

DEGRADATION OF MTBE USING FENTON REAGENT

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ABSTRACT

Methyl tertiary-butyl ether (MTBE) has been commonly used as a fuel additive because of its many favorable properties that allow it to improve fuel combustion. Unfortunately, increased production and use have led to its introduction into the water supplies. Accordingly, research studies have been initiated to investigate the treatment of contaminated water. Degradation of MTBE in aqueous solution by Fenton reagent (Fe^{2+} and H_2O_2) was investigated. This study used Fenton reagent to oxidize MTBE with an attempt to explore the behavior of MTBE decomposition and measure how factors such as pH, $[\text{H}_2\text{O}_2]$ and $[\text{Fe}^{2+}]$ may influence the degradation of MTBE, and finally the optimum conditions were obtained. Under optimum conditions of 50 mL H_2O_2 , 0.65 g/L Fe^{2+} , pH=3-4 and room temperature, the initial 1000 mg/L MTBE solution was reduced by 99% within 120 min. The results showed that application of Fenton reagent was an effective method for degradation of MTBE.

Key words: MTBE, fenton reagent, hydroxyl radical, degradation

INTRODUCTION

In an attempt to reduce the environmental consequences associated with incomplete fuel combustion, the US Clean Air Act Amendments of 1990, required that oxygenates are added to reformulated gasoline. Since 1979, methyl tert butyl ether (MTBE) has been used in the USA as an octane enhancing replacement for lead, primarily in mid and high grade gasoline. It is the most commonly used (85%) fuels oxygenate (Johnson *et al.*, 2000). The reformulated gasoline contains 2.7% oxygen (by weight), which is approximately 11-15% of MTBE by volume (Johnson *et al.*, 2000). The widespread use of MTBE for gasoline oxygenation has led to its introduction into groundwater from spills and leaky underground storage tanks.

The wide application of MTBE is problematic (Franklin *et al.*, 2000). The bad taste and odour of MTBE can be detected down to 0.02 mg/L and inhalation of MTBE vapors may cause headaches and nausea at higher concentration (ppm) (Burgess

et al., 1998). In the USA, MTBE has been classified as a possible human carcinogen and a draft lifetime health advisory limit of 20-35 $\mu\text{g/L}$ issued (Squillace *et al.*, 1996). In addition, MTBE has the undesirable characteristic of being highly mobile in the environment as it is transported in the same velocity as groundwater in the aquifer. MTBE is poorly adsorbed, chemically and biologically stable, and very soluble in water, so making it very persistent in the environment.

Conventional treatment of MTBE contaminated groundwater is inefficient and unsatisfactory. Air stripping is difficult and requires a high air-to-water ratio (>200/l for 95% removal) because of its very low Henry's law constant. The low affinity of MTBE towards granular activated carbon makes this process undesirable and expensive (Anderson, 2000). It can be treated biologically (Bradley *et al.*, 1999) with special bacterial strains or natural isolated under aerobic conditions. However, the bacteria grow slowly with low yields of biomass and sometimes unstable. As a result, a viable bioremediation process for MTBE has not been fully developed.

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Advanced oxidation processes on the other hand, provide promising treatment alternative for MTBE. In these processes, organic compounds are transformed with reactions involving hydroxyl radicals ($\cdot\text{OH}$). Hydroxyl radicals have one unpaired electron and are strong, non selective, highly reactive oxidants, and only second to elemental fluorine in reactivity. Fenton oxidation produces $\cdot\text{OH}$ from Fenton reagent (Fe^{2+} and hydrogen peroxide, H_2O_2) and can degrade MTBE in aqueous solution.

Mechanism of MTBE degradation by Fenton reagent

The ether linkage and tertiary carbon structure are two characteristic features of MTBE. Generally, ethers are relatively uncreative compounds with the ether linkage being quite stable toward bases, oxidizing and reducing reagents. Cleavage usually requires quite strong conditions involving concentrated acids (HI or HBr) and high temperatures.

It is well accepted that oxidation reaction by Fenton reagent is mediated to a large extent by the $\cdot\text{OH}$ formed. Initial $\cdot\text{OH}$ attack MTBE by H abstraction can occur at either the methoxy group or any of the three methyl groups. The carbon centered radical generated after addition of oxygen forming the peroxy radical decomposes to different intermediates (Acero *et al.*, 2001). It is well known that the $\cdot\text{OH}$ is an electrophile and those C-H bonds adjacent to oxygen are responsible for a pronounced stereoelectronic effect that produces high rates of H atom abstraction. Therefore, reaction at the methoxy group is more likely to happen since H abstraction occurs most easily at the position α to the ether function (Reaction 1 and route A). The reaction of pathway A generates TBF, TBA and acetone. The second possible pathway, i.e. pathway B, ($\cdot\text{OH}$ attack on the methyl groups) (Reaction 2 and route B) leads to the formation of MA and acetone.

