valve was immediately sealed after the hydrogen peroxide was introduced. The samples were then mixed for 120 minutes using a Mistral Multi Mixer, Melrose Park, ILL. Rapid bubbling was seen for approximately 10 minutes after the addition of the hydrogen peroxide. As a result, 120 minutes was considered a sufficiently long time for the reaction to take place. After 120 minutes, the reaction was terminated by adding 200 μL of 5N sodium thiosulfate solution (Xu et al., 2004). To get the correct volume of sodium thiosulfate, aliquots of sodium thiosulfate were added gradually until the reaction ceased (as noted by a termination of bubble formation). These vials were then chilled at 4°C for 60 minutes to prevent volatilization losses before analysis. The 2-way valves were then replaced with 20 mm crimp seal with Teflon lined rubber septa, and these samples were then analyzed using the Perkin Elmer Headspace Sampler HS 40 equipped with a Perkin Elmer Auto System Gas Chromatograph (GC) and a photo ionization detector (PID). Chromatograms were read and the data was interpreted using the Turbochrom Navigator software (Perkin Elmer Corp.).

This experiment was conducted three times in triplicate. During the first trial, 15% H_2O_2 was used throughout the experiment and initial results from 60 mg/L (1500 mg/kg soil) to 10,000 mg/L (250000 mg/kg soil) were inaccurate due to experimental error. This series of experiments were then repeated using 15% and 3% hydrogen peroxide. The third set was conducted with a longer run time than the earlier sets to look at the presence of byproducts. The data from the complete second and third sets and half of the first set, from hydrogen peroxide concentrations 10,000 mg/L (250,000 mg/kg soil) to 40,000 mg/L (1,000,000 mg/kg soil) are shown in this chapter. The complete data from the first set is shown in the Appendix. The mean values for each experimental trial are presented in the figure together with vertical error bars indicating the standard deviations.

4.3 Results and Discussion

The initial pH of the reaction mixture was maintained between 2 and 3 (Pignatello, 1992; Burbano et al., 2003; Xu et al., 2004). Xu et al. (2004) found that at pH values greater than 4, the decomposition rate of MTBE decreases due to a reduction in the concentration of free iron species in solution. This could be due to the formation of Fe (II) complexes, which would hinder further reaction between Fe^{2+} and H_2O_2 (Xu et al., 2004). Additionally, at pH greater than 3, retardation of the reaction between MTBE and hydrogen peroxide may occur due to the precipitation of iron oxides such as $Fe_2O_3 \cdot nH_2O$, and $Fe(OH)_3$ (Pignatello, 1992; AMRClearinghouse, 2004). At low pH, the reaction between MTBE and hydrogen peroxide is hindered since at high concentration of H^+, equilibrium would shift towards the left, thus, inhibiting the formation of Fe^{2+} as is seen in reaction (2-9) (Pignatello, 1992).

$$Fe^{3+} + H_2O_2 \longleftrightarrow H^+ + FeOOH^{2+} \longrightarrow Fe^{2+} + HO_2\cdot \qquad (2\text{-}9)$$

Additionally, at very low pH, i.e. at very high concentration of hydrogen ion, H^+ becomes a major hydroxyl radical scavenger. This has been shown in reaction 4-1 (Tang and Huang, 1996). The electrons for this reaction may be obtained from ferrous ions.

$$\cdot OH + H^+ + e^- \longrightarrow H_2O \qquad (4\text{-}1)$$

For this reaction, $k = 7 \times 10^9\ M^{-1}s^{-1}$

4.3.1 Effect of H_2O_2

The only iron present was in the form of mineral iron in the soil, and that amounted to 2 ppm. It was observed that the removal percentage of MTBE increased with an increase in the concentration of the hydrogen peroxide added. This is shown in Figure 4-1.

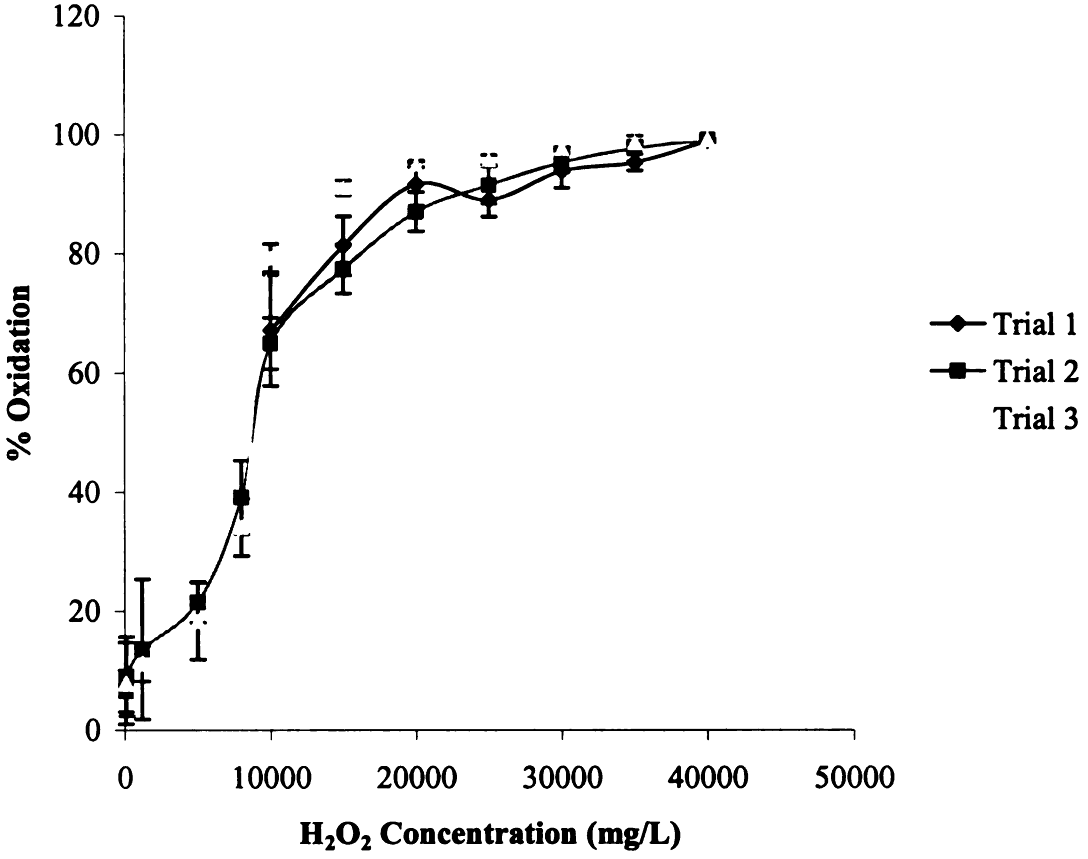


Figure 4-1: Effect of hydrogen peroxide concentration on percent oxidation of MTBE, initial pH = 2-3. Initial concentration of MTBE was between 299.25 and 429.75 mg MTBE/kg soil

The results of Trial 1, 2, and 3 have been shown in Tables 4-1, 4-2, and 4-3. These depict the percent oxidation of MTBE and concentration of MTBE as the concentration of hydrogen peroxide were varied.

Table 4-1. Trial 1. Average initial concentration of MTBE = 429.75 mg/L

H_2O_2 Concentration (mg/L)	H_2O_2 Concentration (mg/kg soil)	% Oxidation ± Standard Deviation	Concentration ± Standard Deviation (mg MTBE/kg soil)
40000	1000000	99.1 ± 0.38	≤ 18.13 ± 1.57
35000	875000	95.4 ± 1.35	33.45 ± 5.63
30000	750000	93.9 ± 2.78	39.57 ± 11.55
25000	625000	89.1 ± 2.82	59.66 ± 11.73
20000	500000	91.7 ± 3.57	48.73 ± 14.84
15000	375000	81.3 ± 4.99	91.79 ± 20.72
10000	250000	67.1 ± 9.32	150.82 ± 38.72

Table 4-2. Trial 2. Average initial concentration of MTBE = 340.25 mg/L

H_2O_2 Concentration (mg/L)	H_2O_2 Concentration (mg/kg soil)	% Oxidation ± Standard Deviation	Concentration ± Standard Deviation (mg MTBE/kg soil)
40000	1000000	≥ 99.3 ± 0.00	ND
35000	875000	97.8 ± 2.16	21.55 ± 4.79
30000	750000	95.4 ± 1.69	28.71 ± 3.39
25000	625000	91.5 ± 3.10	41.75 ± 10.21
20000	500000	87.1 ± 3.28	55.19 ± 6.10
15000	375000	77.5 ± 4.12	87.76 ± 20.21
10000	250000	65.0 ± 4.34	130.07 ± 38.26
8000	200000	39.1 ± 6.19	211.88 ± 39.95
5000	125000	21.5 ± 3.43	268.87 ± 46.10
1200	30000	13.61 ± 11.78	290.47 ± 20.51
120	3000	9.0 ± 6.64	308.41 ± 47.09
60	1500	6.5 ± 3.51	319.40 ± 71.16

