

# Influence of inorganic ions on MTBE degradation by Fenton's reagent

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## Abstract

The effect of selected inorganic anions on the effectiveness of the Fenton advanced oxidative treatment of waters contaminated with methyl *t*-butyl ether (MTBE) was examined. With respect to the chloride or phosphate ions used, inhibition of oxidation was clearly in evidence, whereas addition of sulfates or perchlorates influenced these rates to a much smaller extent. Anions suppress MTBE decomposition in the following sequence:  $\text{ClO}_4^- < \text{SO}_4^{2-} < \text{Cl}^- < \text{H}_2\text{PO}_4^-$ . There are very probably several mechanisms affecting oxidation. Complexation reactions with iron are likely to affect the distribution and reactivity of iron species with  $\text{H}_2\text{O}_2$ . Hydroxyl radicals may also be scavenged from less reactive inorganic radicals. Additionally, in order to explore the degradation mechanism of MTBE by Fenton's reagent in the presence of different salts, four intermediate products of MTBE oxidation were identified: *tert*-butyl formate (TBF), *tert*-butyl alcohol (TBA), acetone, and methyl acetate (MA).

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## 1. Introduction

Since 1979, methyl *tert*-butyl ether (MTBE) has been used commercially as an octane enhancer to replace tetraethyl lead in fuel. For a long time it has been the favorite gasoline oxygenate, mainly because of its numerous desirable properties, such as the high octane rating, low cost and favorable transfer and blending characteristics [1–3]. The major environmental concern stems from its high water solubility. MTBE has been found in the environment, especially in groundwater, as a result of fuel spills, and leaks from gasoline storage tanks and pipelines [4].

The Fenton oxidative system has reported promising results to clean up water contaminated with various organic pollutants. The method is one of the group of homogenous AOPs, involving a mixture of ferrous ions and  $\text{H}_2\text{O}_2$ , which generates highly reactive hydroxyl radicals at room temperature [5]. The process is based on electron transfer between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  acting as a homogenous catalyst. The radical generated is a very strong, non-selective agent with rate constants often in the order of  $10^7$  to  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . Its oxidizing potential of 2.8 V versus normal hydrogen electrode (NHE) is capable of degrading a wide range

of organics in wastewater [6–8]. Table 1 summarizes the Fenton reactions. Furthermore, neither complex instrumentation nor pressurized systems are required for this type of AOP.

However, contaminated waters usually contain not only MTBE, but also substantial concentrations of other substances (chloride, phosphate, sulfate, nitrate). The groundwater contains sulfate and chloride anions at concentrations levels which can vary from 0.1 to 100 mM. The inorganic ions leads to the formation of more or less reactive ferrous and ferric species for the Fenton reaction and it can change the overall efficiency of the system. In the presence of inorganic ions the rate for the reaction  $\text{H}_2\text{O}_2$  with ferrous ion is different. The rate of decomposition of  $\text{H}_2\text{O}_2$  in the presence of sulfate ions was more rapid than in the presence of perchlorate anion. In contrast, the presence of chloride in reaction mixture did not changed the rate of  $\text{H}_2\text{O}_2$  decomposition [8].

Scavenging of  $\text{OH}^\bullet$  by anions is also likely to take place, when inorganic radicals are formed that are less reactive than hydroxyl radicals. A summary of the complex reactions with ferric and ferrous ions in the presence of inorganic ions is presented in Table 2. Usually the effects of inorganic salts on the overall rates of decomposition of  $\text{H}_2\text{O}_2$  and organic compounds have been ignored. In some cases, experiments have been conducted in the presence of only one anion. In view of this, the present work was undertaken in order to compare the effects

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Table 1  
Summary of Fenton reactions [5,18–20]

