Methyl Tert-Butyl Ether (MTBE) Degradation by Ferrous Ion-Activated Persulfate Oxidation: Feasibility and Kinetics Studies

K. F. Chen[1]*, C. M. Kao[2], L. C. Wu[3], R. Y. Surampalli[4], S. H. Liang[2]

ABSTRACT: The objective of this study was to evaluate the feasibility of using ferrous ion-activated persulfate oxidation to remediate groundwater contaminated with methyl tert-butyl ether (MTBE). In this study, batch experiments were conducted to evaluate the effects of various factors on the efficiency of MTBE degradation including persulfate concentrations, ferrous ion concentrations, and persulfate coupled with hydrogen peroxide. Results show that ferrous ion-activated persulfate oxidation was capable of degrading MTBE efficiently. Persulfate and ferrous ion concentrations correlated with MTBE degradation rates. However, excess addition of ferrous ion resulted in decreased MTBE degrading rates most likely because of competition for sulfate free radicals between ferrous ion and MTBE. Two main byproducts of MTBE degradation, tert-butyl formate and tert-butyl alcohol, were detected in the experiments; both were, however, subsequently degraded. Results of sulfate analysis show that proper addition of ferrous ion could prevent unnecessary persulfate decomposition. *Water Environ. Res.*, **81**, 687 (2009).

KEYWORDS: Methyl tert-butyl ether (MTBE), persulfate, ferrous ion, Fenton's reaction, in situ chemical oxidation (ISCO).
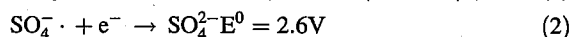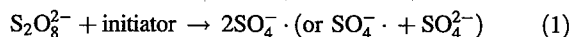
Introduction

Oxygenates such as ethers and alcohols usually are introduced into gasoline as additives to replace lead as an octane index enhancer and to improve air quality. Among the oxygen-containing compounds, methyl tert-butyl ether (MTBE) is the most commonly used gasoline additive because of its low cost and ease of production and blending (Fayolle et al., 2001; Kharoune et al., 2001). However, because of the large amount of MTBE used, contamination has occurred in groundwater, surface water, and air (Juhler and Felding, 2003; Ayotte et al., 2005; Kolb and Püttmann, 2006; Toran et al., 2003; Schmidt et al., 2004; Rosell et al., 2006; Guillard et al., 2003; Lin et al., 2005). Methyl tert-butyl ether has been demonstrated to be an animal carcinogen. As a result, the U.S. Environmental Protection Agency (U.S. EPA) has temporarily classified MTBE as a possible human carcinogen (U.S. EPA, 1997). Methyl tert-butyl ether is an organic chemical with high water solubility and low adsorption to soil. In addition, MTBE is not readily biodegradable because of the tertiary butyl group and ether

linkage on it. Thus, it usually migrates a longer distance than other gasoline components such as benzene, toluene, ethylbenzene, and xylenes (BTEX) (US EPA, 1998; Braids, 2001; U.S. EPA, 2004). For this reason, more active measures may be required to control the movement of MTBE plumes at gasoline-contaminated sites. Chemical oxidation technology is an effective, potent groundwater remedial option capable of breaking down many contaminants in water. Hydrogen peroxide, Fenton's reagent, permanganate, persulfate, and ozone are common oxidants used to remediate organic pollutants (Damm et al., 2002; Mitani et al., 2002; Burbano et al., 2005). Recently, persulfate oxidation has been proposed for in situ chemical oxidation (ISCO) processes [Interstate Technology & Regulatory Council (ITCR), 2005]. The redox potential of persulfate is about 2.01 V, which is higher than those of hydrogen peroxide and permanganate but lower than those of hydroxyl radicals (·OH) and ozone (Huang et al., 2002; ITRC, 2005).

Persulfate can be activated thermally or chemically by initiators such as heat or transition metals (e.g., Fe^{2+}) to produce more powerful sulfate free radicals ($SO_4^-\cdot$) (Block et al., 2004):

$$S_2O_8^{2-} + \text{initiator} \rightarrow 2SO_4^-\cdot \ (\text{or } SO_4^-\cdot + SO_4^{2-}) \quad (1)$$

$$SO_4^-\cdot + e^- \rightarrow SO_4^{2-} \ E^0 = 2.6V \quad (2)$$

Sulfate free radicals are capable of degrading organic compounds to carbon dioxide and water. For example, degradation of MTBE by sulfate free radicals can be illustrated as reaction 3:
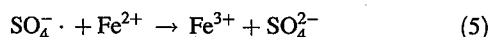
$$30SO_4^-\cdot + C_5H_{12}O + 9H_2O \rightarrow 5CO_2 + 30H^+ + 30SO_4^{2-} \quad (3)$$
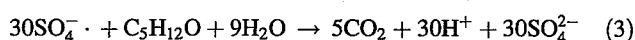
Generally, ferrous ion is a commonly used initiator for persulfate activation (Liang et al., 2004a):

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^-\cdot \quad (4)$$
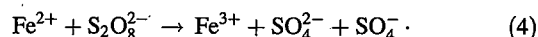
$$k = 2.0 \times 10^1 \ M^{-1} \ s^{-1} \ (\text{Travina et al., 1999})$$

Where,

k = bimolecular rate constant.

$$SO_4^-\cdot + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \quad (5)$$

$$k = 4.6 \times 10^9 \ M^{-1} \ s^{-1} \ (\text{Buxton et al., 1997})$$

From reactions 4 and 5, overall reaction is obtained as reaction 6:

$$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-} \quad (6)$$
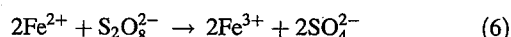
$$k = 3.1 \times 10^4 \ M^{-1} \ s^{-1} \ (\text{Buxton et al., 1997})$$

[1] Department of Civil Engineering, National Chi Nan University, 1 University Rd., Nantou 545, Taiwan; e-mail: kfchen@ncnu.edu.tw.