ND =Not Detected

Table 4-3. Trial 3. Average initial concentration of MTBE = 419 mg/L

H_2O_2 Concentration (mg/L)	H_2O_2 Concentration (mg/kg soil)	% Oxidation ± Standard Deviation	Concentration ± Standard Deviation (mg MTBE/kg soil)
40000	1000000	≥ 99.3 ± 0.00	ND
35000	875000	98.8 ± 0.29	19.13 ± 1.17
30000	750000	97.8 ± 0.19	23.15 ± 0.78
25000	625000	95.8 ± 0.82	31.28 ± 3.30
20000	500000	95.1 ± 0.55	34.14 ± 2.23
15000	375000	91.1 ± 1.29	50.29 ± 5.22
10000	250000	79.3 ± 2.36	98.00 ± 9.57
8000	200000	34.1 ± 4.83	280.88 ± 19.54
5000	125000	18.3 ± 6.47	344.75 ± 26.18
1200	30000	11.1 ± 2.98	373.74 ± 12.07
60	1500	7.8 ± 6.88	387.03 ± 27.84

ND =Not Detected

As can be see from Figure 4-1, the percent removal of MTBE increases with increasing hydrogen peroxide concentration, with almost complete oxidation of MTBE at an H_2O_2 concentration of 40,000 mg/L (1,000,000 mg/kg soil). The results obtained from all experimental runs are very similar. This would mean that at high concentrations of hydrogen peroxide, nearly complete degradation of MTBE is possible if the initial pH is between 2 and 3, and under similar MTBE: H_2O_2 ratios and soil type used. This can be explained because when hydrogen peroxide is in excess, due to the rapid oxidation of Fe^{2+}, Fenton's reaction often written as '$Fe^{2+} + H_2O_2$', is more accurately represented as Fe^{3+}/H_2O_2. This is often missed in literature. The main oxidant in the reaction is believed to be ·OH (Pignatello, 1992).

Pignatello (1992) investigated the degradation of the herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). He discovered that conversion of the organic contaminant to CO_2 was independent of the Fe oxidation state. In his study, conducted at a pH 2.7-2.8, the concentration of 2, 4-D decreased from 0.1 mM to almost 0.0 mM in less than 20 minutes when the Fe^{3+} concentration used was 1.0 mM and that of hydrogen peroxide was 10 mM. The degradation of 2,4,5-T at a pH of 2.8 was slower, which was possibly due to other competing reactions (Pignatello, 1992). He also discovered that 2,4-D ring mineralization increased from 45 to 69% when the hydrogen peroxide concentration was increased from 10 to 500 mM. This trend is consistent with the present study, where it was also observed that the degradation of MTBE increased with increase in hydrogen peroxide concentration.

In the present study, it was observed that approximately 95% or greater degradation of MTBE was obtained when the concentration of H_2O_2 was 30,000 mg/L (750,000 mg/kg soil) or higher. Additionally, the percent degradation of MTBE was approximately 92% when the H_2O_2 concentration was approximately 588 mM (19,992 mg/L or 499,800 mg/kg soil). It can thus be inferred that the nature and the initial concentration of the contaminant, presence of other organic compounds that may be present on the site play a significant role in deciding the hydrogen peroxide dose for nearly complete oxidation of the contaminant.

4.3.2 Effect of Fe^{3+} on MTBE Degradation in Soil

In the presence of Fe^{2+} and Fe^{3+}, hydrogen peroxide forms highly reactive hydroxyl radicals (•OH), and possibly other reactive species (Pignatello, 1992) (Refer Reactions 2-1 to 2-9).

From the experiments conducted in this study, it can be concluded that in the presence of excess peroxide, nearly complete oxidation of MTBE can be achieved using Fe^{3+}/H_2O_2. In the presence of excess peroxide, the concentration of Fe^{2+} is much smaller than that of Fe^{3+} since the rate of decomposition of hydrogen peroxide by ferric ion is slower than that by ferrous ion (Barb, 1951) (Refer Reactions 2-1 and 2-4).

In studies conducted by Pignatello with hydrogen peroxide, he observed that under initial conditions of [2,4-D] = 0.1mM, [Fe] = 1mM, $[H_2O_2]$ = 10mM, pH = 2.7, the percent ^{14}C in solution for ring-^{14}C-2,4-D vs. was almost identical for both Fe^{3+} and Fe^{2+} except during the first few minutes. He concluded that under conditions of excess peroxide, there seemed to be little or no advantage of using Fe^{2+} over Fe^{3+}.

4.3.3 pH Monitoring for Soils Treated with Hydrogen Peroxide

The pH of the reaction mixture for each of the samples was measured before and after the reaction. As mentioned before, the initial pH of the reaction mixture for each sample was maintained between 2 and 3. It was observed that the final pH of the reaction mixture was between 1 and 2 for samples where the hydrogen peroxide added was between 40,000 mg/L (1,000,000 mg/kg soil) and 10,000 mg/L (250,000 mg/kg soil). The pH increased gradually as the amount of hydrogen peroxide added decreased. The final pH of the reaction mixture for a hydrogen peroxide concentration of 60 mg/L (1500 mg/kg soil) was between 7 and 8. Please refer the Figure 4-4 for pH vs. concentration of H_2O_2 table. The controls contained 0.2g of contaminated soil and acidified water, and their initial pH was also maintained between 2 and 3. The final pH of the controls, to which hydrogen peroxide was not added, was around 7. Table 4-4 depicts variation of pH with hydrogen peroxide concentration.

Table 4-4. Variation of pH with hydrogen peroxide concentration for Trials 1, 2, and 3

H_2O_2 Concentration (mg/L)	H_2O_2 Concentration (mg/kg soil)	pH
40000	1000000	Between 1-2
35000	875000	Between 1-2
30000	750000	Between 1-2
25000	625000	Between 1-2
20000	500000	Between 1-2
15000	375000	Between 1-2
10000	250000	Between 1-2
8000	200000	Between 2-3
5000	125000	Between 3-4
1200	30000	Between 5-6
120	3000	Between 7-8
60	1500	Between 7-8

From this data, it can be deduced that in the presence of excess H_2O_2, the pH of the reaction mixture decreases due to the release of protons as is seen from the Reaction (2-4).

$$H_2O_2 + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + HO_2\cdot \qquad (2\text{-}4)$$

When the concentration of the hydrogen peroxide added is low, the pH of the soil increases. This can be explained based on the fact that the soil used in this study is sandy soil (78.9%), which has a pH of 5.43 ± 0.87. Sandy soil is a poor buffer, and hence does not resist changes in pH. The fact that the final pH of the controls was approximately 7 further supports this theory.

The slightly higher pH of the soil treated with low concentrations of hydrogen peroxide than the controls could be due to the generation of HO^- during reaction (2-1).

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + HO^- + \cdot OH \qquad (2\text{-}1)$$

4.4 Formation of Byproducts

As shown in Figure 4-2, it was observed that at the initial higher concentrations of hydrogen peroxide, higher molecular weight byproducts were formed. It is believed that these byproducts may be dimers formed due to the presence of free radicals such as $\cdot C(CH_3)_3$. The formation of these byproducts did not occur at hydrogen peroxide concentrations lower than 15,000 mg/L (375,000 mg/kg soil).

It was also observed that two lower molecular weight byproducts were formed at nearly all concentrations of hydrogen peroxide added. Based on the retention times of the compounds, these compounds were tentatively identified as propionaldehyde and acetone. The concentration of these byproducts increased with the decrease in the concentration of hydrogen peroxide, and this leads to the conclusion that the reaction is less complete at lower concentrations.

Shown below are several chromatograms with varying concentrations of hydrogen peroxide. No formation of dimers at lower hydrogen peroxide concentrations was observed.