Reaction	Constant $k$
$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{HO}^\bullet + \text{HO}^- + \text{Fe}^{3+}$	(1) $k_1 = 55\text{--}76 \text{ M}^{-1} \text{ s}^{-1}$
$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}\text{--}\text{OOH}^{2+} + \text{H}^+$	(2a) $k_{2a} = 3.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$
$\text{Fe}\text{--}\text{OOH}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}(\text{OH})(\text{HO}_2)^+$	(2b) $k_{2b} = 2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
$\text{Fe}\text{--}\text{OOH}^{2+} \rightarrow \text{Fe}^{2+} + \text{HO}_2^\bullet$	(3a) $k_{3a} = 2.3 \times 10^{-3} \text{ s}^{-1}$
$\text{Fe}(\text{OH})(\text{HO}_2)^+ \rightarrow \text{Fe}^{2+} + \text{HO}_2^\bullet + \text{OH}^-$	(3b) $k_{3b} = 2.3 \times 10^{-3} \text{ s}^{-1}$
$\text{HO}^\bullet + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{HO}^-$	(4) $k_4 = 4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$
$2\text{HO}^\bullet \rightarrow \text{H}_2\text{O}_2$	(5) $k_5 = 5.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
$\text{HO}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^\bullet$	(6) $k_6 = 3.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$
$2\text{HO}_2^\bullet \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	(7) $k_7 = 8.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$
$\text{Fe}^{2+} + \text{HO}_2^\bullet \rightarrow \text{Fe}^{3+} + \text{HO}_2^-$	(8) $k_8 = 1.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
$\text{Fe}^{3+} + \text{HO}_2^\bullet \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+$	(9) $k_9 = 1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$
$\text{RH} + \text{HO}^\bullet \rightarrow \text{H}_2\text{O} + \text{R}^\bullet$	(10)
$\text{R}^\bullet + \text{H}_2\text{O}_2 \rightarrow \text{ROH} + \text{HO}^\bullet$	(11)
$\text{R}^\bullet + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{products}$	(12)
$\text{R}^\bullet + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{products}$	(13)
$\text{R}^\bullet + \text{O}_2 \rightarrow \text{ROO}^\bullet$	(14)
$\text{ROO}^\bullet + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{products}$	(15)
$\text{ROO}^\bullet + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{products}$	(16)

Table 2  
Complex reactions with ferric and ferrous ions in the presence of inorganic ions [10,21,22]

Reaction	$\log k$
$\text{Fe}^{2+} + \text{Cl}^- \rightarrow \text{FeCl}^+$	(1) 0.45
$\text{Fe}^{3+} + \text{Cl}^- \rightarrow \text{FeCl}^{2+}$	(2) 0.82
$\text{Fe}^{3+} + 2\text{Cl}^- \rightarrow \text{FeCl}_2^+$	(3) 1.01
$\text{Fe}^{2+} + \text{SO}_4^{2-} \rightarrow \text{FeSO}_4$	(4) 1.36
$\text{Fe}^{3+} + \text{SO}_4^{2-} \rightarrow \text{FeSO}_4^+$	(5) 2.59
$\text{Fe}^{3+} + 2\text{SO}_4^{2-} \rightarrow \text{Fe}(\text{SO}_4)_2^-$	(6) 3.65
$\text{Fe}^{2+} + \text{H}_2\text{PO}_4^- \rightarrow \text{FeH}_2\text{PO}_4^+$	(7) 2.75
$\text{Fe}^{3+} + \text{H}_2\text{PO}_4^- \rightarrow \text{FeH}_2\text{PO}_4^{2+}$	(8) 5.84
$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}(\text{HO}_2)^{2+} + \text{H}^+$	(9) -2.5
$\text{Fe}(\text{HO}_2)^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}(\text{OH})(\text{HO}_2)^+ + \text{H}^+$	(10) -3.7

of chloride, sulfate and dihydrophosphate on the overall rate of MTBE oxidation under the same experimental conditions. The influence of these anions on the oxidation of contaminants is of the highest importance because they are naturally present in different concentrations in contaminated waters.

## 2. Materials and methods

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

Deionized water was obtained in-house by treating tap water with a carbon filter, reversed osmosis, a mixed bed of ion exchangers and an 0.45  $\mu\text{m}$  filter. The stock MTBE solution (10 mM) was prepared and stored at 4 °C for a maximum of 1 week. In order to prevent the oxidation of iron by dissolved oxygen, the solution of ferrous perchlorate was prepared by dissolving the appropriate weight of  $\text{Fe}(\text{ClO}_4)_2$  in  $\text{HClO}_4$  (0.01 M).

