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Decomposition rates of methyl *tert*-butyl ether and its by-products by the Fenton system in saline wastewaters

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Abstract

The primary aim of this study was to gain an understanding of how different concentrations of chloride ions affect the oxidation of methyl *t*-butyl ether (MTBE) in the Fenton system. Oxidation of MTBE in a chloride-free reaction mixture was rapid and very effective, but was inhibited even by the lowest chloride concentrations employed. After 90 min of reaction in the presence of 0.05–1 M of chloride ions, the effectiveness of MTBE degradation dropped to 97–68%, respectively. It was found that the inhibition of Fenton's reaction by chloride ions depends on two factors, thus, complexation and radical scavenging. Under the experimental conditions of the current study, comparison of rate constants for possible degradation reactions showed that most of the $^{\bullet}OH$ radicals formed by the reaction of H_2O_2 with Fe^{2+} were consumed by Cl^-. The influence of chloride ions on the degradation of four intermediate products in identical system was also studied: in chloride-free solution under the same experimental conditions, *t*-butyl alcohol (TBA) was the major by-product, followed by *t*-butyl formate (TBF) and acetone. In the process of degradation, the distribution of MTBE intermediates varied with the different chloride concentrations. Furthermore, by varying the concentrations of Fe^{2+} and H_2O_2, it was possible to track the behavior of MTBE degradation products in the Fenton system in order to find optimal conditions for saline wastewater treatment.

Keywords: Advanced oxidation processes (AOPs); Hydrogen peroxide; Fenton reaction; MTBE; Oxidation; Salinity

1. Introduction

Methyl *t*-butyl ether (MTBE) is widely used as an octane enhancer and fuel oxygenation additive in gasoline to provide a cleaner burning fuel with reduced vehicle exhaust emissions [1–4]. Despite the several technological benefits of using MTBE as a fuel additive, its widespread use, as well as its physicochemical features, have raised a very serious environmental problem with regard to water quality. Nowadays, methyl *t*-butyl ether has become one of the most common contaminants in shallow ground waters and drinking water, mainly as a consequence of petroleum leakage from underground tanks [5]. The environmental fate of MTBE depends closely on its excellent solubility in water and its very low soil sorption coefficient. This means that MTBE is only weakly retained by soil layers and is rapidly transported to ground waters. Another reason for MTBE's persistence is that its molecular structure is difficult to break down. Under normal conditions, the presence of the *t*-butyl group inhibits environmental degradation, thus, effectively retarding natural biodegradation [6,7].

Since, it has been demonstrated that MTBE removal by conventional remediation technologies is costly and ineffective, attention has turned to advanced oxidation processes (AOPs) for its degradation; several studies have indicated their usefulness [8–10]. AOPs are based on the generation of highly reactive hydroxyl radicals, which then rapidly and non-selectively oxidize a broad range of organic pollutants. Hydroxyl radicals are generated by different combinations of oxidizing agents, not to mention a whole range of photocatalytic systems [11–17]. Among these processes, the one involving Fenton's reagent (Fe^{2+}/H_2O_2) has been the subject of numerous investigations into the mechanisms, reaction kinetics and efficiencies of processes for removing organic pollutants [18–21]. The Fenton process depends on electron transfer between H_2O_2 and Fe^{2+}, the latter acting as a homogeneous catalyst [18]. With an oxidizing potential of 2.6 V versus NHE, these $^{\bullet}OH$ radicals are capable of oxidizing a wide range of organics in wastewater. The oxidant used in the process is easy to handle and environmen-

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Abbreviations: AOPs, advanced oxidation processes; DO, dissolved oxygen; FID, flame ionization detector; MA, methyl acetate; MTBE, methyl *tert*-butyl ether; TBA, *tert*-butyl alcohol; TBF, *tert*-butyl formate

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tally friendly, because the final decay products (water, oxygen and ferric hydroxide) exert no harmful effect. The performance of the Fenton system is governed mainly by the concentration of hydroxyl radicals produced in the reaction mixtures. The concentration of hydroxyl radicals formed in the process may be strongly affected by the background impurities present in the wastewater stream. Inorganic anions, such as chloride are very common in most wastewaters [22]. Chloride ion concentration in saline wastewater varies from 0.1 to 1 M. Since the accumulation of chloride ions may inhibit the Fenton process to a significant degree, the formation of more or less reactive ferrous and ferric species for the Fenton reaction is likely, which may affect the overall efficiency of the system [23].

The effect of inorganic salts on overall decomposition rates has usually been ignored in studies of the applicability of AOPs to the degradation of certain groups of contaminants. Recently, we undertook a preliminary examination of the effect of selected inorganic anions on the effectiveness of the Fenton advanced oxidative treatment of waters contaminated with methyl *t*-butyl ether [24]. With respect to chloride, inhibition of oxidation was clearly in evidence, whereas the addition of sulfates or perchlorates influenced these rates to a much lesser extent. The present study was, therefore, undertaken in order to examine in detail the influence of chloride anions on the degradation rates of MTBE and its degradation products in the Fenton system.