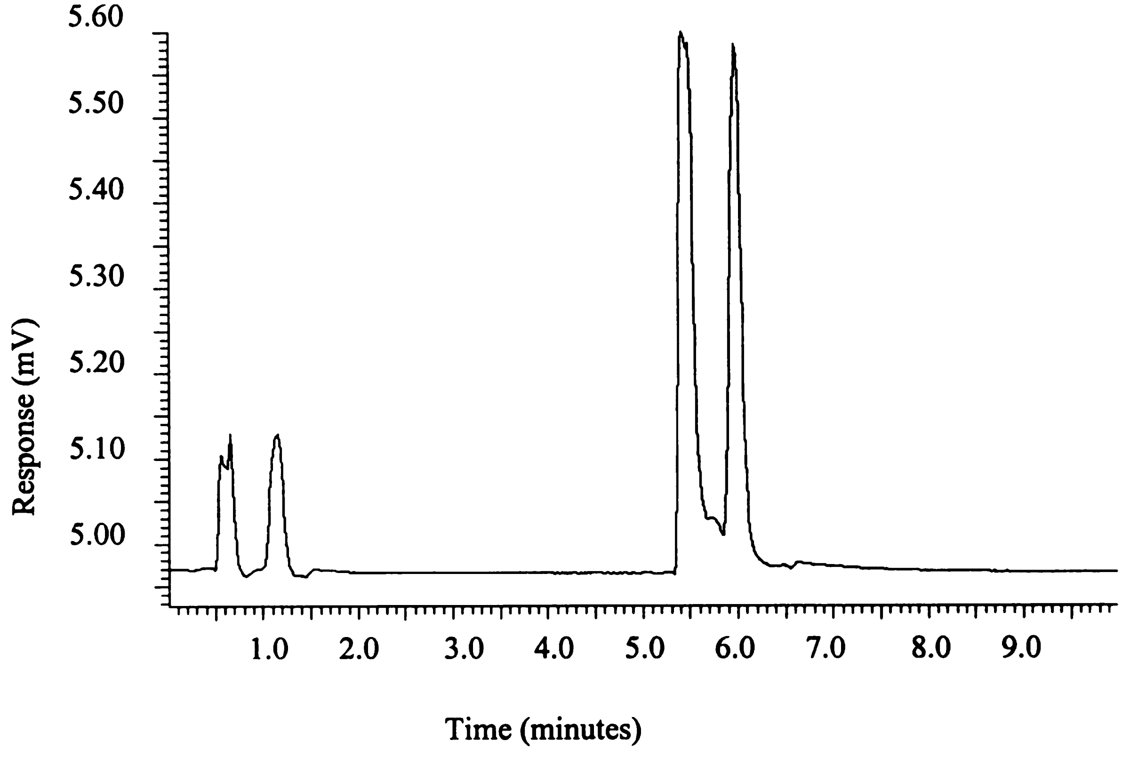


Figure 4-2. Initial [H_2O_2] = 20,000 mg/L (500,000 mg/kg soil), pH = 2-3, no Fe^{2+} added. Chromatogram shows presence of lower molecular weight compounds and dimers

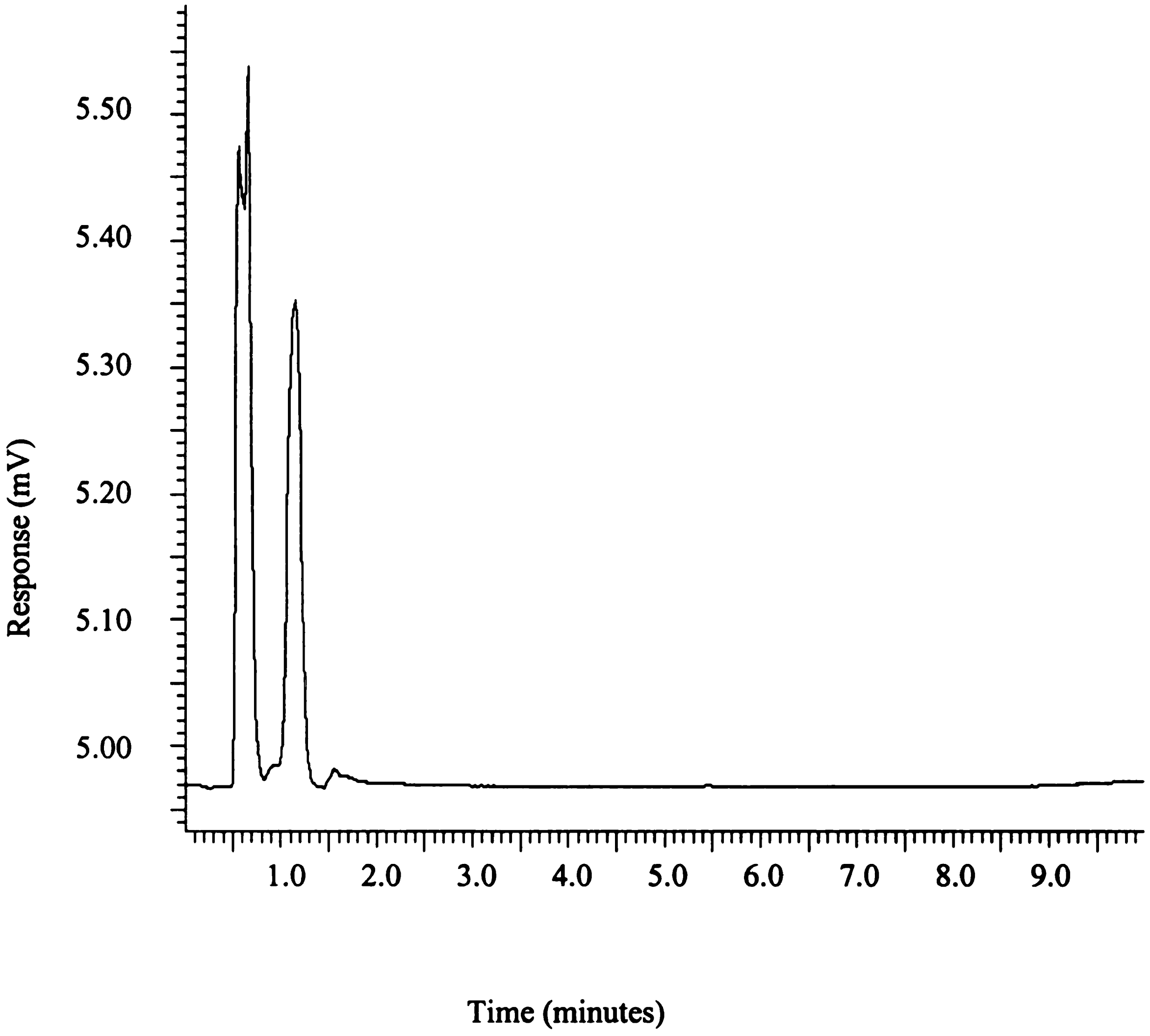


Figure 4-3. **Initial [H_2O_2] = 15,000 mg/L (375,000 mg/kg soil), pH = 2-3, no Fe^{2+} added. Only formation of lower molecular weight compounds was observed**