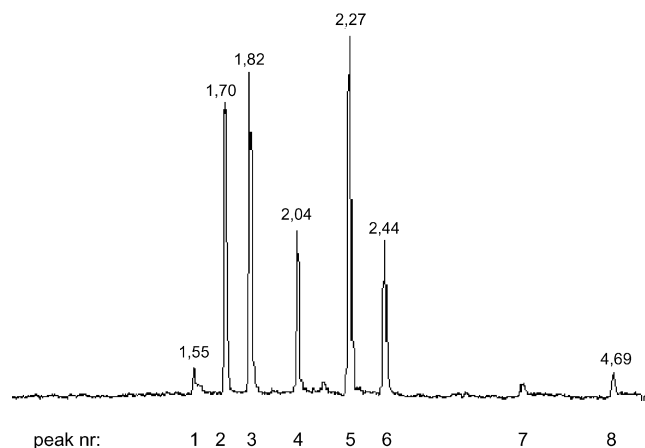


Fig. 1. A GC chromatogram of the test mixture. Numbering of compounds: (2) acetone, (3) *tert*-butyl alcohol (TBA), (4) methyl *tert*-butyl ether, (5) methyl acetate (MA), (6) *tert*-butyl formate (TBF), and (1, 7 and 8) unidentified.

The initial concentration of MTBE was 0.5 mM, that of hydrogen peroxide was 7.5 mM. The ferrous ion:MTBE initial ratio was maintained at 2:1 ( $\text{mol mol}^{-1}$ ) at time 0. The inorganic salt concentrations were 100 mM of NaCl and  $\text{NaClO}_4$ , 33 mM of  $\text{Na}_2\text{SO}_4$  and 17 mM of  $\text{Na}_3\text{PO}_4$ . The ionic strength of all the reaction mixtures was 0.1 M.

The reactions were carried out in a batch reactor ( $V = 0.25$  l). The oxidation experiments were performed in darkness and at  $25 \pm 1$  °C. Reaction mixtures were obtained by taking the appropriate aliquot of MTBE stock solution, adding  $\text{Fe}^{2+}$ , and adjusting the pH with perchloric acid. The reaction was started by the addition of  $\text{H}_2\text{O}_2$ . During the experiment, samples were collected after various reaction times and immediately quenched with 20  $\mu\text{l}$  of 0.1N solution of  $\text{Na}_2\text{S}_2\text{O}_3$ . The degradation of MTBE was stopped after 90 min.

Hydrogen peroxide was determined by iodometric titration. MTBE and its by-products *tert*-butyl formate, *tert*-butyl alcohol, acetone, and methyl acetate (MA) were directly analyzed on a gas chromatograph (Perkin-Elmer Claus 500) coupled to a flame ionization detector (FID), equipped with a 30 m capillary column, 0.32 mm i.d. and film thickness 0.25  $\mu\text{m}$  (Perkin-Elmer Elite Series PE). The inlet and detector temperatures were set at 250 and 180 °C, respectively. The sequence of oven temperatures for analyses was 35 °C for 3 min, 35 °C/min ramp to 110 °C and held for 1 min. One of these chromatograms is shown in Fig. 1 by way of example. The method detection limit for all analysed compounds were 5  $\mu\text{g/l}$ .

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

## 3. Results and discussion

In the experimental setup, the anions originate from two sources: (i) the counter ions of hydrogen and ferrous ions, and (ii) the background ions. In this study we selected four background ions for examination: perchlorate, sulfate, chlorate,

