

# 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  $\text{Cl}^-$  ions has been studied. An anionic surfactant sodium alkylbenzenesulfonate ( $\text{C}_{11}\text{-C}_{14}$ ) has been selected as a model compound. The effect of individual components of the reactive system ( $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2/\text{Cl}^-$ ,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{Cl}^-$ ) on the degree of ABS degradation has been determined. The degree of ABS degradation has been found to be affected by the presence of  $\text{Cl}^-$  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  $\text{Cl}^-$  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  $\text{H}_2\text{O}_2/\text{Cl}^-$ . When only  $\text{H}_2\text{O}_2$  was applied, the concentration of the surfactant was unchanged.

**Keywords:** Fenton reagent, degradation of ABS-type surfactants,  $\text{H}_2\text{O}_2/\text{Cl}^-$  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 million 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 ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) leading to free hydroxyls ( $\cdot\text{OH}$ ) 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-

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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<sup>-</sup> ions on degradation of anionic sodium alkylbenzenesulfonate in the presence of H<sub>2</sub>O<sub>2</sub> as well as hydrogen peroxide and Fe<sup>2+</sup> 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<sup>-</sup> ions on degradation of ABS in the Fenton reagent was studied for model solutions of ABS.

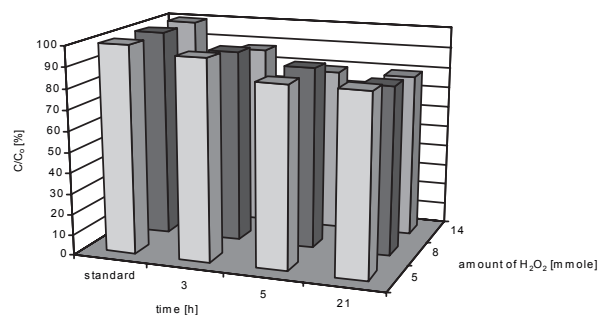


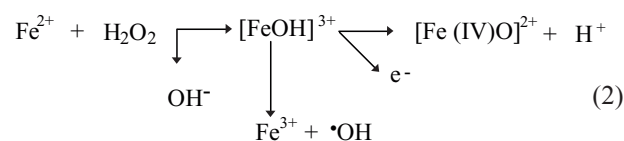
Fig. 1. The effect of the amount of hydrogen peroxide on the degree of ABS degradation.

The effect of individual components of the reaction system (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>/Cl<sup>-</sup>) on the degree of ABS degradation was determined before the experiment. At the first stage, the effect of the presence of H<sub>2</sub>O<sub>2</sub> free of Fe<sup>2+</sup> ions added on ABS degradation was studied.

It was found that ABS reaction with H<sub>2</sub>O<sub>2</sub> run with a very low yield. Application of high concentrations of H<sub>2</sub>O<sub>2</sub> 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 Fe<sup>2+</sup> ions has increased the rate of ABS degradation (see Fig. 2). This fact may be explained as a result of the catalytic activity of Fe<sup>2+</sup> 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 H<sub>2</sub>O<sub>2</sub>.



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 Fe<sup>2+</sup> ion oxidation are [FeOH]<sup>3+</sup> ions, which can undergo further conversions with formation of the free hydroxyls or ferryl cationic-radical [Fe(IV)O]<sup>2+</sup>:



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

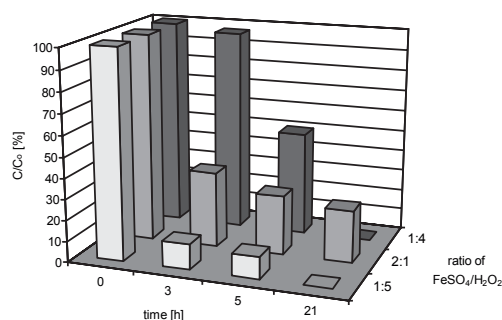
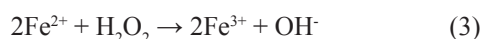


Fig. 2. The effect of FeSO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> weight ratios on the rate of surfactant degradation in the Fenton reagent at pH=3.

different effect on ABS destruction is observed in the presence of excess of  $\text{Fe}^{2+}$  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  $\cdot\text{OH}$  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.

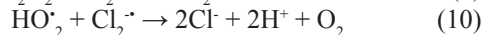
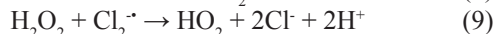
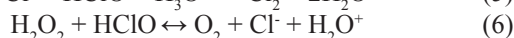
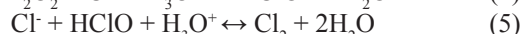
The decreased rate of ABS degradation in the presence of the excess of  $\text{Fe}^{2+}$  ions relative to that in the presence of  $\text{H}_2\text{O}_2$  can be explained by its decomposition in the reactions whose course do not favor formation of free hydroxyls (reaction (3)) [18] or in which these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



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

At first, the process of ABS destruction in the presence of  $\text{H}_2\text{O}_2$  and  $\text{Cl}^-$  ions was studied. It was found that the introduction of  $\text{Cl}^-$  ions into the ABS/ $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2/\text{Cl}^-$  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  $\text{H}_2\text{O}_2$  and  $\text{Cl}^-$  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  $\text{Cl}^-$  ions is lower than that in the classical Fenton reagent used without the addition of  $\text{Cl}^-$  ions (Fig. 4).