[2] Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan.

[3] CPC Corp., Tainan, Taiwan.

[4] U.S. Environmental Protection Agency, Kansas City, Kansas.

Table 1—Parameters of methyl tert-butyl ether (MTBE) oxidation experiments.

Factors Trials	MTBE (mM)	$Na_2S_2O_8$ (mM)	Fe^{2+} (mM)	$MTBE/S_2O_8^{2-}/Fe^{2+}$ (molar ratio)	H_2O_2/Persulfate (molar ratio)
1. Persulfate	0.114	1.13	3.57	1/10/31	0
		5.69		1/50/31	
		11.39		1/100/31	
		34.16		1/300/31	
		56.93		1/500/31	
		11.39	0	1/100/0	
2. Ferrous ion	0.114	11.39	0.36	1/100/3.1	0
			1.79	1/100/15.5	
			3.57	1/100/31	
			11.43	1/100/100	
		1.13	0.18	1/10/1.55	
3. Persulfate with H_2O_2	0.114	11.39	3.57	1/100/31	1.18 mM of H_2O_2 only 0.01/1 (H_2O_2 = 0.11 mM) 0.1/1 (H_2O_2 = 1.18 mM)
4. In situ groundwater	0.114	11.39	1.79	1/100/15.5	0

Persulfate can exist longer than other oxidants (such as O_3 and H_2O_2) resulting in a greater transport distance in the subsurface. In addition, because persulfate reacts less with natural organic matters (NOM), it appears to be more appropriate for the remediation of contaminated aquifers containing high NOM (Brown et al., 2003; Block et al., 2004; ITRC, 2005). Dose demand of persulfate would be less because of its lower affinity for NOM and its longer retention time in the subsurface. As a result, the cost of using persulfate oxidation may be lower compared to other oxidants, making it a promising alternative in site remediation.

Persulfate activated by ferrous ion or heat has been used to treat groundwater contaminants including chlorinated organics and petroleum hydrocarbons (Anipsitakis and Dionysiou, 2004; Liang et al., 2004a, 2004b; Huang et al., 2005). Although degrading efficiency is lower, polycyclic aromatic hydrocarbons, explosives, and pesticides could also be oxidized via persulfate (ITRC, 2005; Rivas, 2006). Recent studies have focused on kinetics and efficiency of trichloroethylene (TCE) removal by persulfate under various environmental conditions (Liang et al., 2004a, 2004b; Liang et al., 2006; Liang et al., 2007). However, few studies have evaluated the feasibility of using persulfate for the degradation of petroleum hydrocarbons such as MTBE and BTEX (Huang et al., 2002; Block et al., 2004; Huang et al., 2005; Liang et al., 2008). Huang et al. (2002) reported that effective removal of MTBE and its degrading intermediates—including TBF, TBA, acetone, and methyl acetate—was achieved via heat-assisted persulfate oxidation. Block et al. (2004) also showed that more than 90% of MTBE was decomposed by persulfate oxidation at 35°C. In addition, 80 to 98% of MTBE was degraded by ferrous iron-activated persulfate at a pH of about 2. Kinetics of MTBE removal by iron-activated persulfate has not been studied.

In this study, batch experiments were conducted to evaluate the various controlling factors—different persulfate and ferrous ion concentrations, nature of solution (deionized water or groundwater), persulfate coupled with hydrogen peroxide—on the efficiency of MTBE degradation. The main objectives of this study were to (1) evaluate the efficiency and kinetics of MTBE degradation via persulfate oxidation under different conditions; (2) evaluate the feasibility of using ferrous ion-activated persulfate oxidation to

remediate MTBE-contaminated groundwater; (3) assess the feasibility of MTBE removal by persulfate coupled with hydrogen peroxide; and (4) determine the formation and removal of byproducts, tert-butyl formate (TBF) and tert-butyl alcohol (TBA), during MTBE degradation.

Materials and Methods

Chemicals. In this study, MTBE (99.97%, TEDIA Company Inc., Fairfield, Ohio) and sodium persulfate ($Na_2S_2O_8$, >99%, Riedel-de Haen, Germany) were selected as the target compound and the oxidant, respectively. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$, 99.5%; Riedel-de Haen, Germany) was used to activate persulfate.

Batch Kinetic Experiments. Volatile organic analysis vials (40 mL) were used as batch reactors. Ten mg/L (0.114 mM) of MTBE was prepared in a 2-L bottle previously and then ferrous ion was introduced into the bottle followed by the addition of persulfate. Each 40-mL vial was then filled with the prepared solution via a dispenser and then placed at 25 ± 1°C. The experiments of persulfate coupled with hydrogen peroxide were conducted by the same procedure with simultaneous addition of hydrogen peroxide and persulfate. Control experiments without the addition of persulfate or hydrogen peroxide also were conducted. No disturbance was applied to the batch reactors to simulate nearly static conditions in aquifers. During the experiments, samples were collected at various reaction times. Typically, most of the experiments were stopped when MTBE, TBA, and TBF were completely removed. The efficiency of MTBE removal was obtained by calculating the percentage of MTBE consumption at the end of the experiment. All batch kinetics experiments were conducted with duplicates. Two aqueous media including deionized water (typically used) and groundwater were applied to evaluate the efficiency of persulfate oxidation on MTBE degradation. The initial pH values of deionized water and groundwater were 5.5 and 7.0, respectively. Table 1 shows the parameters of each experiment of MTBE oxidation.