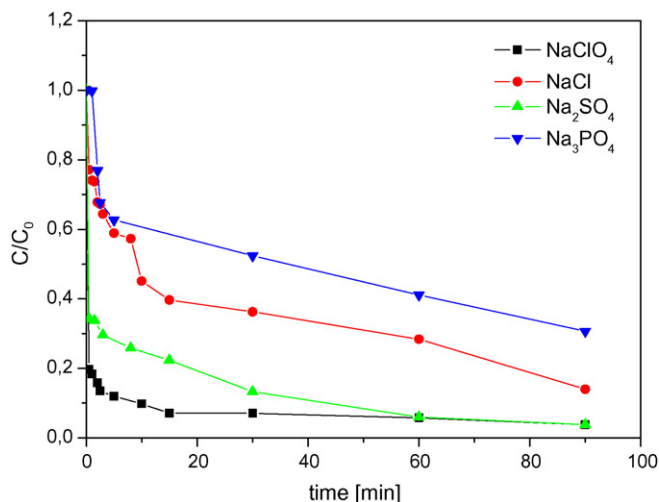


Fig. 2. Effect of inorganic ions on MTBE degradation (experimental condition: [MTBE] =  $5 \times 10^{-4}$  M, [Fe<sup>2+</sup>] =  $1 \times 10^{-3}$  M, [H<sub>2</sub>O<sub>2</sub>] =  $7.5 \times 10^{-3}$  M, [NaClO<sub>4</sub>] = 0.1 M, [NaCl] = 0.1 M, [Na<sub>2</sub>SO<sub>4</sub>] =  $33 \times 10^{-3}$  M, [Na<sub>3</sub>PO<sub>4</sub>] =  $17 \times 10^{-3}$  M, [Na<sub>2</sub>CO<sub>3</sub>] =  $33 \times 10^{-3}$  M, I = 0.1 M, pH = 2.8, T =  $25 \pm 1$  °C).

and phosphate. The counter ions of hydrogen and ferrous ions are ClO<sub>4</sub><sup>-</sup>. Because of the high background ion concentration (approximately 0.1 M), which is far higher than the concentration of ferrous and hydrogen ions ( $1 \times 10^{-3}$  M), the effect of counter ions on the reaction will not be referred to further.

Fig. 2 shows the effect of the background ions on MTBE oxidation in the Fenton system. The initial concentration of ether was  $5 \times 10^{-4}$  M, that of hydrogen peroxide was  $7.5 \times 10^{-3}$  M. The ionic strength of all salts was 0.1 M. The pH was fixed at 2.8 and remained practically constant ( $2.8 \pm 0.08$ ). The Fe<sup>2+</sup>/MTBE initial ratio was maintained to 2 at time 0. This molar ratio proved effective for MTBE oxidation at a controlled rate that made it possible to monitor the progress of the reaction during a 90 min period in the presence of ClO<sub>4</sub><sup>-</sup>. As can be seen from Fig. 2, the Fenton reaction is extremely sensitive to the inorganic anions present in the solution.

In the case of the chloride, and dihydrophosphate ions, oxidation is clearly inhibited, but the addition of sulfate influences the reaction to a much smaller extent. Also, degradation was less effective. After 90 min of the reaction, MTBE in the presence of sulfate is degraded in 96%. When chloride and dihydrophosphate were introduced into the reaction mixture, the amount of degraded MTBE fell to 86 and 65%, respectively. The anions thus suppress the decomposition of MTBE in the following sequence: ClO<sub>4</sub><sup>-</sup> < SO<sub>4</sub><sup>2-</sup> < Cl<sup>-</sup> < H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. There are at least two reasons why ClO<sub>4</sub><sup>-</sup> has a lesser effect on decomposition than the other ions: (a) perchlorate ions do not form complexes with Fe(II) and Fe(III), and (b) they do not react with OH<sup>•</sup> [9]. Therefore, the dominant iron entity under the conditions of this experiment (pH 2.8) represents Fe<sup>2+</sup> in free form [10].

The experiments showed that MTBE decomposition was slower in the presence of sulfate, chloride, and dihydrophosphate than in the presence of ClO<sub>4</sub><sup>-</sup>. Complexation reactions with Fe could be occurring here – these can affect the distribution of the iron species and their reactivity with H<sub>2</sub>O<sub>2</sub> – but

another mechanism might be the scavenging of hydroxyl radicals and the formation of inorganic radicals.

