The Effect of Chloride Ions on Alkylbenzenesulfonate Degradation in the Fenton Reagent

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Abstract
Degradation of sodium alkylbenzenesulfonate (ABS) in the Fenton reagent in the presence of Cl\(^{-}\) ions has been studied. An anionic surfactant sodium alkylbenzenesulfonate (C\(_{11}\)-C\(_{14}\)) has been selected as a model compound. The effect of individual components of the reactive system (H\(_2\)O\(_2\), H\(_2\)O\(_2\)/Cl\(^{-}\), Fe\(^{2+}\)/H\(_2\)O\(_2\), Fe\(^{2+}\)/H\(_2\)O\(_2\)/Cl\(^{-}\)) on the degree of ABS degradation has been determined. The degree of ABS degradation has been found to be affected by the presence of Cl\(^{-}\) ions and the mutual molar ratios of individual components of the system studied. Moreover, it influences on the composition of the post-reaction mixture. The use of the Fenton reagent in the presence of Cl\(^{-}\) ions resulted in the formation of chloroorganic compounds in the solution studied. 2,4,6-trichlorophenol was identified in reaction products and its presence was confirmed using the HPLC - MS method and by HPLC with an internal standard. No chloroproducts were identified during degradation of ABS by the system H\(_2\)O\(_2\)/Cl\(^{-}\). When only H\(_2\)O\(_2\) was applied, the concentration of the surfactant was unchanged.

Keywords: Fenton reagent, degradation of ABS-type surfactants, H\(_2\)O\(_2\)/Cl\(^{-}\) system

Introduction

Growing demand for washing agents, detergents and wetting agents as well as a deficit of natural fats have resulted in increasing production of surfactants. They are applied not only for production of the synthetic washing agents but also employed in various branches of industry such as petroleum, chemical, building, metal processing, cosmetic, dairy, textile industries and other. For example, in North America alone, 800 milion pounds of alkylbenzene sulfonate are produced each year.

Surfactants contained in wastes are an obstacle in exploitation of sewage-treatment plants and cause foaming in rivers and water pipes. Wastewater treatment reduces the contents of detergents only to a small degree [1]. Their presence in water affects its physicochemical properties and they are toxic for living organisms [2, 3]. Therefore, different methods of their removal from wastes have been sought. Biodegradation of these groups of compounds as well as their chemical destruction by classical methods, such as coagulation [4, 5, 6, 7], oxidation [8, 9, 10] or oxidation by Fenton reagent [11, 12] have been described by many authors [13, 14, 15, 16].

However, not much interest has been paid to the effect of various compounds in the wastes or agents applied for waste treatment on the possible conversions of surfactants. During the waste treatment process, the surfactants can undergo various “by-reactions”, e.g. as a result of iron salt application for coagulation. The Fenton reagent (Fe\(^{2+}\)/H\(_2\)O\(_2\)) leading to free hydroxyls (OH\(^{-}\)) formation can occur under favorable values of pH.

As the presence of surfactants in the environment is confirmed, the question arises about their behavior in the presence of various substances occurring in the environ-
ment, for instance the effect of chloride ions or peroxides. Peroxides can be introduced into the environment in the form of waste products and furthermore, they are also the intermediate products formed during oxidation reactions. In view of the above, a study on the effect of Cl⁻ ions on degradation of anionic sodium alkylbenzenesulfonate in the presence of H₂O₂ as well as hydrogen peroxide and Fe²⁺ ions, i.e. the (Fenton reagent), has been undertaken.

**Experimental**

**Analytical Methods**

Sodium alkylbenzenesulfonate (Fluka) being a mixture of (C11-C14) homologues was used as a model compound in our investigations. Concentrations of the surfactant in the analyzed samples were determined by liquid chromatography and spectrophotometric method with methylene blue (PN-85/C-04550/02). Samples were analyzed by chromatography on a Merck Hitachi (UV detector (L-4250), λ= 230nm) and Waters 2690 with an MS detector of ZQ Waters Micromas type (with ESI ionization); column: diameter -4mm, length -25mm, packing -Hypersil ODS (C-18) 5m, eluent: methanol/water (65/35 v/v), flow rate: 1ml/min.

**Preparation of Samples for Chromatographic Analysis**

Samples of the solutions studied were injected into a column packed with solid phase (SPE) C18 (6ml Supelclean LC-18). The bed was conditioned with methanol (7ml) and distilled water (3ml); the sample (100ml) was passed through the sorbent at the rate of 5ml/min. Then, the bed was dried in a stream of air and analytes were eluted with ethanol (2ml). The extract was analyzed by the chromatographic method.