Analytical Methods. Organics including MTBE, TBF, and TBA samples were pretreated by a headspace autosampler (G1888 Network Headspace Sampler, Agilent Technologies, Santa Clara, California), and then analyzed using gas chromatography (6890N, Agilent Technologies) equipped with flame ionization detector

and capillary column (HP-5, 5% phenyl methyl siloxane, 30 m × 0.25 mm × 0.25 µm, Agilent Technologies). Oven temperature was started at 50°C for 1 minute, and then increased 5°C per minute to a final temperature of 80°C and held for 1 minute. A split ratio of 75:1 was used, and the injector and detector temperatures were both maintained at 250°C. Method detection limits of MTBE, TBF, and TBA were 0.01, 0.04, and 0.05 mg/L, respectively. Sulfate analysis was performed by an ion chromatography (ICS-1500, Dionex Corp., Sunnyvale, California) equipped with an analytical column (IonPac AS14, 4 × 250 mm, Dionex). A dissolved oxygen meter (ORION Model 1810A+, Thermo Fisher Scientific Inc., Waltham, Massachusetts) was used to measure dissolved oxygen. Oxidation-reduction potential (ORP) and the potential of hydrogen (pH) were measured by an ORP meter (ORION Model 250A+, Thermo Fisher Scientific) and a pH meter (TES 1380, Taiwan), respectively.

Results and Discussion

Persulfate Activation by Ferrous Ion. In a preliminary test, MTBE oxidation by persulfate with and without the addition of ferrous ion was conducted to determine the effectiveness of ferrous ion on persulfate activation. The initial MTBE concentrations in the reactors were approximately 0.114 mM, and ferrous ion of 3.57 mM was applied. Results show that MTBE was removed completely within 78 hours in the presence of ferrous ion; 7% of MTBE was degraded in the system with persulfate alone (data not shown). No MTBE degradation was observed when only ferrous ion and MTBE existed in the reactors. Results reveal that the oxidative power of persulfate was enhanced by ferrous ion because of production of sulfate free radicals (Liang et al., 2004a). Subsequent experiments were conducted with the addition of ferrous ion to accelerate MTBE oxidation.

Effects of Persulfate Concentrations. Figure 1 presents the results of MTBE degradation under different persulfate concentrations. As shown in Figure 1a, complete MTBE oxidation was accomplished with the molar ratios of $MTBE/S_2O_8^{2-}/Fe^{2+}$ ranging from 1/50/31 to 1/500/31. However, no MTBE degradation was observed with a $MTBE/S_2O_8^{2-}/Fe^{2+}$ molar ratio of 1/10/31 during 70 hours of reaction time. Theoretically, 15 mole of persulfate is capable of degrading one mole of MTBE based on the stoichiometry illustrated below:

$$15S_2O_8^{2-} + C_5H_{12}O + 9H_2O \rightarrow 5CO_2 + 30H^+ + 30SO_4^{2-} \quad (7)$$
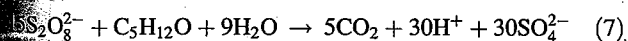
Although the $MTBE/S_2O_8^{2-}/Fe^{2+}$ molar ratio of 1/10/31 was not sufficient for the complete degradation of MTBE, some removal was expected to occur according to reaction 7. Nevertheless, no MTBE degradation was observed under this molar ratio. The competition of ferrous ion for sulfate free radicals (reaction 5) was responsible for the ineffectiveness of MTBE removal because the ratio of ferrous ion to persulfate in this experiment was much higher than those of other four experiments (Table 1) (Liang et al., 2004a). The kinetics of contaminant removal using persulfate oxidation is commonly proposed as a pseudo-first-order reaction (Huang et al., 2002; Huang et al., 2005; Liang et al., 2007). Results revealed that pseudo-first-order reaction rate constants (k) of $MTBE/S_2O_8^{2-}/$ molar ratios of 1/50/31, 1/100/31, 1/300/31, and 1/500/31 were 1.2 × 10⁻², 4.4 × 10⁻², 8.4 × 10⁻², and 20.8 × 10⁻² h⁻¹, respectively. As shown in Figure 1b, persulfate concentration has linear correlation with MTBE degradation rate. Higher persulfate concentration caused more efficient MTBE degradation. However, MTBE reaction rates were less than the rates in an MTBE
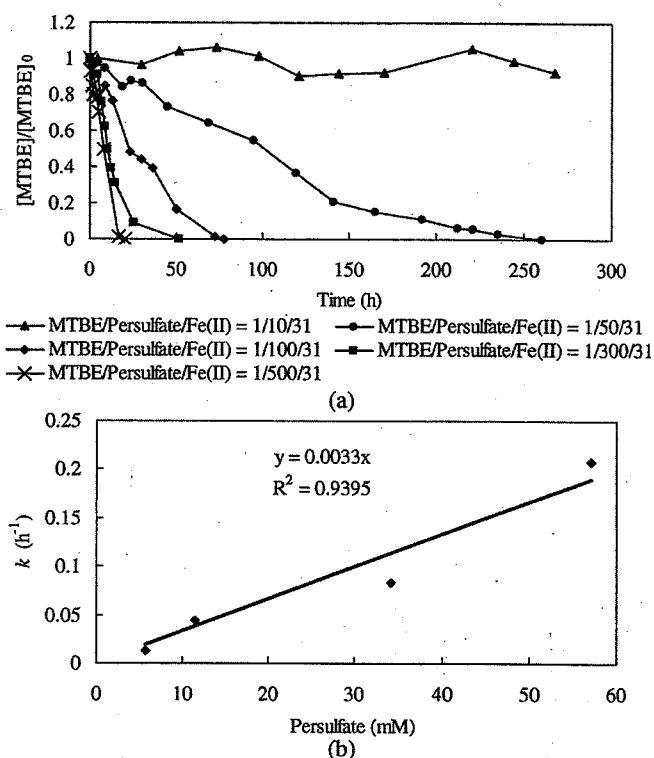