The presence of SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, ions leads to competition between the organics and the hydroxyl radicals, which retards MTBE oxidation. The inorganic ions react with hydroxyl radicals to generate inorganic radicals.

In the presence of SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, various radicals may be formed. In between may of them the dichlorine (Cl<sub>2</sub><sup>•-</sup>), the sulfate (SO<sub>4</sub><sup>•-</sup>) and dihydrophosphate (H<sub>2</sub>PO<sub>4</sub><sup>•</sup>) radicals represent the predominant radicals in acidic solution (pH < 3). Cl<sub>2</sub><sup>•-</sup>, SO<sub>4</sub><sup>•-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>•</sup>, are strong oxidant species. The second-order rate constants for their reactions with most of the organic solutes lie within the range of 10<sup>6</sup> to 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> for H<sub>2</sub>PO<sub>4</sub><sup>•</sup>, 10<sup>3</sup> to 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> for Cl<sub>2</sub><sup>•-</sup>, and 10<sup>6</sup> to 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> for SO<sub>4</sub><sup>•-</sup> [11,12]. These values indicate that H<sub>2</sub>PO<sub>4</sub><sup>•</sup>, Cl<sub>2</sub><sup>•-</sup> and SO<sub>4</sub><sup>•-</sup> are less or much less reactive than the OH<sup>•</sup> radical (10<sup>7</sup> to 10<sup>10</sup>) M<sup>-1</sup> s<sup>-1</sup> [13]. The inhibiting effect of anions on the rates of conversion of organic compounds depends not only on the scavenging of OH<sup>•</sup> radicals. The complexation of ferrous ions which take place in the generation of OH<sup>•</sup> radicals. The influence of inorganic ions on the formation of OH<sup>•</sup> (reaction (1) in Table 1) strongly depends on regeneration of ferrous ions (Fe(III) to Fe(II)) as shown in reactions (3a) and (3b) [14]. The inorganic ions decrease the rates of formation of OH<sup>•</sup> radicals because the rates of regeneration of ferrous ion (reactions (3a) and (3b)) is decreased due the formation of chloro-, sulfato-complexes of ferric ion, that competes with the formation of peroxocomplexes (reactions (2a) and (2b)).

The initial concentrations of ferrous ion H<sub>2</sub>O<sub>2</sub> were 1 and 7.5 Mm, respectively. These values meant that H<sub>2</sub>O<sub>2</sub> is in excess. The oxidation of MTBE with Fenton's reagent in our experiment is a two-stage reaction. The first stage is a Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> reaction in which Fe<sup>3+</sup> and OH<sup>•</sup> are produced rapidly (reaction (1) in Table 1) and MTBE decomposes swiftly. In the second stage, MTBE now decomposes more slowly because of the lower concentrations of Fe<sup>2+</sup> and OH<sup>•</sup> formed during the reaction. Additionally, OH<sup>•</sup> attacks other compounds (e.g. decomposition products) besides MTBE. The second stage can be regarded as a series of Fenton-like reactions, since iron (III) species are predominately present in the solution (reactions (2)–(9) in Table 1).

Ions such as Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> may undergo complex reactions with ferric and ferrous ions, as shown in reactions (1)–(6) summarized in Table 2. The forms of the phosphate ions present in solution are determined by the pH. When pH ≤ 3, phosphate exist primarily in the form of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and they too can undergo complex reactions with ferrous and ferric ions (reactions (7)–(11) in Table 2). These complexes retard the reaction, as a result of which hydroxyl radicals are produced and the rate of oxidation falls.

Inspection of Table 2 shows that the oxidation rate by Fenton's reagent is correlated with the concentration of free ferrous and ferric ions. The values of log K for the ferrous ion complexes are much lower than those for the ferric types. This means that free ferrous ions are still present in the solution, and the generation of hydroxyl radicals is still possible. When the initial amount of ferrous ions is  $1 \times 10^{-3}$  M (our experimental conditions) the concentration of non-complexed Fe<sup>2+</sup> will decrease in