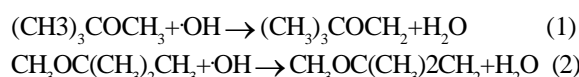


Fig. 1 shows the mechanism of MTBE decomposition by Fenton reagent and generation of the primary detected intermediates, which involves two different

pathways (route A and route B, respectively), corresponding to the two possible sites for the attack of the $\cdot\text{OH}$ on the MTBE molecule. The tetraoxides in route A and B, respectively, were formed by self termination reactions of the corresponding peroxy radicals. In route A, the main initial product of the reaction of Fenton reagent with MTBE is TBF. TBF can be generated by a series of chain reaction with radicals. In route B, the occurrences of $\cdot\text{OH}$ attack the methyl group of the tert carbon in MTBE (Xu *et al.*, 2003).

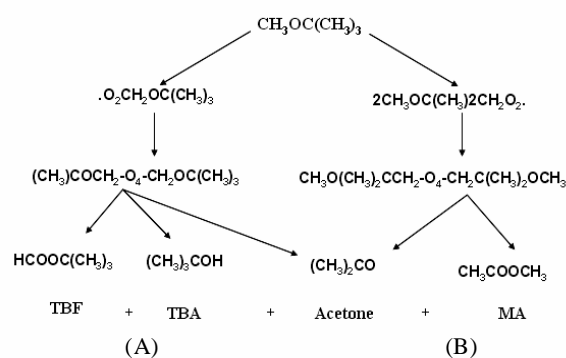


Fig. 1: Proposed pathways for the decomposition of MTBE by Fenton reagent

MATERIALS AND METHODS

The reagent of MTBE (99.9 %), FeSO_4 , 7 H_2O and H_2O_2 were obtained from Merck. Aqueous solution used for oxidation reactions were prepared using Millipore Milli-Q system. All glasswares were rinsed sequentially, with 10% nitric acid, tap water, methanol and distilled water. MTBE stock solution was prepared and stored at 4 °C. Calibration standards were prepared by serial dilution of the stock solutions.

Test samples for MTBE degradation studies were prepared from appropriate stock solution immediately before use.

The reaction was carried out in glass vials with 50 mL volume. The final volume reaction mixture was 10 mL in each vial. Taking an appropriate amount of MTBE stock solution, adding FeSO_4 and adjusting the pH value with dilute HCl 0.1N or sodium hydroxide 1N were conducted afterwards. The initial concentration of MTBE, in most cases, was 1000 mg/L. Because MTBE reduction depends on the concentrations of H_2O_2

and Fe^{2+} , the concentration of these chemicals were also varied in this study.

Excess $\text{Na}_2\text{S}_2\text{O}_3$ solution was added to vials to remove any residual H_2O_2 and terminate Fenton reaction. pH measurements were conducted before the addition of $\text{Na}_2\text{S}_2\text{O}_3$. In the experiment of the optimum conditions for degradation of MTBE by Fenton reagent, the reaction was stopped after 120 min.

To determine the optimum concentration of Fe^{2+} and H_2O_2 , several series of tests according to Table 1, were carried out. Various concentrations of Fe^{2+} (0.15, 0.25, 0.35, 0.45, 0.55, 0.65 and 0.75 g/L) with three concentrations of H_2O_2 (10, 30, 50 ml/L) were added the solution. The concentration of Fe^{2+} and H_2O_2 with maximum removal percentage was chosen as optimum value. All reactions were conducted at room temperature, 20 ± 1 °C. In this experiment, we chose 15, 30, 45, 60, 75, 90, 105, 120 min as the reaction time for analysis.

Table 1: Test series for obtaining optimum amount of $[\text{Fe}^{2+}]$ and H_2O_2 for MTBE decomposition

Fe^{2+} (g/L)	H_2O_2 (mg/L)
0.00	0
0.15	10
0.25	30
0.35	50
0.45	-
0.55	-
0.65	-
0.75	-

MTBE concentration was analyzed using a purge and trap gas chromatography mass selective detector system. The GC was a Philips PU-4410 equipped with a FID detector and packed (10% SE-30) capillary column (25.0 m 0.2 mm 1.5 m film thickness).

The temperature was programmed at 35 °C for 4 min, then increased to 180 °C at a rate of 10 °C/min, and held at 200 °C. The carrier gas used was helium. The injection port temperature was 180 °C and samples were injected using split mode 10:1. A sample was taken from the headspace of each vial and immediately injected into the GC/FID.

The experiment was conducted three separate times, and each individual assay was conducted in duplicate. The mean values are presented in the figs.