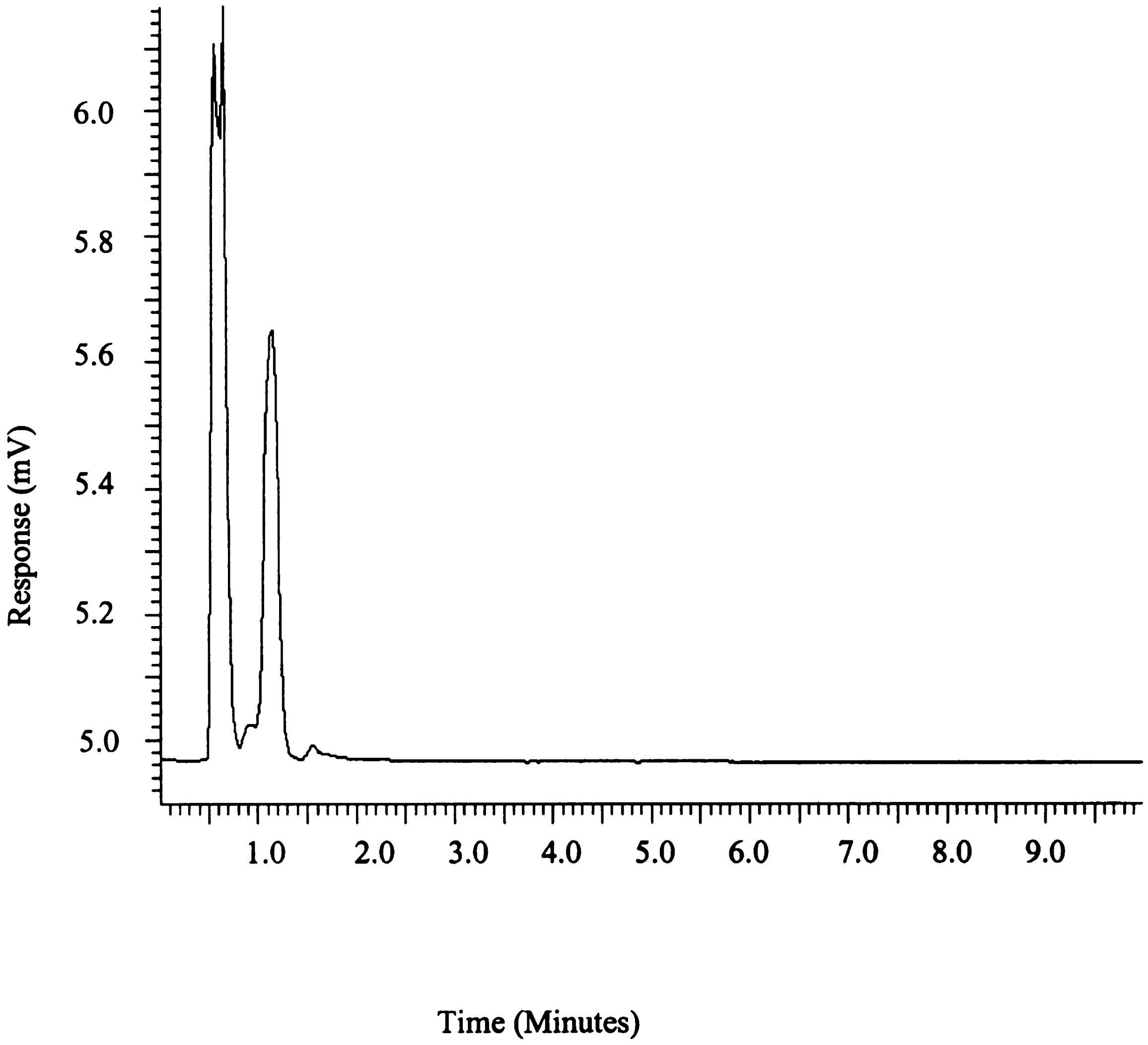


Figure 4-4. Initial [H_2O_2] = 10,000 mg/L (250,000 mg/kg soil), pH = 2-3, no Fe^{2+} added

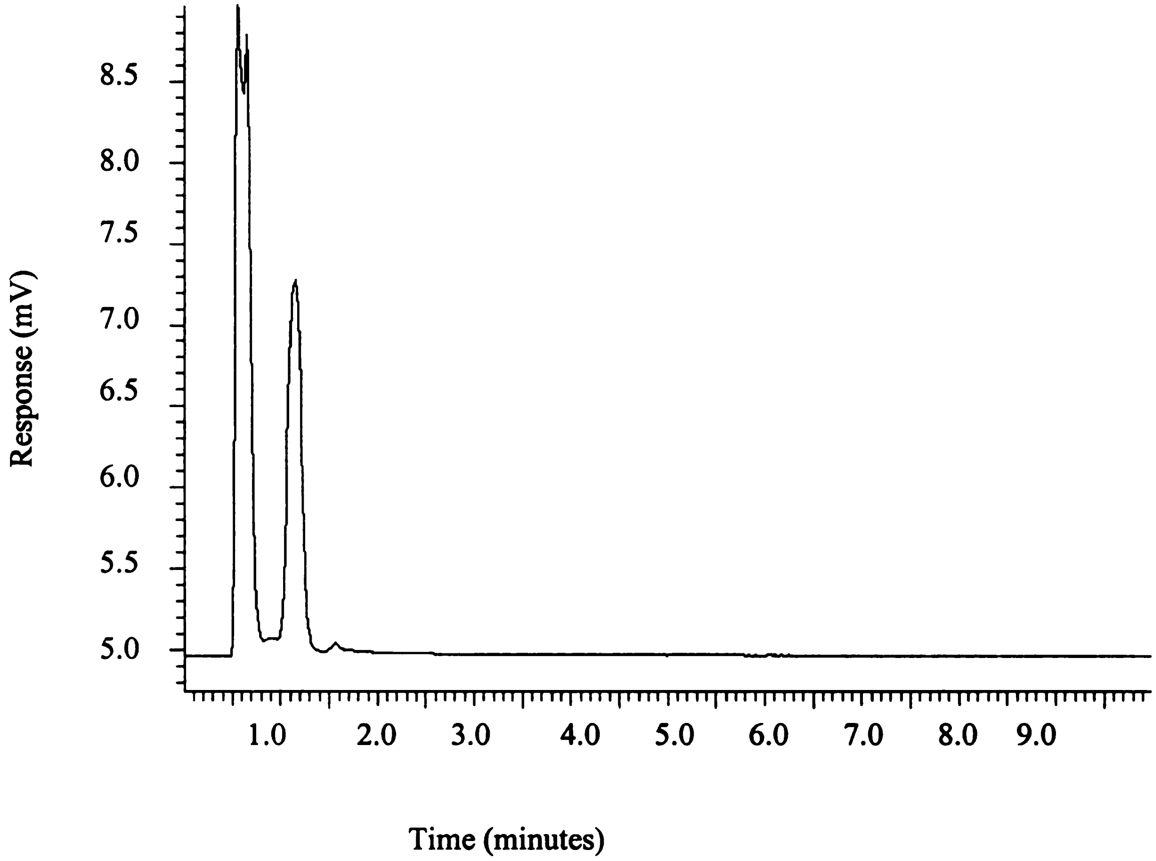


Figure 4-5. **Initial $[H_2O_2]$ = 8000 mg/L (200,000 mg/kg soil), pH = 2-3, no Fe^{2+} added**

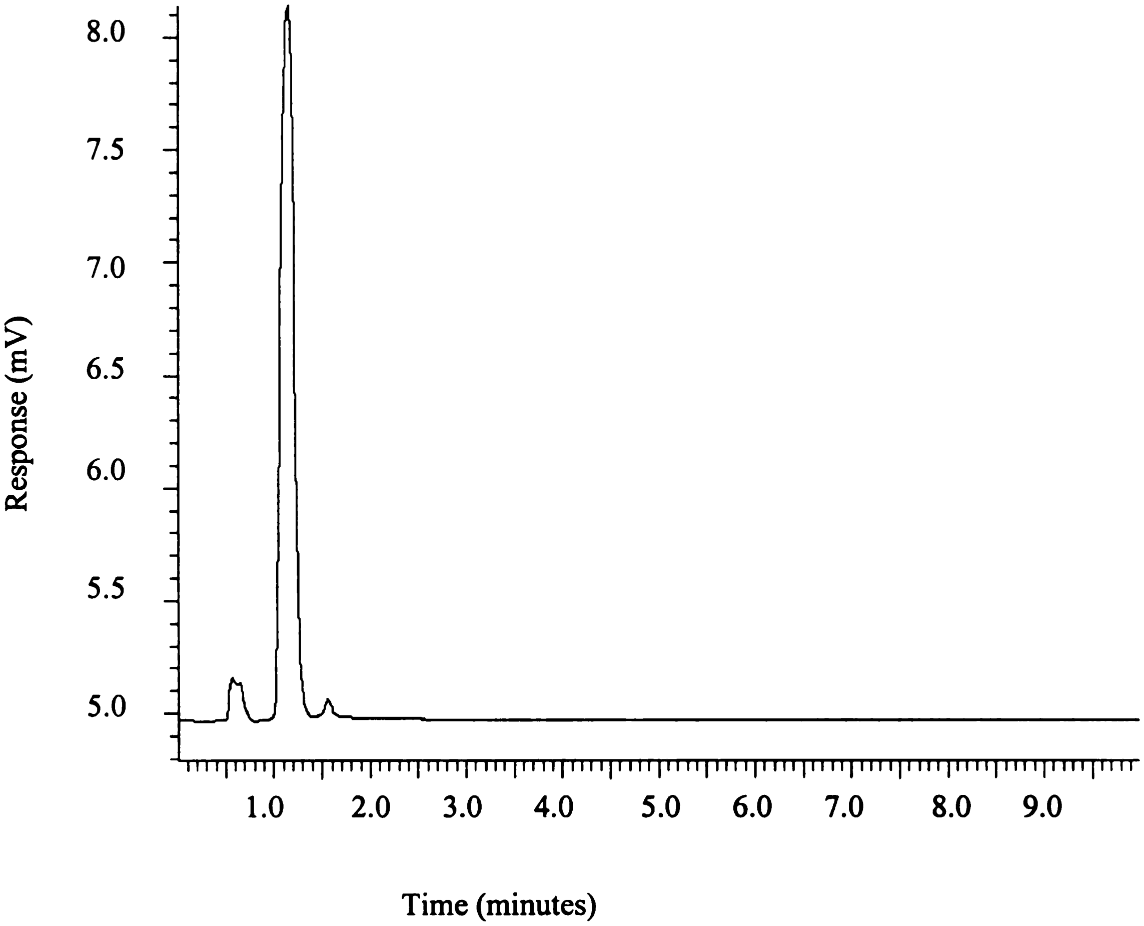


Figure 4-6. Initial [H_2O_2] = 5000 mg/L (125,000 mg/kg soil), pH = 2-3, no Fe^{2+} added

The concentration of the lower molecular weight byproducts decreased when the hydrogen peroxide concentration reached 5000 mg/L (125,000 mg/kg soil). This may have occurred because hydrogen peroxide becomes the limiting reagent at these lower concentrations.

Tables 4-5 and 4-6 depict the percent conversion of MTBE to propionaldehyde and acetone on a molar basis. However, as can be seen from Table 4-7, the total conversion does not add to 100%. Thus, a more complete study of the byproducts needs to be done to identify and quantify all of the byproducts and intermediates.