the following sequence:  $\text{ClO}_4^- > \text{Cl}^- \sim \text{SO}_4^{2-} > \text{H}_2\text{PO}_4^-$ . This indicates that with a lower concentration of free ferrous ions, MTBE degradation is slower. Additionally, in the  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  stage, most of the ferric ions were present as an  $\text{Fe(III)-complex}$ . Ferric ion is able to form the complexation species with  $\text{H}_2\text{O}_2$  as well as with chloride or other inorganic anions. At  $\text{pH} < 3$  ferric ions react spontaneously with  $\text{H}_2\text{O}_2$ , which preliminary leads to the formation of two iron(III)-peroxo-complexes, thus  $\text{Fe}^{\text{III}}(\text{OH}_2)^{2+}$  and  $\text{Fe}^{\text{III}}(\text{OH})(\text{HO}_2)^+$  that compete with formation of complexes with other inorganic anions. These complexes are assumed to slowly decomposed in a unimolecular way to yield  $\text{Fe}^{2+}$  and  $\text{HO}_2^\bullet$ . The values of  $\log K$  for the equilibrium for ferric-peroxo complexes are much lower than those for the ferric chloro- or sulfo-complexes;  $\log K$  values are  $-2.5$  and  $-3.7$  for  $\text{Fe}^{\text{III}}(\text{OH}_2)^{2+}$  and  $\text{Fe}^{\text{III}}(\text{OH})(\text{HO}_2)^+$ , respectively. Therefore, in the presence of different salts, the rate of MTBE oxidation decreased as  $\log K$  for the reaction of ferric and ferrous complex species with inorganic ions increased. On the other hand the chloro-complexes of  $\text{Fe(II)}$  are characterized by the same reactivity as the free ferrous ions for the overall reaction with  $\text{H}_2\text{O}_2$  [10]. However, sulfo-complexes of  $\text{Fe(II)}$  decompose of  $\text{H}_2\text{O}_2$  faster than free  $\text{Fe(II)}$ . It may suggest that in the presence

of chloride and sulphate ions the rate of MTBE degradation decreased because regeneration of ferrous ions was inhibited by formation of unreactive ferric complexes. De Laat et al. while modeling  $\text{Fe(III)}/\text{H}_2\text{O}_2$  system in the presence of sulfate, indicated that the decrease of rate of the oxidation of atrazine can be mostly attributed to a decrease of the formation of unreactive  $\text{Fe(III)-sulphato}$  complexes [8].

To explore the degradation mechanism of MTBE by Fenton's reagent in the presence of different salts, four intermediate products of MTBE oxidation were identified by GC analysis: *tert*-butyl formate, *tert*-butyl alcohol (TBA), acetone, and methyl acetate (MA). These degradation products were also identified in previous studies when other  $\text{OH}^\bullet$  producing AOPs were applied, [15,16].

During the first 3–5 min of the reaction, when the concentration of  $\text{OH}^\bullet$  was in the highest range, MTBE was consumed rapidly: 35–87% of the initial MTBE concentration was converted to products, depending on the kind of inorganic anion present. After 3–5 min, the rate of oxidation was significantly less, but  $5 \times 10^{-4}$  M of the MTBE solution was nevertheless reduced by 65–96% during 90 min of the experiment.

