



Impact of activation methods on persulfate oxidation of methyl *tert*-butyl ether



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HIGHLIGHTS

- Persulfate activated conditions influenced MTBE removal kinetics.
- Persulfate activated conditions influenced degradation of MTBE daughter products.
- Persulfate oxidation of MTBE primarily happened via non-oxygen demand pathways.

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ABSTRACT

To provide guidance on the selection of proper persulfate processes for the remediation of MTBE contaminated groundwater, MTBE aqueous solutions were treated with three common field persulfate processes including heat activated persulfate, Fe(III)-EDTA activated persulfate and alkaline persulfate, respectively. The results were compared with MTBE oxidation by Fenton's reagent and persulfate alone at 25 °C. The impact of the activating conditions on the fate of MTBE and its daughter products was investigated. Heat activation at 40 °C offered the most rapid removal of MTBE and its daughter products, while Fe(III)-EDTA activation showed higher efficiency of MTBE removal but low removal efficiency of its daughter products. On the other hand, alkaline persulfate showed slower kinetics for the removal of MTBE and less accumulation of the daughter products. Furthermore, *tert*-butyl alcohol and acetone were observed as the main purgeable daughter products along with a small amount of *tert*-butyl formate in persulfate oxidation of MTBE, while *tert*-butyl formate, *tert*-butyl alcohol and acetone were the main products in Fenton oxidation. Mechanistic analysis suggests that degradation of MTBE by persulfate most likely happens via non-oxygen demand pathways, different from the dominant oxygen demand degradation pathways observed in Fenton oxidation.

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1. Introduction

Methyl *tert*-butyl ether (MTBE) is a volatile, flammable and colorless liquid with high solubility in water (51.26 g/l at 25 °C) [1], which is produced in large quantities (~18 million tons in 2005 worldwide) [2] and is extensively used as a fuel additive. MTBE can easily enter the environment through leaking underground storage tanks and fuel spills [3]. Due to its high solubility in water, high vapor pressure and the ability to travel rapidly through the soil [4], MTBE leakage has resulted in more than 200,000 contaminated sites in the United States alone [3]. In particular, groundwater near a substantial number of leaking underground tanks has been highly

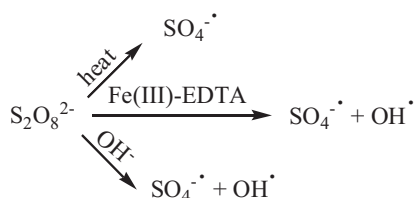
contaminated with MTBE. Data from California shows that 4.5% of the leaking underground tank sites reported a maximum MTBE concentration higher than 1000 ppm in groundwater [5]. Due to its offensive taste and odor and possible health impact (potential carcinogen [6]) to the public, US EPA issued a drinking water advisory limit of 20–40 ppb for MTBE in 1997 [7] and many states (25 states in 2005) in the US have banned or limited the use of MTBE since 2004 and have called for the remediation of MTBE from contaminated groundwater [8]. It is estimated that \$2.0 billion is needed to remediate MTBE from existing leaking underground tanks in the US alone [9], showing the prevalence of the MTBE problems. Therefore, it is very important to identify cost-effective methods for the remediation of MTBE contaminated groundwater, especially groundwater with high levels of MTBE, which is the focus of the current study.

In situ chemical oxidation (ISCO) is increasingly employed for the remediation of organic contaminated soil and groundwater, especially for the treatment of source zones (hot spots) [10]. In ISCO, environmental friendly inorganic oxidants are injected into the

Abbreviations: MTBE, methyl *tert*-butyl ether; ISCO, In situ chemical oxidation; TBA, *tert*-butyl alcohol; TBF, *tert*-butyl formate; MA, methyl acetate; Fe(III)-EDTA, ethylenediaminetetraacetic acid iron(III) sodium salt; ETBE, ethyl *tert*-butyl ether.

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Scheme 1. Main reactive radical species in the three common persulfate activation processes.

subsurface to degrade organic contaminants into carbon dioxide or other less toxic products [11]. Two common oxidants applied in ISCO are hydrogen peroxide (Fenton's reagent) and persulfate, both of which oxidize organic contaminants by generating highly reactive radical species, such as hydroxyl and sulfate radicals. Previous studies indicate that Fenton's reagent is an effective oxidant for MTBE in aqueous solutions [12,13], but when hydrogen peroxide is injected into the subsurface, it decomposes very quickly and can produce substantial heat, which not only induces potential safety problems but also causes the escape of volatile organic compounds. As a result, persulfate has been increasingly used in recent years for the remediation of organic contaminated sites, as persulfate tends to have much longer lifetime in the subsurface and it is safer to handle and more applicable to subsurface than hydrogen peroxide [14].

When designing a persulfate-based field remediation project, a major consideration is the selection of proper activation methods. When applied in the field, persulfate is generally activated by heat or Fe(III)-EDTA, and in recent years, alkalines. All these processes rely on the generation of sulfate and/or hydroxyl radicals to oxidize the organic contaminants (Scheme 1) [15–17].