Figure 1—Methyl tert-butyl ether (MTBE) degradation under different persulfate concentrations: (a) normalized MTBE concentrations versus reaction time ([MTBE] ≈ 0.114 mM; [Fe²⁺] = 3.57 mM); (b) pseudo-first-order reaction rate constants (k) of MTBE oxidation ([MTBE] ≈ 0.114 mM; [Fe²⁺] = 3.57 mM).

oxidation study conducted with thermal activation under similar conditions (Huang et al., 2005). This may be because of the undisturbed system of this study, which resulted in lower reaction rate constants.

Effects of Ferrous ion Concentrations. Figure 2 shows the results of MTBE degradation under different ferrous ion concentrations. Results revealed that MTBE could be totally consumed with the molar ratios of $MTBE/S_2O_8^{2-}/Fe^{2+}$ ranging from 1/100/3.1 to 1/100/100 (Figure 2a). Additionally, no significant differences were observed in required MTBE oxidation time with the molar ratios of $MTBE/S_2O_8^{2-}/Fe^{2+}$ between 1/100/3.1 and 1/100/15.5. This indicates that persulfate activation could be achieved even with the addition of a low concentration of ferrous ion. However, MTBE oxidation rate decreased significantly at $MTBE/S_2O_8^{2-}/Fe^{2+}$ molar ratio of 1/100/100. This could because high concentrations of ferrous ion caused competition for sulfate free radicals between ferrous ion and MTBE (reactions 3 and 5) (Liang et al., 2004a). According to available literature, the concentration of ferrous ion between 100 mg/L and 250 mg/L was suggested for persulfate activation (Block et al., 2004; ITRC, 2005). Removal efficiency of contaminants would drop because of the rapid decomposition of persulfate if the concentration of ferrous ion exceeded 750 mg/L. Thus, results of this study were similar to other reports (Block et al., 2004; ITRC, 2005). Figure 2b presents the pseudo-first-order reaction rate constants (k) of MTBE oxidation under various ferrous ion concentrations. The reaction rate constants with the molar ratios of $MTBE/S_2O_8^{2-}/Fe^{2+}$ of 1/100/3.1, 1/100/

(a)

(b)

—▲— MTBE/Persulfate/Fe (II) = 1/10/31   —■— MTBE/Persulfate/Fe (II) = 1/10/1.5
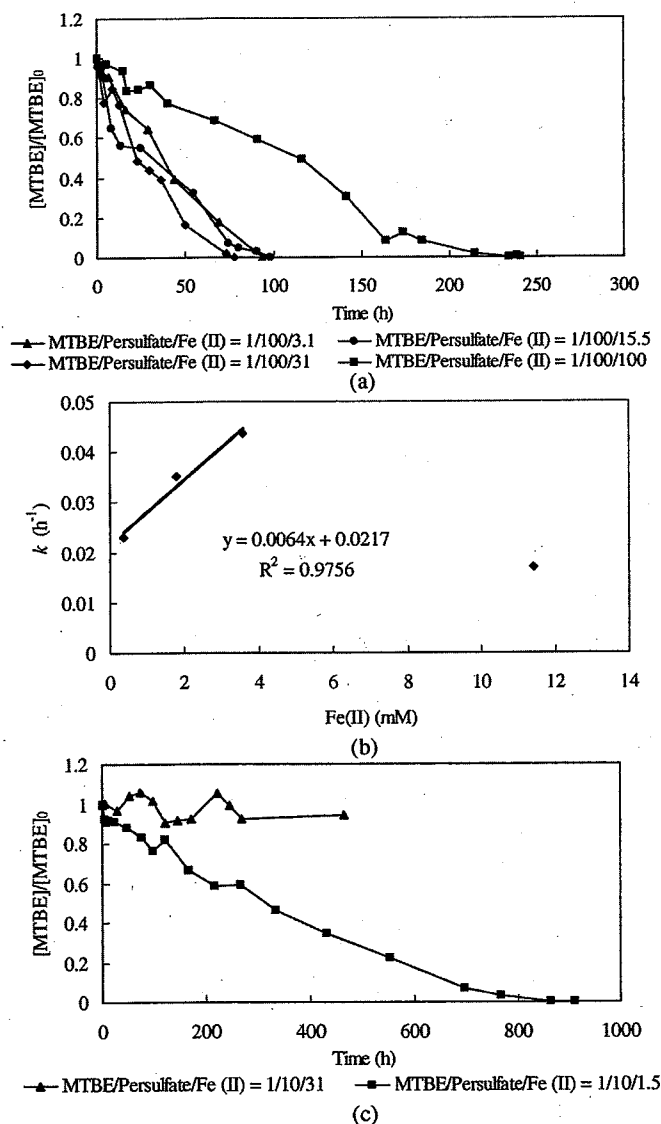
(c)

Figure 2—Methyl tert-butyl ether (MTBE) degradation under different ferrous ion concentrations: (a) normalized MTBE concentrations versus reaction time ([MTBE] ≈ 0.114 mM; [Na₂S₂O₈] = 11.39 mM); (b) pseudo-first-order reaction rate constants (k) of MTBE oxidation ([MTBE] ≈ 0.114 mM; [Na₂S₂O₈] = 11.39 mM); (c) normalized MTBE concentrations versus reaction time under high and appropriate ferrous ion addition ([MTBE] ≈ 0.114 mM; [Na₂S₂O₈] = 1.13 mM).