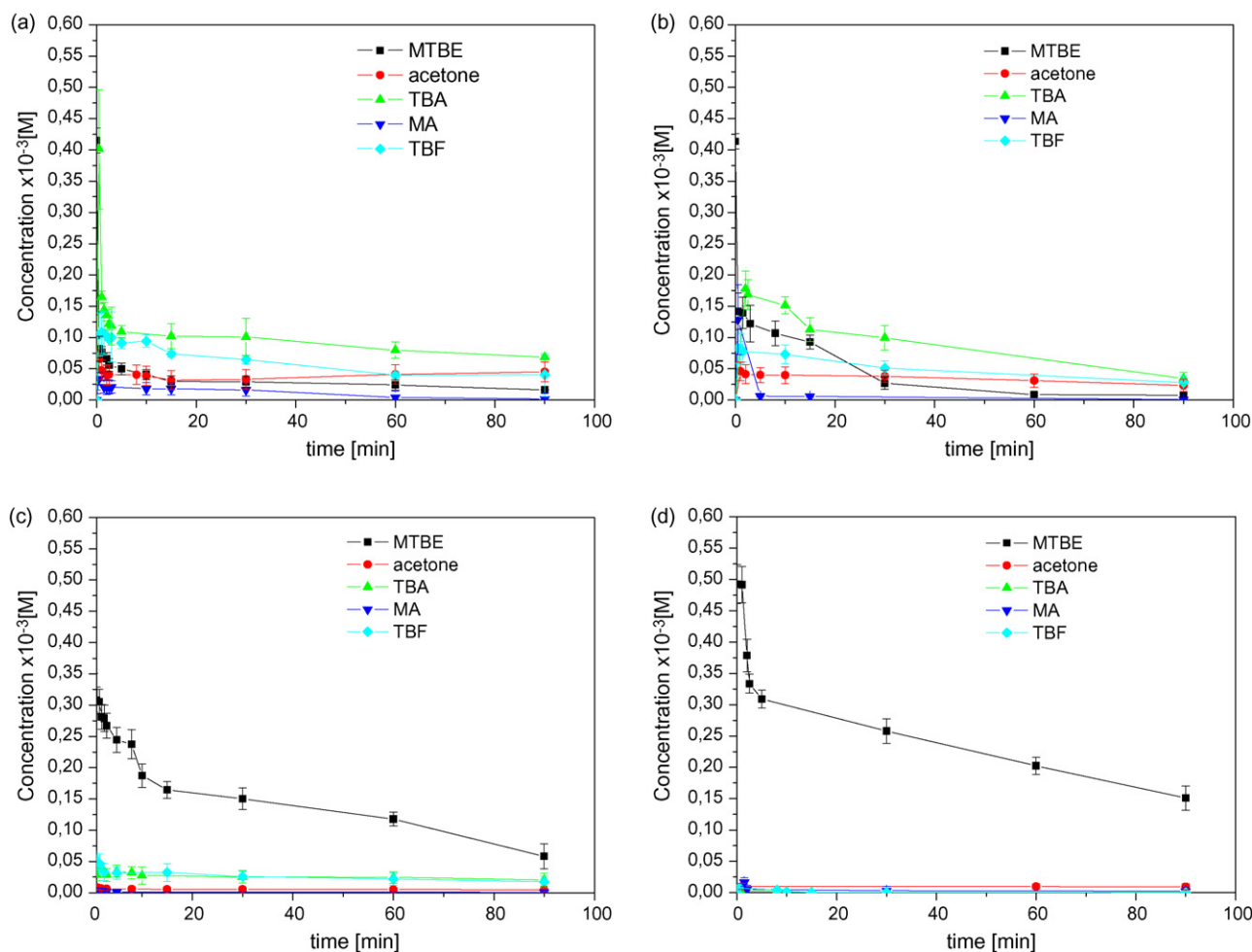


Fig. 3. MTBE degradation with Fenton's reagent in the presence of (a)  $[\text{NaClO}_4] = 0.1 \text{ M}$ , (b)  $[\text{Na}_2\text{SO}_4] = 33 \times 10^{-3} \text{ M}$ , (c)  $[\text{NaCl}] = 0.1 \text{ M}$ , (d)  $[\text{Na}_2\text{CO}_3] = 33 \times 10^{-3} \text{ M}$ , (e)  $[\text{Na}_3\text{PO}_4] = 17 \times 10^{-3} \text{ M}$ , (experimental condition:  $[\text{MTBE}] = 5 \times 10^{-4} \text{ M}$ ,  $[\text{Fe}^{2+}] = 1 \times 10^{-3} \text{ M}$ ,  $[\text{H}_2\text{O}_2] = 7.5 \times 10^{-3} \text{ M}$ ,  $I = 0.1 \text{ M}$ ,  $\text{pH} 2.8$ ,  $T = 25 \pm 1^\circ \text{C}$ ).