Each persulfate activation process has its pros and cons, which are further complicated by the matrix effects of soil and groundwater. Heat activation is a simple and effective activation method for persulfate, but heat activation suffers from the potential high cost in raising the temperature of soil and groundwater [14]. An activation temperature of ~40 °C is commonly used in field application [10]. Fe(III)-EDTA is used to maintain a sufficient iron concentration in the solution to activate persulfate and minimize the loss of activation due to immobilization of Fe by surface sorption, precipitation or co-precipitation encountered in ferrous ion activation. However, the organic ligand of Fe(III)-EDTA may compete with the target contaminants for persulfate [16,18]. Moreover, the addition of base to the persulfate system may neutralize the protons produced from persulfate decomposition, but some recent studies indicate that persulfate at high pH may suffer from slow kinetics [19].

The degradation of MTBE using persulfate has been investigated using heat activation [20], ferrous iron activation [21] or pyrite activation [22], respectively, in aqueous solutions. However, the remediation of MTBE contaminated water by Fe(III)-EDTA activated persulfate and alkaline persulfate, two of the three common applied field persulfate processes, has not been fully explored. Therefore, the current study investigated and compared the performance of the three common field persulfate activation processes, heat-activated persulfate, Fe(III)-EDTA activated persulfate and alkaline persulfate, for the remediation of MTBE, aiming to provide potentially valuable guidance on the selection of appropriate conditions for field application.

In designing a proper process for the remediation of organic contaminants, another important consideration is the toxicity of the daughter products. Therefore, it is crucial to identify potential intermediates and characterize the degradation pathways of the target contaminants. *Tert*-butyl alcohol (TBA), acetone, methyl

acetate (MA), and *tert*-butyl formate (TBF) have been identified as the products in persulfate oxidation of MTBE [20–22], but there is limited information on the effects of activation methods on the occurrence, distribution and fate of the daughter products. The current study also systematically investigated this effect, hoping to provide useful guidance on this matter.

In this work, degradation of MTBE using persulfate with heat, Fe(III)-EDTA, or alkaline activation, respectively, was studied and compared. An MTBE aqueous solution of ~1000 ppm was used to investigate the feasibility of persulfate for the remediation of groundwater contaminated by high levels of MTBE. For comparison purposes, oxidation of MTBE was also carried out with persulfate alone at 25 °C as well as with Fenton's reagent. The main objectives of the current study were to (1) evaluate the impact of different persulfate processes on the degradation efficiency and kinetics of MTBE and its daughter products; (2) determine potential degradation mechanisms of MTBE by persulfate oxidation, with special focus on the impact of non-oxygen demand and oxygen demand degradation pathways on the fate of MTBE and its daughter products, which has been rarely noticed and investigated before in persulfate oxidation of organic contaminants.

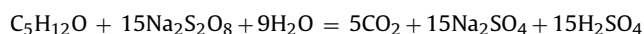
2. Materials and methods

2.1. Materials

Methyl *tert*-butyl ether (MTBE, 98%), ethyl *tert*-butyl ether (ETBE, 99%), *tert*-butyl alcohol (TBA, 99.5%), *tert*-butyl formate (TBF, 99%), methyl acetate (MA, 99.5%), acetone (99.5%), ethylenediaminetetraacetic acid iron(III) sodium salt hydrate (Fe(III)-EDTA, 12–14% Fe base), iron(II) sulfate heptahydrate (FeSO₄·7H₂O, 99%), sodium persulfate (Na₂S₂O₈, 98%), sodium hydroxide (pellets, 98%) and hydrogen peroxide (35%) were all analytical grade and used as received. Deionized water (18 MΩ cm) was used to prepare all solutions.

2.2. Persulfate oxidation of MTBE in aqueous solutions

MTBE was added into deionized water to prepare a stock solution of ~11.34 mmol/L (~1000 ppm). The solution was treated at a persulfate dosage of ~170 mmol/L or 40.5 g/L, equal to 1.5 equiv. of the theoretical persulfate dosage needed to achieve complete mineralization of MTBE (reaction (1)). The oxidant dosage used in the current study was also similar to those used in field applications and pilot studies [23]. Persulfate dosage was kept constant in each persulfate activation process for comparison purpose. For persulfate oxidation at 25 °C and 40 °C, sample vials were kept in covered cardboard boxes at 25 °C or put into a covered water bath maintained at 40 °C. For alkaline persulfate oxidation, sodium hydroxide at two molar equivalents of the persulfate was also added into the MTBE stock solution. For Fe(III)-EDTA activation, Fe(III)-EDTA concentration was ~4.48 mmol/L (~250 ppm Fe), while a typical iron dosage of 100–250 ppm is normally recommended for the persulfate activation [23]. Once prepared, each reaction mixture was dispensed into 20-mL amber vials and sealed with open top screw-on caps with Teflon septa, and care was taken to ensure minimal headspace left in the vials. Samples vials were kept in the dark to avoid potential interference of sunlight on the persulfate activation. At desired time intervals, sample vials were taken out and the concentrations of MTBE and its daughter products were measured by purge/trap-GC/MS, and pH and dissolved oxygen were also monitored by a pH meter and a dissolved oxygen meter, respectively



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