15.5, 1/100/31, and 1/100/100 were 2.3×10^{-2}, 3.5×10^{-2}, 4.4×10^{-2}, and 1.7×10^{-2} h^{-1}, respectively. As shown in Figure 2b, ferrous ion concentration had a linear correlation with MTBE removal with ferrous ion concentrations of 0.36 to 3.6 mM. The molar ratio of MTBE/$S_2O_8^{2-}$/Fe^{2+} of 1/100/100 resulted in the data point outlier. As discussed, the overdose of ferrous ion resulted in a lower MTBE degradation rate because of competition for sulfate free radicals between ferrous ion and MTBE.

Results from the experiments indicated that molar ratios of $S_2O_8^{2-}$/Fe^{2+} between 1/0.031 and 1/0.31 demonstrated good MTBE degradation efficiency. Results in Figure 1a show that
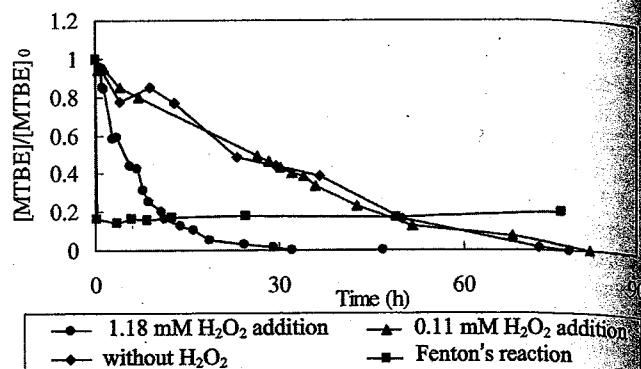

Figure 3—Methyl tert-butyl ether (MTBE) degradation using persulfate coupled with hydrogen peroxide ([MTBE] ≈ 0.114 mM; [Na₂S₂O₈] = 11.39 mM; [Fe²⁺] = 3.57 mM; Fenton's reaction: [H₂O₂] : 1.18 mM + [Fe²⁺]: 3.57 mM).

MTBE was not degraded with a MTBE/$S_2O_8^{2-}$/Fe^{2+} molar ratio of 1/10/31 ($S_2O_8^{2-}$/Fe^{2+} molar ratio 1/3.1). This likely was because of the effect of the high ratio of ferrous ion that was added to the system, which would react with sulfate radicals and decrease the oxidation power. To test this hypothesis, a test with MTBE/$S_2O_8^{2-}$/Fe^{2+} molar ratio of 1/10/1.55 ($S_2O_8^{2-}$/Fe^{2+} molar ratio of 1/0.155) was conducted for comparison. Figure 2c presents the comparison of MTBE degradation under high and appropriate ferrous ion addition. More than 60% of MTBE was removed within 430 hours with $S_2O_8^{2-}$/Fe^{2+} molar ratio of 1/0.155, and complete degradation was observed after 912 hours (38 days) with a reaction rate constant of 0.5×10^{-2} h^{-1}. However, no MTBE degradation was observed with $S_2O_8^{2-}$/Fe^{2+} molar ratio of 1/3.1 during a 460-hour reaction time. Results of the experiment suggested that excess addition of ferrous ion was the major factor inhibiting MTBE degradation in the system.

According to reaction 7, 1.14 mM of persulfate theoretically is capable of degrading 0.076 mM of MTBE. However, 0.114 mM of MTBE was completely removed in the test with MTBE/$S_2O_8^{2-}$/Fe^{2+} molar ratio of 1/10/1.55. The degrading efficiency of MTBE was approximately 1.5 times higher than the theoretical value. In fact, the oxidation of contaminants in a persulfate system involves a complicated chain reaction including initiation, propagation, and termination reactions (House, 1961). It has been reported that if the chain termination reactions are slower than chain propagation processes, then even small amounts of sulfate radicals can result in significant contaminant removal. For this reason, consumption of persulfate for contaminant treatment will be lower than the stoichiometric quantities (ITRC, 2005). Although stoichiometric equations such as reaction 7 were commonly used to predict the reaction of persulfate with contaminants, results from this study suggest that it is necessary to construct a more detailed mechanism of the reaction between persulfate and contaminants (ITRC, 2005; Liang et al., 2007). Results also showed that MTBE could be degraded effectively with appropriate ferrous ion addition even if low concentration of persulfate was applied. Therefore, molar ratio of $S_2O_8^{2-}$/Fe^{2+} in a persulfate oxidation system was the most important controlling factor to achieve effective MTBE removal.