As can be seen in Fig. 3, TBF, TBA, MA, and acetone were identified and quantified as major reaction intermediates during the degradation of contaminated water. In the presence of perchlorate and sulfate, TBA was found to be the major product, followed by TBF and acetone. TBA was produced immediately and reached its highest concentration after 3 min of the reaction. Over the next 90 min the concentration dropped fairly quickly, then gradually decreased to a trace level at 180 min (data not presented here). During this period, detectable concentrations of TBF and acetone were also present.

It is well known that a reaction at the methoxy group is likely to occur since H-abstraction takes place most easily at the position  $\alpha$  to the ether functional group. Therefore, the main pathway of MTBE degradation is related to TBF, TBA and acetone generation. Furthermore, TBA is generated from MTBE and TBF. Hence, the low TBF concentration indicates that it too was oxidized to a significant extent in the presence of perchlorate and sulfate. Only in the first stage was TBF involved in the competition between  $\text{OH}^\bullet$  and MTBE, so from 91 to 96% of the MTBE was degraded, depending on the kind of anion ( $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ ) present.

The degradation process in the presence of dihydrophosphate and chloride, as presented in Fig. 3, shows a different distribution of MTBE intermediates. At an early stage of the experiment, the reaction reached a point where  $\text{OH}^\bullet$  started to degrade all the intermediates (TBF, TBA, acetone), since much of the MTBE had not yet been degraded. In addition, the lower rate of MTBE oxidation compared to that in the presence of perchlorate and sulfate caused intermediate concentrations to be very low for the entire duration of the experiment. This resulted in lower respective degradation values of 65 and 81% for the experiments with dihydrophosphate and chloride.

The results summarized in Table 3 show that in comparison with the MTBE content, the concentration of intermediates was lower after 90 min in the experiments with dihydrophosphate and chloride than in the ones with  $\text{ClO}_4^-$ , or  $\text{SO}_4^{2-}$ . The table also gives pseudo-first-order rate constants for the first stage of the reaction. In contrast, Fig. 3 shows the deviation from pseudo-first-order reaction behavior. Deviations from pseudo-first-order MTBE oxidation by Fenton's reagent were observed by other authors too [17]. As described above, after a very fast reaction for 3–5 min (described by  $k'$ ), a noticeably slower stage was initiated. The pseudo-first-order rate constant  $k'$  was calculated separately for the first ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) stage of reaction.

Table 3  
Concentrations of MTBE and intermediates (mg C/l) and pseudo-first-order rate constants for the first stage ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ )

After 90 min of reaction	Perchlorate	Sulfate	Chlorate	Phosphate
MTBE (mg C/l)	1.00	0.60	3.50	8.70
tBC (mg C/l)	5.70	3.20	1.10	0.40
All intermediates + MTBE (mg C/l)	8.30	4.60	4.80	9.70
$k'$ ( $\text{min}^{-1}$ ) for first stage (3–5 min) of reaction	3.24	2.14	0.12	0.13

tBC: it is a total amount of by-products included *t*-butyl group (TBF and TBA).

#### 4. Conclusion

In this study, we have shown that the Fenton reaction is extremely sensitive to inorganic anions present in the solution. In the case of chloride and dihydrophosphate, oxidation is evidently inhibited, while the addition of sulfates affects the rate of oxidation to a much smaller extent. Possible complexation reactions with Fe are postulated as a main of the mechanisms, but scavenging of hydroxyl radicals and the formation of inorganic radicals may also plays a role. The study has shown that in the presence of different salts the oxidation rate of MTBE decreases as  $\log K$  increases for the reactions of ferric and ferrous complex species with inorganic ions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ). It suggested that the inhibitory effect of anions on the rates of conversion of organic compounds is connected with complexation of ferric ion by them and less or non reactivity of these species with  $\text{H}_2\text{O}_2$ . Four intermediate products of MTBE oxidation were identified: TBF, TBA, acetone, and MA. In the presence of perchlorate and sulfate, TBA was found to be the major product, followed by TBF and acetone. If the degradation of MTBE is carried out in the presence of dihydrophosphate and chloride, the concentration of intermediates are very low at all time of reaction. Deviations from pseudo-first-order MTBE oxidation by Fenton's reagent were also observed.

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