RESULTS

Effect of initial pH

In the degradation of MTBE with the addition of Fe^{2+} and H_2O_2 , the initial pH of the solution (pH=6.8) dropped gradually with time of reaction and after 15 min reached to 2.8-3, suggesting that H^+ are generated during this process. Fig. 2 shows pH variation after adding Fenton reagent.

Fig. 3 shows the relationship between MTBE removal percentage and pH under $\text{Fe}^{2+} = 0.65$ g/L and $\text{H}_2\text{O}_2 = 0.5$ mL. At higher pH (3 to 7) and $\text{pH} > 9$, the decomposition rate of MTBE noticeably declines because of the formation of Fe (II) complexes which hinder the further reaction of Fe^{2+} with H_2O_2 .

It can be observed from Fig. 3 that the best pH for the MTBE oxidation was 3. Therefore the best reaction pH value for the MTBE oxidation was chosen 3. In addition, it can be observed from Fig. 2 that pH after adding Fenton reagent dropped 2.8-3, hence it was not needed to adjust pH during next stages (Fe^{2+} and H_2O_2 optimization).

Effect of Fe^{2+} and H_2O_2

While addition of H_2O_2 without Fe^{2+} could not oxidize the MTBE, Fe^{2+} is the main ion that can catalyze H_2O_2 to generate $\cdot\text{OH}$. It was observed that removal percentage MTBE changed according to the amount of added Fe^{2+} . The amount of remaining MTBE decreased with increase of the concentration of Fe^{2+} in the solution.

Moreover it was observed that adding of only Fe^{2+} could not oxidize the MTBE. On the other hand Fe^{2+} alone could not decompose MTBE. The remaining MTBE decreased with the H_2O_2 concentration increased. The removal percentage of MTBE reached about 99% when $[\text{Fe}^{2+}] = 0.65$ g/L and $[\text{H}_2\text{O}_2] = 0.5$ mL (Fig. 4).

From this study described above, the maximal reaction efficiency in the chemical degradation of MTBE by Fenton reagent occurred under the following experimental conditions: solution containing up to 1000 mg/L were mixed the appropriate amount of FeSO_4 to and the reaction was initiated by adding H_2O_2 (final concentration was 0.5 mL) at pH 3. Under these conditions, MTBE removal could reach around 99% at room temperature. For control of MTBE degradation,

time points of 15, 30, 45, 60, 75, 90, 105, 120 min degradation was completed (Fig. 5). were used. After 120 min contact time, MTBE

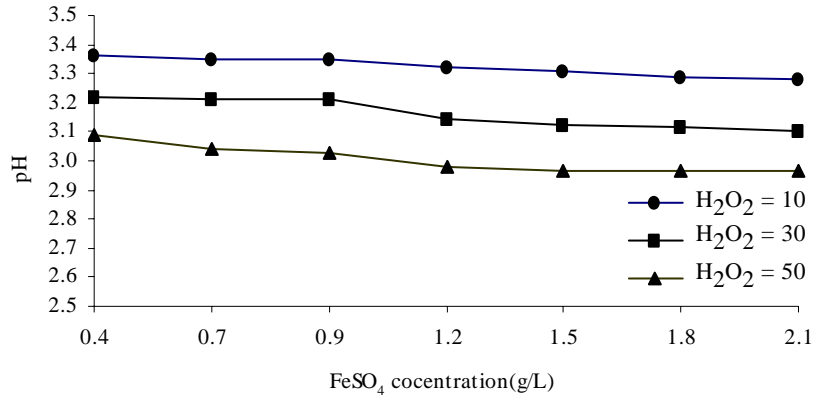


Fig. 2: Effect of FeSO₄ and H₂O₂ on pH of the solution

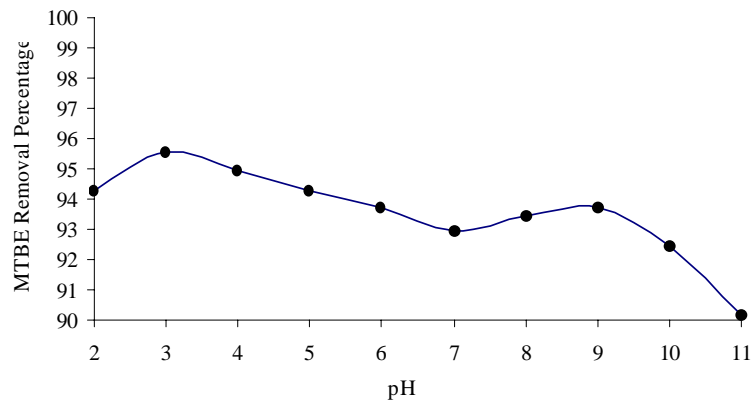


Fig. 3: Effect of pH on the oxidation of MTBE by Fenton reagent
[MTBE]=1000 mg/L, [Fe²⁺]=0.55 g/L, [H₂O₂]= 0.5 mL/L