2. Materials and methods

2.1. Chemicals and reagents

MTBE (99.9%), *t*-butyl formate (TBF 99%), *t*-butyl alcohol (TBA 99%), methyl acetate (MA 99%), acetone (99%) and iron(II) perchlorate hydrate (98%) were purchased from Aldrich. Analytical grade sodium chlorate and perchlorate were obtained from Standard (Lublin, Poland), and 30% hydrogen peroxide from Techmar (Poland).

Stock solution of H_2O_2, MTBE and ferrous salt were prepared in deionized water (TOC < 5 ppb, 5 μS/cm). Deionized water was obtained in-house by treating tap water with a carbon filter, reversed osmosis, a mixed bed of ion exchangers and a 0.45 μm filter. The stock MTBE solution (10 mM) was prepared and stored at 4 °C for a maximum of 1 week. To prevent the oxidation of iron by dissolved oxygen, the ferrous perchlorate solution was prepared by dissolving the appropriate weight of $Fe(ClO_4)_2 \times H_2O$ in 0.01 M $HClO_4$.

2.2. Degradation experiment

Oxidation of MTBE has been conducted in dilute aqueous solution of MTBE 5×10^{-4} M. The initial concentration of hydrogen peroxide was 7.5×10^{-3} M. Chloride concentrations were adjusted to 0.05, 0.1, 0.2 and 1 M with NaCl. Experiments were conducted in a well stirred and thermostated batch reactor (volume = 0.25 L) at 25 ± 1 °C. All reactions were performed in the darkness in order to avoid photo-reactions. Reaction mixtures were obtained by taking the appropriate aliquot of MTBE stock solution, adding Fe^{2+} and adjusting the pH with perchloric acid to pH 2.8. The reaction was started by the addition of H_2O_2. During the experiment, samples were collected after various reaction times and immediately quenched with 20 μL of 0.01N $Na_2S_2O_3$. The degradation of MTBE was stopped after 90 min.

2.3. Analytical procedures

Analysis of Fe(II) was carried out by using *o*-phenantroline colorimetric method at 510 nm. The molar extinction coefficient of Fe(II)-phenantroline complex was $1.11 \times 10^4\ M^{-1}\ cm^{-1}$.

Hydrogen peroxide was determined iodometrically ($[H_2O_2] > 10^{-3}$ M) or spectrophotometricaly using TiCl method (Eisenberg, 1943) ($[H_2O_2] < 10^{-3}$ M). No interferences have been noticed with the concentration of ferric ions used. The molar absorption coefficient of the titanium peroxo complexes was measured as $714\ M^{-1}\ cm^{-1}$. pH measurememnt were made with pH-meter (HACH EC 20) calibrated at 25 °C with acidic standard buffers 3.0. MTBE and its by-products *t*-butyl formate, *t*-butyl alcohol, acetone and methyl acetate were analyzed directly on a gas chromatograph (Perkin-Elmer Claras 500) coupled to a flame ionization detector (FID) equipped with a 30 m capillary column of i.d. 0.32 mm and film thickness 0.25 μm (Perkin-Elmer Elite Series PE). The inlet and detector temperatures were set at 250 and 180 °C, respectively. The sequence of oven temperatures for the analyses was 35 °C for 3 min, 35 °C/min ramp to 110 °C and held for 1 min. The detection limit of the method for all the compounds analyzed was 5 μg/L.

The experiment was conducted on three separate occasions, and each individual assay was performed in duplicate. In the figures, mean values are presented together with vertical error bars indicating the standard deviation of the three experiments.

3. Results and discussion

3.1. Oxidation of MTBE in the presence of chloride ions

A comparison was made between MTBE oxidation in a chloride-free solution and in solutions with final chloride concentrations from 0.05 to 1 M (Fig. 1). In the absence of chloride ions, oxidation was rapid and very effective. After 10 min, the MTBE concentration dropped to 10% of the initial level, and after 90 min to 3% of that level. With 0.05, 0.1 or 0.2 M of Cl^- in the oxidation mixture (the respective $[Cl^-]/[Fe^{2+}]$ ratios = 50, 100 and 200), inhibition of degradation was clearly in evidence. The effectiveness of degradation also varied. After 90 min of the reaction in the presence of 0.05–0.2 M of chloride ions, the effectiveness of MTBE degradation dropped to 85–87%. With a 1 M concentration of chloride ions (the $[Cl^-]/[Fe^{2+}]$ ratio raised to 1000), the decomposition of MTBE after 90 min of reaction dropped to 68%. In a chloride-free solution, the Fenton process takes place in two phases: first, ferrous ions react very quickly with hydrogen peroxide to produce a large number of hydroxyl radicals (see Table 1—reaction (1.1)), which then react rapidly with MTBE to initiate degradation. In addition, the ferric ions produced in the first stage can react with hydrogen peroxide to produce hydroperoxyl radicals and ferrous ions (reactions