Removal by Persulfate and Hydrogen Peroxide. Hydrogen peroxide was added into batch reactors to enhance the efficiency of MTBE oxidation because it can activate persulfate (Block et al., 2004). Figure 3 shows the results of MTBE degradation by

persulfate coupled with hydrogen peroxide. The addition of 1.18 mM of hydrogen peroxide enhanced MTBE removal efficiency, although 0.11 mM of hydrogen peroxide showed no significant improvement. This indicates that 0.11 mM of hydrogen peroxide was not sufficient to improve persulfate activation. Because ferrous ion was present in the system, formation of hydroxyl free radicals would generate more sulfate free radicals to accelerate MTBE degradation according to reaction 8 (House, 1961):

$$\cdot OH + S_2O_8^{2-} \rightarrow SO_4^- \cdot + HSO_4^{1-} + 1/2O_2 \qquad (8)$$
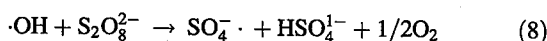
In addition, formation of hydroxyl free radicals also would contribute to MTBE consumption. Block et al. (2004) reported that synergistic attributes caused by hydrogen peroxide and persulfate would enhance removal of contaminants. Furthermore, heat generated from the decomposition of hydrogen peroxide may also thermally activate persulfate (Waldemer et al., 2007).

When 1.18 mM of hydrogen peroxide was added alone with ferrous ion of 3.57 mg/L (Fenton's reaction), more than 80% of MTBE was degraded efficiently within 15 minutes. However, further MTBE removal was not observed because of complete consumption of hydrogen peroxide in the system. It has been reported that two stages of MTBE decomposition were observed in Fenton's reaction (Sun and Pignatello, 1993; Xu et al., 2004). In the first stage, MTBE is degraded rapidly with large amount of hydroxyl free radicals, which are generated from quick reaction of ferrous ions and hydrogen peroxide. In the second stage, a lower rate of MTBE degradation occurred because ferric ions react much more slowly with hydrogen peroxide than ferrous ions. Thus, if hydrogen peroxide was still in the system, continuous but slow MTBE degradation should be observed because of the catalyst of ferric ions. In this study, however, MTBE was not further degraded until the end of the experiment. Results revealed that hydrogen peroxide was no longer present in the system.

Low concentration of hydrogen peroxide (1.18 mM) was added to enhance persulfate oxidation in this study. Thus, Fenton's reaction was conducted with 1.18 mM of hydrogen peroxide to compare to the combined persulfate/peroxide system. In this study, although MTBE degradation via Fenton's oxidation was much faster than the combined persulfate/peroxide system, it could not remove MTBE completely. Thus, persulfate in the combined system could be used to remove the residual MTBE. The results also indicate, however, that Fenton's reaction was stalled because of persulfate. In fact, using Fenton's system with higher concentrations of hydrogen peroxide can improve the efficiency of MTBE removal. However, in the case of improving a persulfate system, application of Fenton's reaction with proper hydrogen peroxide concentrations (e.g., 1.18 mM) followed by persulfate oxidation is an appropriate ISCO combination to readily and completely degrade contaminants.

Degradation of Oxidation Byproducts. Figure 4 shows the variation in MTBE and its byproducts, TBF and TBA, during the oxidation processes. Firsts TBF, then TBA were produced while MTBE degraded. Huang et al. (2002) and Xu et al. (2004) proposed a similar degrading pathway of MTBE by hydroxyl or sulfate free radicals. The two studies also reported that acetone and methyl acetate were formed during MTBE degradation process (Huang et al., 2002; Xu et al., 2004). Table 2 summarizes the results of MTBE oxidation. As shown in Table 2, TBA was more persistent than TBF in the system. In addition, complete degradation of TBA was not observed with low concentration of oxidant (MTBE/$S_2O_8^{2-}$/Fe^{2+} = 1/50/31 and 1/10/1.55) or high concentration of
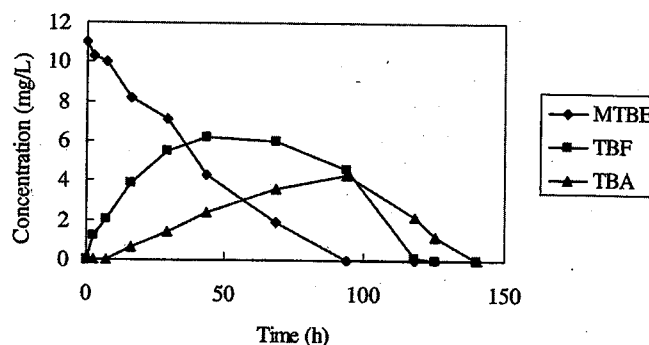

Figure 4—Oxidation of methyl tert-butyl ether (MTBE) and its byproducts, tert-butyl formate (TFB) and tert-butyl alcohol (TBA) (MTBE/$S_2O_8^{2-}$/Fe^{2+} = 1/100/3.1; [MTBE] ≈ 0.114 mM; [$Na_2S_2O_8$] = 11.39 mM; [Fe^{2+}] = 0.36 mM).

ferrous ion (MTBE/$S_2O_8^{2-}$/Fe^{2+} = 1/100/31). This indicates that higher oxidant concentration and proper ferrous ion addition are necessary to achieve complete TBA removal. Moreover, results of TBA degradation from MTBE/$S_2O_8^{2-}$/Fe^{2+} molar ratio of 1/10/1.55 also suggest that persulfate was able to sustain the oxidation power in the system more than 43 days because TBA concentration dropped from 4.0 mg/L on day 43 (data not shown) to 0.6 mg/L on day 96 (Table 2). Continuous oxidative ability of persulfate occurred in the system after a 1.5-month oxidation period.