Table 4-5. Percent conversion of MTBE to propionaldehyde

H_2O_2 Concentration (mg/L)	**H_2O_2 Concentration (mg/kg soil)**	**Initial MTBE concentration (mmoles)**	**Propionaldehyde formed (mmoles)**	**% Conversion to propionaldehyde**
8000	200000	8.82×10^{-4}	1.65×10^{-5}	1.9
10000	250000	8.82×10^{-4}	1.41×10^{-5}	1.6

Table 4-6. Percent conversion of MTBE to acetone

H_2O_2 Concentration (mg/L)	**H_2O_2 Concentration (mg/kg soil)**	**Initial MTBE concentration (mmoles)**	**Acetone formed (mmoles)**	**% Conversion to acetone**
8000	200000	8.82×10^{-4}	1.79×10^{-5}	2.0
10000	250000	8.82×10^{-4}	ND	NA

ND = Not detected, NA = Not applicable

Table 4-7. Total conversion

H_2O_2 Concentration (mg/L)	H_2O_2 Concentration (mg/kg soil)	Initial MTBE concentration (mmoles)	Total conversion to byproducts (%)
8000	200000	$8.82\text{x}10^{-4}$	3.9
10000	250000	$8.82\text{x}10^{-4}$	1.6

4.5 Volatilization Losses

In this current study, Metea soil had initially been contaminated with MTBE at a concentration of 50,000mg/kg in December in the lab. This concentration dropped to approximately 1280 mg MTBE/kg soil in April. The soil finally leveled off to a concentration of approximately 416 mg MTBE/kg soil. These losses have been attributed to volatilization. This proves that MTBE is very volatile in the environment.

In a study conducted by Callender and Davis, they calculated the Henry's constant to be 0.032 at 25°C, indicating that MTBE was more volatile than previously reported, which reported a value of 0.022 at 25°C (Callender and Davis, 2001).

Due to the volatility of MTBE, experiments must be designed so as ensure that losses due to volatilization of MTBE are minimized during the experiments. Only then can one make correct judgments about degradation of MTBE using a particular treatment technology.

It can be concluded that although the oxidation of MTBE is almost complete at high concentrations of hydrogen peroxide, there are byproducts that are formed that must be identified before hydrogen peroxide should be used in the field for the treatment of MTBE. Additionally, these byproducts must be analyzed for their toxicity, and their fate and transport in the environment before this technology is recommended for use in the field for the remediation of MTBE.

CHAPTER 5

TREATMENT OF MTBE USING FENTON'S REAGENT (II)

5.1 Introduction

As was seen in the previous chapter, in the presence of mineral iron and at optimum pH conditions, MTBE was effectively degraded under conditions of excess hydrogen peroxide. Further experiments were conducted by adding Fenton's Reagent, i.e., Fe^{2+} and hydrogen peroxide solution to the MTBE contaminated soil. This chapter discusses the results obtained from these experiments.

5.2 Materials and Methods

5.2.1 Materials

Hydrogen peroxide (purity, 30%) Baker analyzed ® ACS reagent (Stabilized) diluted to 3% using reagent water, sterile filtered, obtained from Sigma-Aldrich Co., was used for the reaction. Aqueous solutions of 0.1M ferrous ammonium sulfate (obtained from Sigma) and 5N solution of sodium thiosulfate (obtained from Sigma) were prepared using double deionized water (Ultra Pure Water System, Technic Central Systems). Sulfuric acid (> 51% acid, Baker Analyzed ® ACS reagent) was used to acidify water, hydrogen peroxide, and ferrous ammonium sulfate solutions to obtain an initial pH of 1.8 for all the solutions. When 4.65 ml of the pH 1.8 solutions was added to 0.2 grams of soil, a final pH of 2-3 resulted. The 3% solution of hydrogen peroxide was prepared fresh before each reaction. The solution pH was measured using Orion Model SA 720A pH meter. The initial and final pH of the soil slurry was measured using pH paper.

5.2.2 Experimental Method

To evaluate if the degradation of MTBE occurred in the presence of soluble ferrous iron catalyzed hydrogen peroxide, this set of experiments was conducted by adding freshly prepared ferrous ammonium sulfate solution, its final concentration between 0.1 mM (140 mg/kg soil) and 50 mM (70,000 mg/kg soil) in the reaction mixture. The oxidation reaction with Fenton's Reagent was carried out in clear, flat bottom 20 ml headspace vials. The pH of the initial reaction mixture was maintained between 2 and 3 for optimum reaction conditions (Pignatello, 1992; Burbano et al., 2003; Xu et al., 2004) by using acidified water, ferrous ammonium sulfate, and hydrogen peroxide. An aliquot (0.2 grams) of the contaminated soil, which had been stored at 4°C, was added to these headspace vials, which already contained appropriate volumes of acidified water and ferrous ammonium sulfate solution, using a spatula. The soil was introduced into the vials gently to reduce agitation, which might drive off volatile compounds, and the vials were then sealed immediately using a Mininert 2-way valve. Only 0.2 g of soil was chosen due to the exothermic nature of the reaction.

The reaction was initiated by adding acidified hydrogen peroxide, which was introduced into these vials via a syringe that could pass through the auxiliary septum of the valve. The concentration of Fe^{2+} in the reaction mixture was varied from 0.1 mM (140 mg/kg soil) to 50 mM (70,000 mg/kg soil). The initial concentration of hydrogen peroxide was kept constant at 510 mg/L (12,750 mg/kg soil) for all samples. 3% H_2O_2 was used for all reactions. The volumes of acidified water, ferrous ammonium sulfate, and the hydrogen peroxide were adjusted so that the final volume of the reaction mixture in the headspace vials was 5 ml. The 2-way valve was immediately sealed after the introduction of the hydrogen peroxide. The samples were mixed for 120 minutes using a Mistral Multi Mixer, Melrose Park, ILL. Rapid bubbling was seen for approximately 10 minutes after the addition of the hydrogen peroxide. As a result, 120 minutes was considered a sufficiently long time for the reaction to take place. After 120 minutes, the residual hydrogen peroxide was quenched using 200 µL of 5N sodium thiosulfate solution (Xu et al., 2004). This volume of sodium thiosulfate was arrived at after several trials of gradually increasing volumes until the reaction finally ceased (as noted by a termination of bubble formation). These vials were then chilled at 4°C for 60 minutes to prevent volatilization losses before analysis. The 2-way valves were then replaced with 20 mm crimp seal with Teflon lined rubber septa, and these samples were then analyzed using the Perkin Elmer Headspace Sampler HS 40 equipped with a Perkin Elmer Auto System Gas Chromatograph (GC) and a photo ionization detector (PID). Chromatograms were read and the data was interpreted using the Turbochrom Navigator software (Perkin Elmer Corp.).

This experiment was conducted in triplicate. The mean values have been presented in the figure together with vertical error bars indicating the standard deviations of the three experiments.

5.3 Results and Discussion

The initial pH of the reaction mixture was maintained between 2 and 3 to ensure optimum conditions (Pignatello, 1992; Burbano et al., 2003; Xu et al., 2004). At pH values greater than 4, the decomposition rate of MTBE decreases due to the reduction in the free iron species in solution. This could be due to the formation of Fe (II) complexes, which would hinder further reaction between Fe^{2+} and H_2O_2 (Xu et al., 2004). Additionally, at pH values greater than 3, retardation of the reaction between MTBE and hydrogen peroxide may occur due to the precipitation of iron oxides such as $Fe_2O_3 \cdot nH_2O$, and $Fe(OH)_3$ (Pignatello, 1992; AMRClearinghouse, 2004). At low pH, the reaction between MTBE and hydrogen peroxide is hindered since at high concentration of H^+, equilibrium would shift towards the left, thus inhibiting the formation of Fe^{2+} as is seen in the Reaction (2-9) (Pignatello, 1992).

$$Fe^{3+} + H_2O_2 \longleftrightarrow H^+ + FeOOH^{2+} \longrightarrow Fe^{2+} + HO_2\cdot \qquad (2\text{-}9)$$

5.3.1 Effect of Fe^{2+} on Degradation of MTBE in Soil

The relative oxidizing power of hydroxyl radical from Fenton's Reagent is 2.06, while that of hydrogen peroxide is 1.31 ($Cl_2 = 1$) (Jacobs et al., 2001). As a result, hydroxyl radicals generated from Fenton's Reagent can non-selectively attack organic compounds and initialize oxidation pathways to eventually yield complete degradation pathways of the parent organics (Burbano et al., 2003).

Fe^{2+} can catalyze the production of $\cdot OH$ from H_2O_2 (Reaction 2-4) (Xu et al., 2004; Barb et al., 1951).

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + HO^- + \cdot OH \qquad (2\text{-}1)$$

Since the concentration of Fe^{2+} influences the production of $\cdot OH$, it has a significant effect on the degradation of MTBE.