**Results and Discussion**

The effect of Cl⁻ ions on degradation of ABS in the Fenton reagent was studied for model solutions of ABS. The effect of individual components of the reaction system (H₂O₂/Fe²⁺/Cl⁻) on the degree of ABS degradation was determined before the experiment. At the first stage, the effect of the presence of H₂O₂ free of Fe²⁺ ions added on ABS degradation was studied. It was found that ABS reaction with H₂O₂ run with a very low yield. Application of high concentrations of H₂O₂ had practically no effect on the degree of ABS degradation (Fig. 1). At the next stage, hydrogen peroxide was replaced with the Fenton reagent. Introduction of Fe²⁺ ions has increased the rate of ABS degradation (see Fig. 2). This fact may be explained as a result of the catalytic activity of Fe²⁺ ions, whose presence has significantly increased the rate of decomposition of peroxide according to reaction (1), leading to the formation of free hydroxyls characterized by an oxidative potential twice as high as that of H₂O₂.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH} \tag{1}
\]

In fact, the reaction runs in a more complicated manner than is shown by the total equation, and can be presented by reaction (2) [17]. The intermediate product of Fe²⁺ ion oxidation are [FeOH]²⁺ ions, which can undergo further conversions with formation of the free hydroxyls or ferryl cationic-radical [Fe(IV)O]²⁺:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow [\text{FeOH}]^{2+} \rightarrow [\text{Fe (IV)O}]^{2+} + \text{H}^+ + \cdot\text{OH}^- \tag{2}
\]

The rate of ABS destruction in the Fenton system was considerably higher as compared with that caused by hydrogen peroxide. It proves that the reactive oxidation agent such as 'OH radicals plays an essential role in the process. They are created in this process and may react with ABS by abstraction of the hydrogen atoms from alkyl chain, which results in the formation of an organic radical. Moreover, the study has shown that the rate of degradation of the surfactant agent by the Fenton reagent depends on the mutual ratios of the reagents. An increase in the excess of the Fenton reagent increases the rate of ABS degradation (Fig. 2). A

![Fig. 1. The effect of the amount of hydrogen peroxide on the degree of ABS degradation.](image1)

![Fig. 2. The effect of FeSO₄/H₂O₂ weight ratios on the rate of surfactant degradation in the Fenton reagent at pH=3.](image2)
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The different effect on ABS destruction is observed in the presence of excess of Fe$^{2+}$ ions. An increase in their amount decreases the efficiency of surfactant destruction. Taking into account the fact that ABS destruction is limited by the presence of OH radicals, the increase in the amount of the destructed surfactant means a decrease in the amount of the above-mentioned radicals in the system analyzed.

The decreased rate of ABS degradation in the presence of the excess of Fe$^{2+}$ ions relative to that in the presence of H$_2$O$_2$ can be explained by its decomposition in the reactions whose course do not favor formation of free hydroxyls (reaction (3)) [18] or in which these radicals are converted into an agent characterized by a significantly lower oxidation potential.

$$2\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow 2\text{Fe}^{3+} + \text{OH}^-$$ (3)

At the next stage of our study the effect of Cl$^-$ ions in the system containing H$_2$O$_2$ and the Fenton reagent on the process of ABS destruction was determined.

At first, the process of ABS destruction in the presence of H$_2$O$_2$ and Cl$^-$ ions was studied. It was found that the introduction of Cl$^-$ ions into the ABS/H$_2$O$_2$ system leads to an increase in the rate of ABS destruction (Fig. 3).

The degree of ABS degradation depends on the mutual proportions of reagents in the H$_2$O$_2$/Cl$^-$ system. An increase in the amount of peroxide causes a decrease in the degree of surfactant degradation (Fig. 3). Changes in the activity of the system can result from violation of the stoichiometry of the reaction between H$_2$O$_2$ and Cl$^-$ ions, which involves a series of secondary reactions leading to the formation of the reactive forms of chlorine (reactions (4)-(10)). However, the degree of ABS degradation caused by application of peroxide with participation of Cl$^-$ ions is lower than that in the classical Fenton reagent used without the addition of Cl$^-$ ions (Fig. 4).

$$\text{H}_2\text{O}_2 + \text{Cl}^- + \text{H}_2\text{O}^- \leftrightarrow \text{HClO} + 2\text{H}_2\text{O}$$ (4)

$$\text{Cl}^- + \text{HClO} + \text{H}_2\text{O}^- \leftrightarrow \text{Cl}_2^- + 2\text{H}_2\text{O}$$ (5)

$$\text{H}_2\text{O}_2 + \text{HClO} \leftrightarrow \text{O}_2 + \text{Cl}^- + \text{H}_2\text{O}^-$$ (6)

$$\text{OH}^- + \text{Cl}^- \rightarrow \text{OH}^- + \text{Cl}^-$$ (7)

$$\text{Cl}^- + \text{Cl}^- \rightarrow \text{Cl}_2^-$$ (8)

$$\text{H}_2\text{O}_2 + \text{Cl}_2^- \rightarrow \text{HO}_2^- + 2\text{Cl}^- + 2\text{H}^+$$ (9)

$$\text{HO}_2^- + \text{Cl}_2^- \rightarrow 2\text{Cl}^- + 2\text{H}^+ + \text{O}_2$$ (10)

Then, Cl$^-$ ions were introduced into the solution in order to determine their effect on the process of ABS degradation in the Fenton system. It was found that degradation of ABS was slower (Fig. 5).