Oxidation Efficiency in Groundwater. Uncontaminated groundwater spiked with MTBE was used for further evaluation to determine the efficiency of in situ persulfate oxidation. The initial conditions of the groundwater were: pH = 6.99; dissolved oxygen = 3.0 mg/L; ORP = 459 mV; and total organic carbon (TOC) = 21.8 mg/L. As shown in Table 2, complete MTBE depletion in groundwater was observed within a 116-hour persulfate reaction (98 hours in deionized water) with a first-order reaction rate constant of $3.1 \times 10^{-2} h^{-1}$ ($3.5 \times 10^{-2} h^{-1}$ in deionized water). In addition, byproducts of MTBE degradation (TBF and TBA) also could be degraded completely in groundwater within a similar oxidation time to that in deionized water (Table 2). Although TOC in groundwater was higher than the concentration of MTBE, little effect was observed on removal of MTBE and its byproducts in the tests with groundwater addition. This likely is because the reaction between persulfate and NOM is limited (ITRC, 2005). The slightly decrease in the MTBE removal rate also may result from the presence of natural radical scavengers in groundwater (e.g., carbonate, bicarbonate, chlorides) (ITRC, 2005; Liang et al., 2007).

Effects of Persulfate Oxidation on Water Quality Parameters. In this study, two aqueous media including deionized water (typically used) and groundwater were applied to evaluate the efficiency of persulfate oxidation on MTBE degradation. The initial conditions of deionized water were pH = 5.5, dissolved oxygen = 3.5 mg/L, and ORP = 459 mV (see previous section for groundwater). Overall, ORP increased dramatically (more than 700 to 800 mV) because of production of sulfate free radicals. In addition, pH values in deionized water dropped rapidly from 5.5 to less than 3.0 (2.3 to 2.9) by the end of all experiments except for those with the MTBE/$S_2O_8^{2-}$/Fe^{2+} molar ratio of 1/10/1.55 (pH = 3.4) (Table 2). Although groundwater showed a stronger buffering capacity during the first 70 hours of reaction (data not shown), the final pH in groundwater also dropped to 2.8 in the reactors. The results indicate that the application of in situ persulfate oxidation

Table 2—Results of methyl tert-butyl ether (MTBE) oxidation by persulfate [TBF = tert-butyl formate; TBA = tert-butyl alcohol; ORP = oxidation-reduction potential].

| Trials	MTBE/$S_2O_8^{2-}$/Fe^{2+} (molar ratio)	Total reaction time of complete MTBE degradation (hours)	Total reaction time of complete TBF degradation (hours)	Total reaction time of complete TBA degradation (hours)	Final pH	Final ORP (mV)	Final dissolved oxygen (mg/L)	Final SO_4^{2-} (mg/L)	k_{MTBE} × 10³ (h⁻¹)
1	1/10/31	463.8 (no degradation)	—[1]	—	2.9	545	3.8	402	—
	1/50/31	260.0	141.3	> 338.0	2.6	778	3.5	1,197	1.2
	1/100/31	77.5	72.5	170.0	2.5	839	3.5	1,085	4.4
	1/300/31	51.6	51.6	97.8	2.3	844	4.5	1,614	8.4
	1/500/31	20.3	29.3	55.8	2.5	893	3.9	1,291	20.8
2	1/100/3.1	93.8	125.5	149.0	2.9	825	3.3	219	2.3
	1/100/15.5	98.0	110.0	173.5	2.4	770	5.6	751	3.5
	1/100/31	77.5	72.5	170.0	2.5	839	3.5	1,085	4.4
	1/100/100	241.0	40.5	> 360.5	2.5	812	3.6	2,807	1.7
	1/10/1.55	912.0	864.0	> 2,304.0	3.4	477	4.6	171	0.5
3	H_2O_2 1.18 mM	> 268.0 (≈ 80% removal)	49.0	> 268.0	2.6	467	5.3	—	61.2
	1/100/31 without H_2O_2	77.5	72.5	170.0	2.5	839	3.5	1,085	4.4
	1/100/31 with H_2O_2 0.11 mM	81.0	166.0	> 169.0	2.3	741	5.2	1,256	3.4
	1/100/31 with H_2O_2 1.18 mM	47.0	47.0	167.5	2.4	596	5.6	1,550	16.6
4	1/100/15.5 (in situ groundwater)	115.8	115.8	178.5	2.8	701	3.8	731	3.1

[1] Not available.

has the potential to lower the pH of groundwater. In a persulfate oxidation system, high concentrations of sulfate may be produced to form sulfuric acid. Although not as severe in aquifers because of the buffering capacity of aquifer sediments, reductions in pH should still be considered when persulfate oxidation is applied in situ (ITRC, 2005). Liang et al. (2007) have investigated TCE degradation by persulfate oxidation under various pH values. The results suggested that maximum TCE degradation occurred at pH 7. The TCE degradation rates were higher at pH 9 than at pH 4. Because pH values were not controlled in this study, further studies need to be conducted to determine the optimum pH for MTBE degradation.
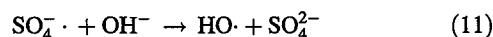
Dissolved oxygen did not noticeably increase except for when hydrogen peroxide was added. Studies have reported that the hydrolysis of persulfate in alkaline, neutral, and dilute acid solutions could generate oxygen (Kolthoff and Miller, 1951):

$$S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + 1/2O_2 \qquad (9)$$
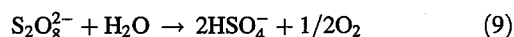
However, based on the results of pH measurement (pH < 3), conditions in the batch reactors were unfavorable for oxygen generation. Hydroxyl free radicals produced from the reaction of sulfate free radicals with water (reaction 10) or hydroxyl ion (reaction 11) potentially could generate oxygen (Al-Ananzeh et al., 2006).