In this experiment, the initial concentration of hydrogen peroxide was 510 mg/L (12,750 mg/kg soil), while the initial concentration of Fe^{2+} was varied between 0.1 and 50 mM (i.e., 140 mg/kg soil and 70,000 mg/kg soil, respectively). It was observed that the percent oxidation of MTBE increased abruptly as the concentration of Fe^{2+} in the reaction mixture was increased. The MTBE concentration was below limits of detection for Fe^{2+}/H_2O_2 molar ratios between 0.27 and 1.3. As shown in Figure 5-1, the degradation of MTBE using Fenton's Reagent gradually decreased as the Fe^{2+}/H_2O_2 ratio was increased beyond 1.3.

In studies conducted by Xu et al., 2004, the reactions were carried out at an initial MTBE concentration of 1 mM, hydrogen peroxide concentration of 10 mM and a pH of 2.8. It was observed that the percent of MTBE removal increased as the concentration of Fe^{2+} was increased. The MTBE removal peaked at a Fe^{2+} concentration of 2 mM, where the percent MTBE degradation was approximately 94%. The percent degradation started to decrease beyond this Fe^{2+} concentration. This agrees with the results obtained in the current study.

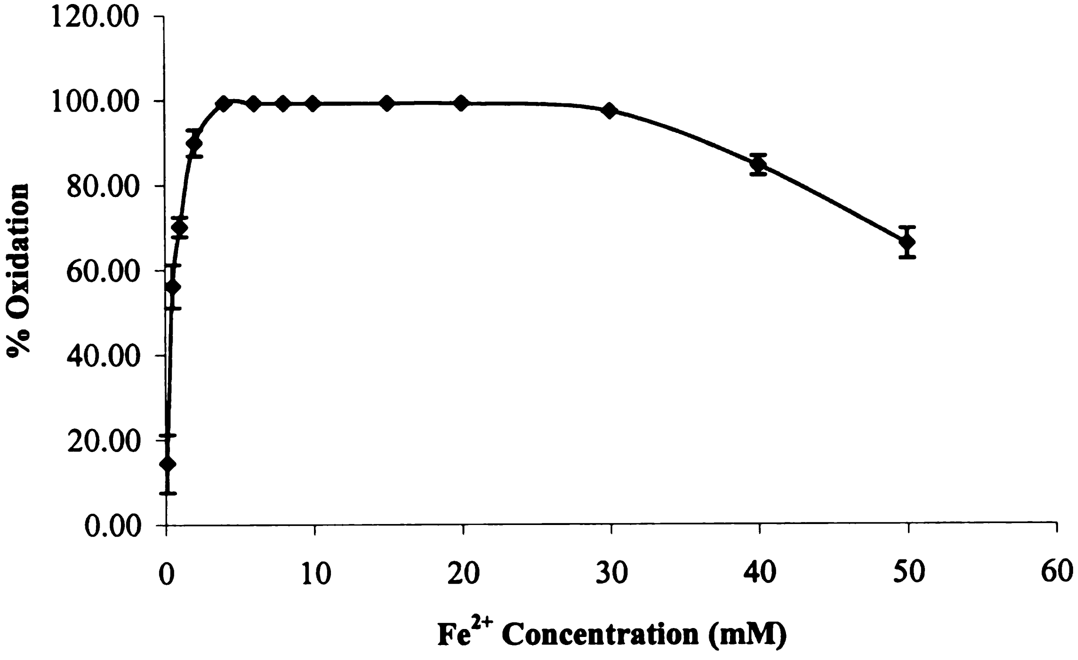


Figure 5-1. **Effect of Fe^{2+} concentration on percent oxidation of MTBE. Initial concentration of MTBE was approximately 388.75 mg MTBE/kg soil, $[H_2O_2]_0$ = 510 mg/L (12,750 mg/kg soil), pH = 2-3.**

Under similar experimental conditions of pH and initial MTBE concentration, when no Fe^{2+} was added to the reaction mixture, only approximately 15% of MTBE was degraded with a hydrogen peroxide concentration of 510 mg/L (12750 mg/kg soil) as was seen in the experiments conducted without the addition of Fe^{2+}. It can be concluded that the addition of Fe^{2+} to hydrogen peroxide can greatly enhance the oxidation of MTBE.

Table 5-1. Variation of MTBE concentration and percent oxidation with Fe^{2+} concentration. Average initial concentration of MTBE = 388.75 mg MTBE/kg soil.

H_2O_2 Concentration (mg/L)	Fe^{2+} Concentration (mM)	Fe^{2+} Concentration (mg/kg soil)	% MTBE Oxidation	MTBE Concentration (mg MTBE/kg soil)
510	0.1	140	14.4 ± 6.83	334.74 ± 25.57
510	0.5	700	56.2 ± 5.09	178.21 ± 19.07
510	1	1400	70.2 ± 2.32	125.80 ± 8.69
510	2	2800	90.0 ± 3.08	51.80 ± 11.54
510	4	5600	≥ 99.3 ± 0.00	ND
510	6	8400	≥ 99.3 ± 0.00	ND
510	8	11200	≥ 99.3 ± 0.00	ND
510	10	14000	≥ 99.3 ± 0.00	ND
510	15	21000	≥ 99.3 ± 0.00	ND
510	20	28000	≥ 99.3 ± 0.00	ND
510	30	42000	97.4 ± 0.13	23.97 ± 0.50
510	40	56000	84.6 ± 2.25	71.81 ± 8.43
510	50	70000	66.2 ± 3.55	140.79 ± 13.29

ND = Not detected

Table 5-1 depicts the percent oxidation and concentration of MTBE as Fe^{2+} concentration is varied from 0.1 mM (140 mg/kg soil) to 50 mM (70,000 mg/kg soil). The H_2O_2 concentration was 510 mg/L (12,750 mg/kg soil) for all samples.

In studies conducted by Pignatello (1992), complete transformation of 0.1 mM 2,4-dichlorophenoxyacetic acid (2,4-D) was complete in less than 1 minute when the concentrations of Fe^{2+} and hydrogen peroxide were greater than 1 mM. It was also observed that when Fe^{2+} and H_2O_2 were present at lower concentrations of 0.25 mM each, the reaction was over in less than 2 minutes and resulted in 76-88% transformation of the contaminant. This would suggest that one or both of the reactants could have been limiting. In the present study, the percent destruction of MTBE was increased from 70% to 90% when the Fe^{2+} concentration was increased from 1 mM (1400 mg/kg soil) to 2 mM (2800 mg/kg soil). Since the MTBE concentration was not detectable when the Fe^{2+} concentration was increased to 4 mM (5600 mg/kg soil), it is possible that Fe^{2+} was the limiting reagent at lower concentrations.

The concentration of Fe^{2+} and hydrogen peroxide to cause complete destruction of the parent compound seems to depend on its nature and initial concentration, other competing organic compounds that may be present, and presence of metals, which may lead to additional reactions such as complexation and precipitation. It is thus imperative that a bench-scale study be conducted on a site before this technology as actually applied.

5.3.2 Effect of Fe^{2+}/H_2O_2 Ratio

As discussed above, the degradation of MTBE increased when the concentration of Fe^{2+} in the reaction mixture was increased. This may be due to the fact that when the concentration of Fe^{2+} in the reaction mixture is low, Fe^{2+} is the limiting reagent in the reaction between H_2O_2 and Fe^{2+} (Equation 2-1), which limits the amount of ·OH produced for the reaction.

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + HO^- + \cdot OH \qquad (2\text{-}1)$$

At higher concentrations of Fe^{2+}, i.e., when the Fe^{2+}/H_2O_2 ratio was greater than 1.3, a decrease in the degradation of MTBE was observed. Although more ·OH could be generated due to a higher concentration of Fe^{2+} present, ·OH may have been scavenged by another Fe^{2+} due to the reaction between Fe^{2+} and the hydroxyl radical (Xu et al., 2004).

$$\cdot OH + Fe^{2+} \longrightarrow Fe^{3+} + HO^- \qquad (5\text{-}1)$$

Additionally, if a large amount of ·OH is generated as a result of excess Fe^{2+}, the oxidation of MTBE may be suppressed due to the reaction of ·OH with H_2O_2, or by the combination of two ·OH groups to form H_2O_2 as is depicted in the reactions 5-2 and 5-3 (Xu et al, 2004).

$$\cdot OH + H_2O_2 \longrightarrow H_2O + HO_2\cdot \qquad (5\text{-}2)$$

$$\cdot OH + \cdot OH \longrightarrow H_2O_2 \qquad (5\text{-}3)$$

5.3.3 Two Stages of MTBE Degradation

It is believed that the degradation of MTBE using Fenton's Reagent is a two-stage reaction (Xu et al., 2004). During the first stage of the reaction, Fe^{2+} reacts rapidly with H_2O_2 to produce a large amount of $\cdot OH$. The generated $\cdot OH$ reacts with MTBE, which, as a result, is degraded very quickly during this first stage. This is known as the Fe^{2+}/ H_2O_2 stage. During this first stage, the Fe^{3+} produced can react with H_2O_2 to generate Fe^{2+} and $HO_2\cdot$ as seen in Reactions 2-4 through 2-8 (Xu et al., 2004)

The rate constant for the reaction between H_2O_2 and Fe^{2+} is 53 $Lmole^{-1}s^{-1}$ (Barb et al., 1950), while that of the reaction between H_2O_2 and Fe^{3+} is 0.02 $Lmole^{-1}s^{-1}$ (Sun et al., 1993). It can be deduced that, unless the concentration of Fe^{3+} is approximately three orders of magnitude greater than that of Fe^{2+}, the reaction between Fe^{2+} and H_2O_2 is much faster than that between Fe^{3+} and H_2O_2, resulting in a greater rate of $\cdot OH$ formation and hence rapid degradation of the organic contaminant during the first stage of the reaction. The ratio of $Fe^{3+}:Fe^{2+}$ would depend on the pH and the redox potential of the system.