This effect can be explained by the occurrence of competitive reactions of Cl$^-$ ions with H$_2$O$_2$ and further the products of these reactions with hydrogen peroxide (reactions (4)-(10)). Hypochlorous acid formed in reactions (4)-(6) is characterized by a lower oxidation potential (1.10V) than OH radical (2.07V). The inhibitory effect of Cl$^-$ ions results also from the fact that they react with free OH radicals (see reactions (11) and (12)), which can explain the slower rate of the degradation process [19].

The conclusion that Cl$^-$ ions are responsible for the slower rate of the degradation process is also confirmed by the fact that an increase in their content in the system under study results in a lower degree of ABS degradation, as shown in Fig. 5. The decrease in the degree of organic compounds degradation in the Fenton reagent in the presence of Cl$^-$ ions was also observed by Dutta et al. [20]. Malik and Saha [19] showed a significant effect of Cl$^-$ ions on degradation of dyes by the Fenton reagent.

$$\text{Cl}^- + \text{OH} \rightarrow \text{ClO}^- + \text{H}^-$$ (11)

$$\text{ClO}^- + 2\text{Fe}^{2+} \rightarrow \text{Cl}^- + \text{OH}^- + 2\text{Fe}^{3+}$$ (12)

Fig. 3. Effect of HCl/H$_2$O$_2$ ratio on the rate of ABS degradation at pH=3.

Fig. 4. Comparison between the effects of ABS degradation in water solution under the action of hydrogen peroxide applied in various systems (amount of H$_2$O$_2$ = 14mmole/dm$^3$).

Fig. 5. The effect of chloride ions addition on the rate of surfactant degradation by Fenton reagent.
Introduction of Cl\(^{-}\) ions into the Fenton reagent affects not only the rate and yield of ABS degradation but also the composition of the post-reaction mixture. It has been shown that chloroorganic compounds are formed in the presence of Cl\(^{-}\) ions in the system under study. Their formation can be a consequence of the above-described reactions (reactions (4)-(12)) leading to the formation of the reactive forms of chlorine, which, in turn, are able to react with ABS or with products formed during ABS degradation. 2,4,6-trichlorophenol was identified in the post-reaction mixture and its presence was confirmed by mass spectrum after separation by HPLC (mass ions: 196 (M\(^{+}\)), 198 (M\(^{+}\)), 200 (M\(^{+}\)), 202 (M\(^{+}\)) (see Fig. 6) as well as with the use of an internal standard. Formation of phenols was also confirmed by J.P. Hage et al. [21], who proved that phenols could be products of degradation of aromatic compounds with alkyl chain in the Fenton reagent. Iron salts in the H\(_2\)O\(_2\)/Cl\(^{-}\) system can play the role of catalyst both in the reactions of peroxide with Cl\(^{-}\) ions and chlorination of aromatic ring [22, 23]. It was confirmed by the fact that no products of chlorination were identified while applying H\(_2\)O\(_2\)/Cl\(^{-}\) system [24].

Conclusions

It has been found that sodium alkylbenzenesulfonate is easily degraded in the Fenton reagent. The degree of ABS degradation depends on the mutual proportions between H\(_2\)O\(_2\) and Fe\(^{2+}\) ions. The best effects of degradation have been achieved by applying the excess of peroxide relative to iron (FeSO\(_4\)/H\(_2\)O\(_2\)= 1:5). Introduction of Cl\(^{-}\) ions into the Fenton reagent causes a reduction in the degree of conversion and ABS degradation rate, and affects the composition of the post-reaction mixture. Chloroorganic compounds were identified in the studied solutions while applying Fenton reagent in the presence of Cl\(^{-}\) ions.

As follows from results of our investigation, chloroorganic compounds identified in the environment by Asplund et al. [25] can be derived not only from natural halogenations of an organic matter but also from processes of purification in the presence of Cl\(^{-}\) ions. Moreover, besides enzymes, metal ions also can act as catalysts in these processes. The formation of chloroorganic compounds while applying Fenton reagent in the presence of Cl\(^{-}\) ions can be an important restriction in application of this reagent for sewage treatment.

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