$$SO_4^- \cdot + H_2O \rightarrow \cdot OH + HSO_4^- \qquad (10)$$
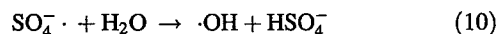
k [H_2O] < 2 × 10⁻³ s⁻¹ (Pennington and Haim, 1968)

$$SO_4^- \cdot + OH^- \rightarrow HO \cdot + SO_4^{2-} \qquad (11)$$

$k = 7.3 \times 10^7$ M⁻¹s⁻¹ (Chawla and Fessenden, 1975)

Nevertheless, reaction 10 has a low reaction rate constant while reaction 11 requires alkaline conditions to increase the production of hydroxyl free radicals. Thus, oxygen generation via hydroxyl free radicals was not predominant in the system. The presence of hydrogen peroxide in the system seems to be another critical source of oxygen. Generally, hydrogen peroxide could be produced from monopersulfuric acid (H_2SO_5), which is formed from the decomposition of persulfate in strong acidic solutions (> 0.5 M $HClO_4$) (Kolthoff and Miller, 1951):

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4 \qquad (12)$$
$$H_2SO_5 + H_2O \rightarrow H_2O_2 + H_2SO_4 \qquad (13)$$
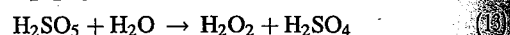
Although pH values in the reactors were less than 3, it did not meet conditions for predominant hydrogen peroxide production. This resulted in unfavorable effects on oxygen production. Based on the above discussion, significant oxygen generation would not take place in the systems. In addition, field applications also showed that the increase of pressure in injection wells was not observed, indicating a limited release of gases from persulfate (ITRC, 2005). Results of this study were in accordance with the data obtained from the field demonstration.

Production of Sulfate during Oxidation. Final sulfate concentrations were analyzed in the experiments because sulfate production is related to persulfate decomposition and consumption. Experimental results reveal that no significant differences in sulfate production were observed under various MTBE concentrations except for the MTBE/$S_2O_8^{2-}$/Fe^{2+} molar ratio of 1/10/31 (Table 2). However, ferrous ion caused a significant effect on final sulfate

centrations. Experiments with higher ferrous ion concentrations sulted in higher sulfate production (Figure 5). Table 2 shows that although 2710 mg/L of persulfate degraded MTBE completely under different ferrous ion concentrations, sulfate production increased with higher ferrous concentrations. This indicates that persulfate decomposition rates would increase when higher concentration of ferrous ion was added. Thus, proper addition of ferrous ion could prevent unnecessary persulfate decomposition.

Conclusions

In this study, MTBE oxidation using ferrous ion-activated persulfate oxidation was investigated. Results from the experiments show that persulfate oxidation was capable of degrading MTBE efficiently. Persulfate concentration correlated with MTBE degradation rate. Higher persulfate concentration caused more efficient MTBE degradation. No significant dissolved oxygen increase was observed in most experiments because of unfavorable conditions ($pH = 2.3$ to 2.9).

Ferrous ion concentration presents a near-linear effect on MTBE removal (between 0.36 and 3.57 mM of ferrous iron addition). However, when excess ferrous ion was applied (11.43 mM), degrading efficiency of MTBE decreased because of competition for sulfate free radicals between ferrous ion and MTBE. Results from the experiments showed that MTBE could be degraded effectively under appropriate ferrous ion addition (molar ratios of $S_2O_8^{2-}/Fe^{2+}$ between 1/0.031 and 1/0.31) even if low concentration of persulfate was applied (1.13 mM). Thus, the molar ratio of $S_2O_8^{2-}/Fe^{2+}$ in a persulfate oxidation system is the most important controlling factor to achieve effective MTBE removal. Moreover, the results of sulfate analysis revealed that persulfate decomposition would be increased if higher concentration of ferrous ion was applied. Thus, appropriate addition of ferrous ion should be controlled to prevent unnecessary persulfate decomposition. The results of TBA degradation show that low concentration of persulfate (approximately 1.13 mM) was able to remain in the system for more than 43 days. This indicates that persulfate is a stable oxidant in water. In addition, the degrading efficiency of MTBE was higher than that predicted from the stoichiometric equation. This may result from the complicated chain reactions of sulfate free radicals.

The combined system with the addition of persulfate and peroxide simultaneously is able to enhance the efficiency of MTBE degradation effectively. The first-order reaction rate of the combined system was approximately four times higher than that of the experiment without hydrogen peroxide addition. Results also indicate that application of Fenton's reaction followed by persulfate oxidation has the potential to be developed into a more effective ISCO system. Results of this study could aid in designing systems to remediate MTBE-contaminated sites.

Acknowledgments

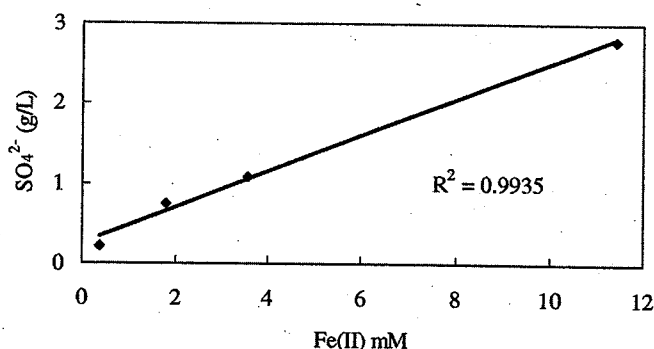**Figure 5—Sulfate production under various ferrous ion concentrations ([MTBE] ≈ 0.114 mM; [$Na_2S_2O_8$] = 11.39 mM) (MTBE = methyl tert-butyl ether).**

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