The second stage, which is the Fe^{3+}/H_2O_2 stage, is much slower (Barb et al., 1951; Xu et al., 2004) due to the fact that the decomposition of hydrogen peroxide by ferric ions is much slower than that by ferrous ions (Barb et al., 1951). This would also agree with the findings from the previous chapter, where only approximately 15% oxidation of MTBE was observed when no Fe^{2+} was added to the reaction mixture, other reaction conditions remaining unchanged.

5.3.4 pH Monitoring for Soils Treated with Fenton's Reagent

The pH of the reaction mixture for each of the samples was measured before and after the reaction. As mentioned before, the initial pH of the reaction mixture for each sample was maintained between 2 and 3. It was observed that the final pH of the reaction mixture was between 7 and 8 for samples where the concentration of Fe^{2+} added was between 0.1 mM (140 mg/kg soil) and 10 mM (14,000 mg/kg soil). The pH decreased gradually as the concentration of Fe^{2+} was increased. The final pH of the reaction mixture for a Fe^{2+} concentration of 50 mM (70,000 mg/kg soil) was between 4 and 5. Please refer Table 5-2 for pH vs. concentration of Fe^{2+} table. The controls contained 0.2g of contaminated soil and acidified water, and their initial pH was maintained between 2 and 3. The final pH of the controls, which did not have any Fenton's Reagent added to them, was approximately 7.

Table 5-2. Variation of pH with concentration of Fe^{2+}

H_2O_2 Concentration (mg/L)	H_2O_2 Concentration (mg/kg soil)	Fe^{2+} Concentration (mM)	Fe^{2+} Concentration (mg/kg soil)	Final pH
510	12750	0.1	140	Between 7-8
510	12750	0.5	700	Between 7-8
510	12750	1	1400	Between 7-8
510	12750	2	2800	Between 7-8
510	12750	4	5600	Between 7-8
510	12750	6	8400	Between 7-8
510	12750	8	11200	Between 7-8
510	12750	10	14000	Between 7-8
510	12750	15	21000	Between 5-6
510	12750	20	28000	Between 5-6
510	12750	30	42000	Between 4-5
510	12750	40	56000	Between 4-5
510	12750	50	70000	Between 4-5

When the concentration of the hydroxyl radicals is low, the pH of the soil increases. This can be explained based on the fact that the soil used in this study is sandy soil (78.9%), which has a pH of 5.43 ± 0.87. Sandy soil is a poor buffer, and hence does not resist changes in pH. Another factor that could lead to an increase in the pH at low concentrations of Fe^{2+} is the release of HO^- when Fe^{2+} reacts with hydrogen peroxide (Reaction 2-1).

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + HO^- + \cdot OH \qquad (2\text{-}1)$$

The fact that the pH of the controls was approximately 7 further supports this theory.

In the presence of excess Fe^{2+}, a large amount of Fe^{3+} is produced as is seen in reaction 2-1. The generated Fe^{3+} can react with H_2O_2 to form H^+, which would lower the pH of the system (Reaction 2-4).

$$H_2O_2 + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + HO_2\cdot \qquad (2\text{-}4)$$

Pignatello, 1992, also observed that within seconds of addition of peroxide, the initial pH of 4.5 and 6.0 dropped to 3.2-3.4, which may have been a result of release of protons from hydrolysis of the Fe^{3+} product.

5.4 Formation of Byproducts

It was observed that when Fe^{2+} was added to the reaction system, there was no formation of higher molecular weight compounds such as those seen without the addition of Fe^{2+}. It was also seen that the byproducts formed when Fe^{2+} was added were different from the case when it was not. This has been shown in the Figures 5-2 and 5-3. The byproducts based on the retention time were tentatively identified as formaldehyde, propionaldehyde and acetone.

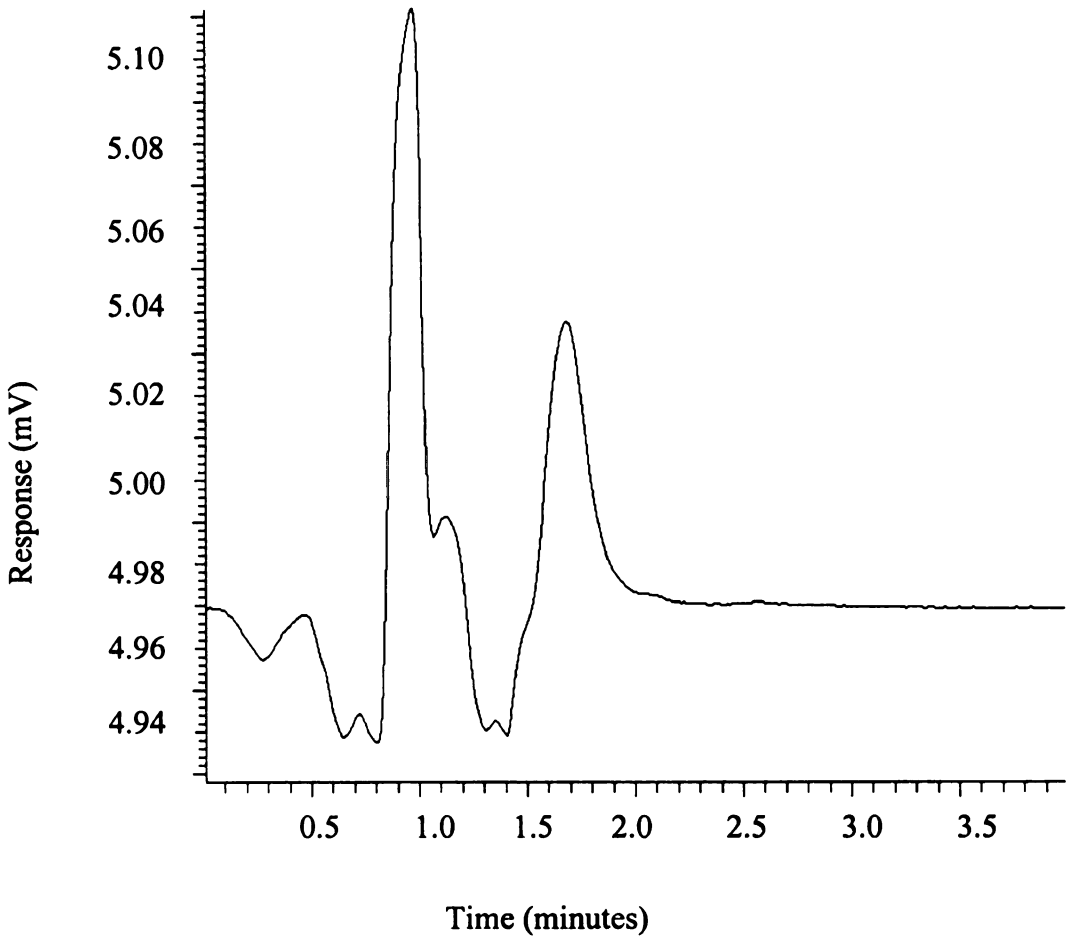


Figure 5-2. $[Fe^{2+}]$ = 4 mM (5600 mg/kg soil), pH = 2-3, $[MTBE]_0$ = 388.75 mg/kg soil, $[H_2O_2]$ = 510 mg/L (12,750 mg/kg soil)

It can be seen that at times around 1.7 minutes, the baseline does not come down, as it should. This suggests the presence of a compound that elutes slowly from the column.