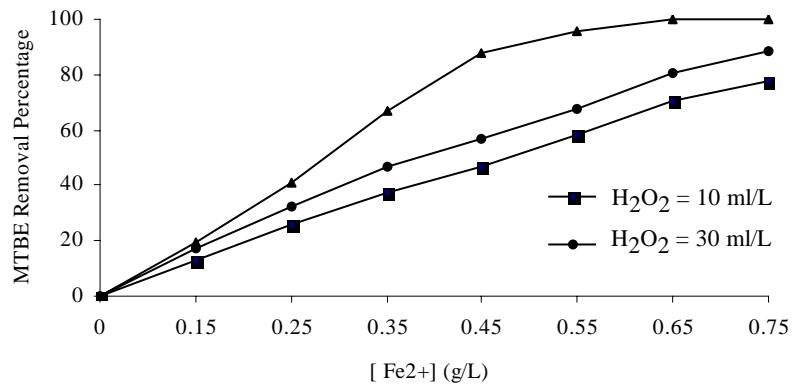


Fig. 4: Effect of Fe²⁺ and H₂O₂ on the oxidation of MTBE by Fenton reagent

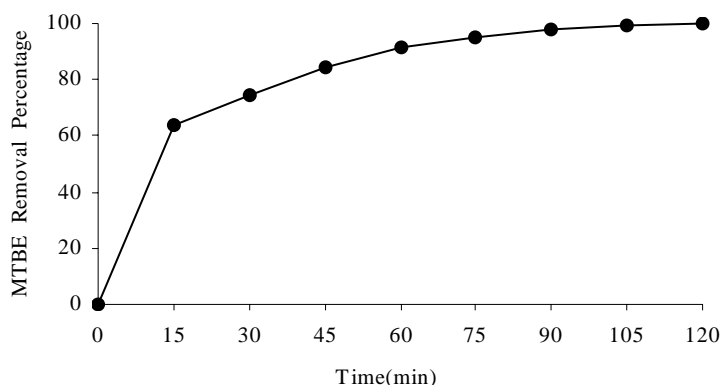


Fig. 5: Change MTBE removal percentage with time

DISCUSSION

This study demonstrated that Fenton reagent was successful in reducing MTBE concentration in water from 1000 mg/L to the proposed regulatory level of 20 µg/L. This reduction was achieved with a contact time of 120 min in room temperature. The reaction was found to be dependent on the pH of reaction and the amount of Fe²⁺ as well as H₂O₂ in the Fenton reagent.

Similar results were also reported by several authors. Basu and Wei (1988) found that the optimum pH using Fenton reaction for 2, 4, 6-trichlorophenol degradation was between 2.0 and 3.5. Sedlak and Andren (1991) pointed out that the best pH for chlorodiphenyl and chlorobenzene was between 2 and 4 and also due to the precipitation of ferric oxyhydroxides which have low activity and could impede the reaction of Fe³⁺ with H₂O₂ to regenerate Fe²⁺. Both aspects are favoured at higher pH and this precipitation is experimentally confirmed by the presence of turbidity in the samples of experiments carried out at pH 5. On the other hand, the lower efficiency at pH < 2.5 is due to the formation of complex species [Fe(II)(H₂O)₆]²⁺ which reacts more

slowly with H₂O₂ than [Fe(II)(OH)(H₂O)₅]⁺, and therefore, generate less ·OH. In addition, the scavenging effect of ·OH by H⁺ becomes important at a very low pH and the reaction of Fe³⁺ with H₂O₂ is then inhabited.

In this study, the maximum reaction efficiency in the chemical degradation of MTBE by Fenton reagent occurred under the following experimental conditions: solution containing 1000 mg/L were mixed with the appropriate amount of FeSO₄ and the reaction was initiated by adding H₂O₂ (molar ratio of 1:1) at pH 3. Under these conditions, MTBE removal could reach around 99% at room temperature. After 120 min contact time, MTBE degradation was completed.

Observations of Barreto *et al.*, (1995) that the reduction of MTBE by Fenton reagent is independent of Fe²⁺ concentration are in contrast to pervious findings (Ray *et al.*, 2000 and Xu *et al.*, 2004), and the findings of the present study. Optimum conditions for generating the OH· radical by Fenton reagent depends on pH conditions and concentration of H₂O₂ and Fe²⁺.

In this study, under optimum conditions; 50 mL/l H₂O₂, 0.65 g/L Fe²⁺, pH=3-4 and room temperature, the initial 1000 mg/L MTBE solution was reduced by 99% within 120 min.

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