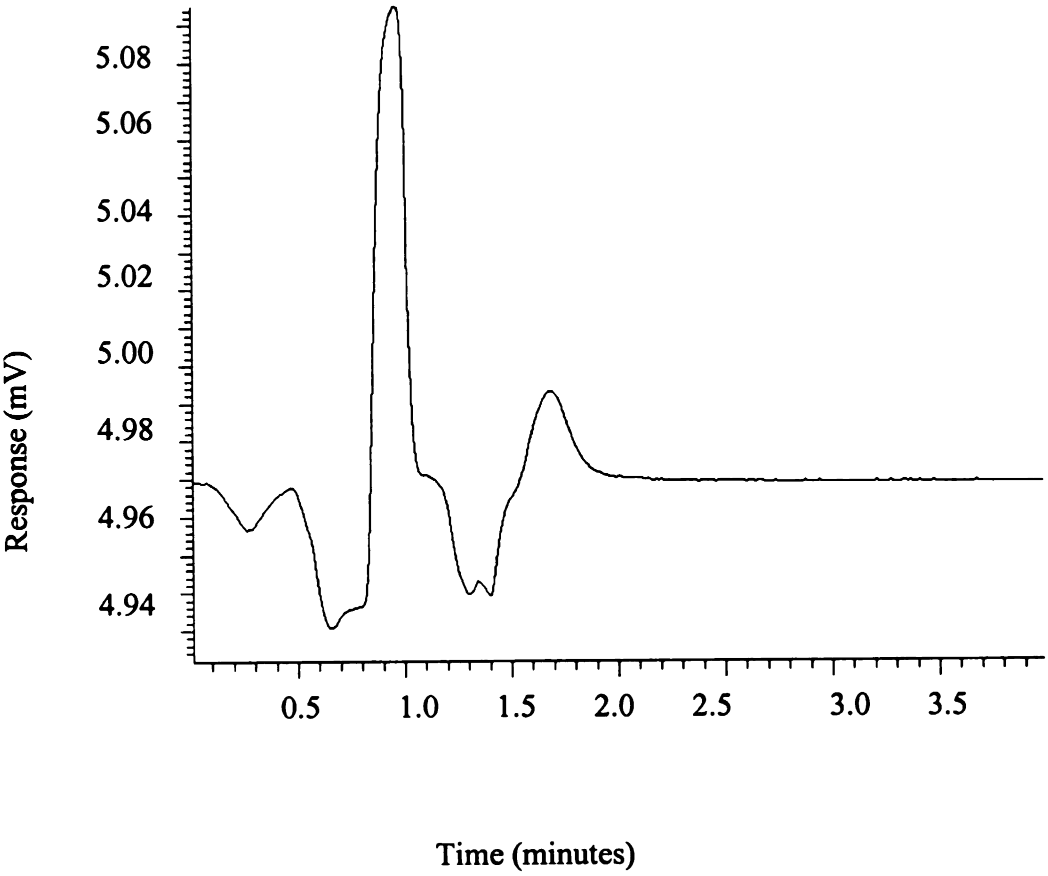


Figure 5-3. **$[Fe^{2+}]$ = 6 mM (8400 mg/kg soil), pH = 2-3, $[MTBE]_0$ = 388.75 mg/kg soil, $[H_2O_2]$ = 510 mg/L (12,750 mg/kg soil)**

Due to the different byproducts obtained in cases where Fe^{2+} was and was not added to the reaction mechanism, it is reasonable to assume that different reactions occur during both cases. This could be due to the formation of different intermediates or could be different stages of oxidation since the rate of the reaction between the contaminant and the hydroxyl radical is faster in the presence of Fe^{2+}.

Tables 5-3, 5-4, and 5-5 depict the percent conversion of MTBE to formaldehyde, propionaldehyde, and acetone on a molar basis. However, as can be seen from Table 5-6, the total conversion does not add to 100%. Thus, a more complete study of the byproducts needs to be done to identify and quantify all of the byproducts and intermediates.

Table 5-3. Percent conversion of MTBE to formaldehyde

Fe^{2+} Concentration (mM)	Fe^{2+} Concentration (mg/kg soil)	Initial MTBE Concentration (mmoles)	Formaldehyde formed (mmoles)	% Conversion to formaldehyde
4	5600	8.82×10^{-4}	6.33×10^{-5}	7.2
15	21000	8.82×10^{-4}	4.31×10^{-4}	48.9
30	42000	8.82×10^{-4}	6.93×10^{-5}	7.8

Table 5-4. Percent conversion of MTBE to propionaldehyde

Fe^{2+} Concentration (mM)	Fe^{2+} Concentration (mg/kg soil)	Initial MTBE concentration (mmoles)	Propionaldehyde formed (mmoles)	% Conversion to propionaldehyde
4	5600	8.82×10^{-4}	2.52×10^{-5}	2.8
15	21000	8.82×10^{-4}	8.58×10^{-6}	0.9
30	42000	8.82×10^{-4}	1.07×10^{-5}	1.2

Table 5-5. Percent conversion of MTBE to acetone

Fe^{2+} Concentration (mM)	Fe^{2+} Concentration (mg/kg soil)	Initial MTBE concentration (mmoles)	Acetone formed (mmoles)	% Conversion to acetone
4	5600	8.82×10^{-4}	5.52×10^{-6}	0.6
15	21000	8.82×10^{-4}	4.17×10^{-5}	4.7
30	42000	8.82×10^{-4}	1.68×10^{-5}	1.9

Table 5-6. Total conversion

Fe^{2+} Concentration (mM)	Fe^{2+} Concentration (mg/kg soil)	Initial MTBE concentration (mmoles)	Total conversion to byproducts (%)
4	5600	8.82×10^{-4}	10.6
15	21000	8.82×10^{-4}	54.5
30	42000	8.82×10^{-4}	10.9

However, due to the presence of byproducts, it is imperative that these compounds are identified and a complete understanding of their toxicity effects, environmental fate and transport is made before this treatment is applied to contaminated sites. It is also important to conduct a bench-scale study before actually applying this technology to any contaminated site due to variation among different sites due to factors such as organic content, type of soil, presence of other contaminants, and presence of metals.

CHAPTER 6

CONCLUSIONS AND SCOPE FOR FUTURE WORK

Form this study, it was seen that the effective degradation of MTBE using Fenton's Reagent is possible, with and without the addition of Fe^{2+}. MTBE was almost completely oxidized under conditions of excess peroxide when no Fe^{2+} was added to the reaction mixture. When Fe^{2+} was added, almost complete oxidation of MTBE could be achieved even at low concentrations of hydrogen peroxide.

In the presence of mineral iron, at pH values between 2 and 3, and reaction time of 120 minutes, MTBE was effectively degraded under conditions of excess hydrogen peroxide. Greater than 95% of MTBE destruction was achieved when the hydrogen peroxide added was equal to or greater than 30,000 mg/L (750,000 mg/kg soil). The initial MTBE concentration in the soil was between 299.25 and 429.75 mg MTBE/kg soil.

Although the degradation of MTBE was almost complete under these experimental conditions and soil type, higher molecular weight byproducts were formed at high concentrations of hydrogen peroxide. In addition, it was also observed that lower molecular weight byproducts were formed at nearly all concentrations of hydrogen peroxide added. Based on the retention times of the compounds, the lower molecular weight compounds were tentatively identified as propionaldehyde and acetone.

When Fe^{2+} was added to the reaction mixture, nearly complete degradation of MTBE was obtained when the Fe^{2+} concentration was between 4 and 20 mM (i.e., 5600 and 28,000 mg/kg soil). The reaction had been conducted at pH values between 2 and 3, initial hydrogen peroxide concentration of 510 mg/L (12,750 mg/kg soil), and a reaction time of 120 minutes. It was also observed that there was no formation of higher molecular weight compounds as was seen in the case where no Fe^{2+} was added to the reaction mixture. Based on the retention times of the compounds, these byproducts were tentatively identified as formaldehyde, propionaldehyde, and acetone.

It is recommended that additional work be done for complete identification and quantification of all the byproducts and intermediates formed during the reaction of MTBE with Fenton's Reagent (with and without the addition of Fe^{2+}). It is imperative that a thorough analysis of these byproducts, which would include their toxicity, fate and transport in the environment, be conducted before this technology is recommended for use at a contaminated site.

Since nearly complete degradation of MTBE is possible in soil without the addition of external iron, this technology could prove very beneficial provided the byproducts formed are less toxic than the parent compound.

Additionally, the formation of intermediates and byproducts of the reaction should be evaluated at different times so as to develop a complete reaction mechanism for MTBE degradation.

The degradation of MTBE using similar reaction conditions as those employed in this study, but different soil types can also be conducted, which would help us understand the effect of different parameters on reaction rates and the byproduct formation.

It is recommended that for a contaminated site, a bench-scale experiment be conducted so as to optimize reaction conditions such as pH, Fe^{2+} and H_2O_2 dose, and reaction time, since these parameters will vary with each site. Additionally, it is imperative that effective mixing of all reagents is ensured at the site so that the contaminants can react with the hydroxyl radicals generated. The concentration of the hydrogen peroxide should be sufficiently low so that it does not cause any explosive hazard at the site.

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