Then,  $\text{Cl}^-$  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  $\text{Cl}^-$  ions with  $\text{H}_2\text{O}_2$  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  $\cdot\text{OH}$  radical (2,07V). The inhibitory effect of  $\text{Cl}^-$  ions results also from the fact that they react with free  $\cdot\text{OH}$  radicals (see reactions (11) and (12)), which can explain the slower rate of the degradation process [19].

The conclusion that  $\text{Cl}^-$  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  $\text{Cl}^-$  ions was also observed by Duta et al. [20]. Malik and Saha [19] showed a significant effect of  $\text{Cl}^-$  ions on degradation of dyes by the Fenton reagent.

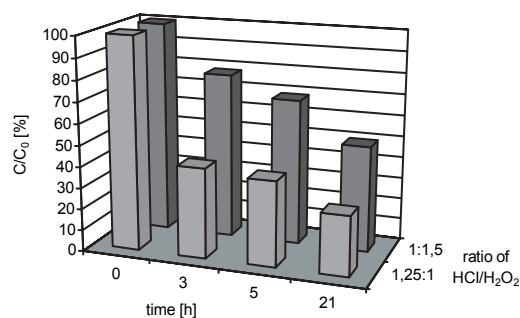
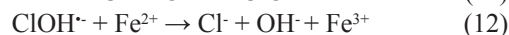


Fig. 3. Effect of  $\text{HCl}/\text{H}_2\text{O}_2$  ratio on the rate of ABS degradation at  $\text{pH}=3$ .

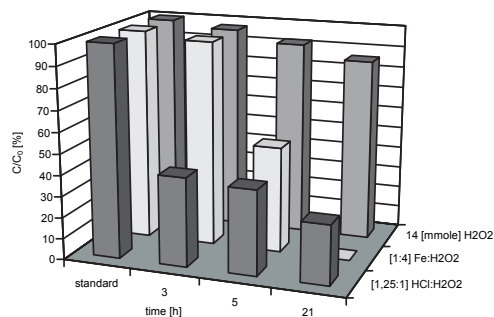


Fig. 4. Comparison between the effects of ABS degradation in water solution under the action of hydrogen peroxide applied in various systems (amount of  $\text{H}_2\text{O}_2 = 14\text{mmole}/\text{dm}^3$ ).

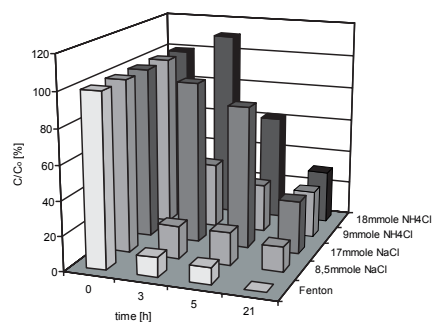


Fig. 5. The effect of chloride ions addition on the rate of surfactant degradation by Fenton reagent.

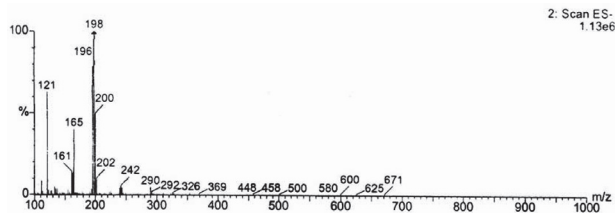


Fig. 6. Mass spectrum of 2,4,6-trichlorophenol obtained by HPLC-MS analysis.

Introduction of  $\text{Cl}^-$  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  $\text{Cl}^-$  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 ( $\text{M}^+$ ), 198 ( $\text{M}^{2+}$ ), 200 ( $\text{M}^{4+}$ ), 202 ( $\text{M}^{6+}$ ) (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  $\text{H}_2\text{O}_2/\text{Cl}^-$  system can play the role of catalyst both in the reactions of peroxide with  $\text{Cl}^-$  ions and chlorination of aromatic ring [22, 23]. It was confirmed by the fact that no products of chlorination were identified while applying  $\text{H}_2\text{O}_2/\text{Cl}^-$  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  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  ions. The best effects of degradation have been achieved by applying the excess of peroxide relative to iron ( $\text{FeSO}_4/\text{H}_2\text{O}_2 = 1:5$ ). Introduction of  $\text{Cl}^-$  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  $\text{Cl}^-$  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  $\text{Cl}^-$  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  $\text{Cl}^-$  ions can be an important restriction in application of this reagent for sewage treatment.

### References

1. IMHOFF K.K., Municipal sewage system and sewage treatment, Warsaw, **1982** (in Polish)
2. WYRWAS B., SZYMAŃSKI A., ŁUKASZEWSKI Z., Tensammetric determination of non-ionic surfactants combined with the BiAS separation procedure: Part 3. Determination in the presence of hydrocarbons, *Talanta*, **47**, 325, **1998**
3. WALIGÓRSKA M., Biodegradability of Anionic Surfactants in Anoxic Conditions, *Polish J. Environ. Stud.*, **11**, (1), 55, **2002**
4. PAPAPOPOULOS A., SAVVIDES C., LOIZIDIS M., HARALAMBOUS, K. J., LOIZIDOU, M., An assessment of the quality and treatment of detergent wastewater, *Wat. Sci. Tech.* **36**, (2-3), 377, **1997**
5. VARO P., RODRUGUEZ M., PRATS D., MORENO A., BERNA J.L., Biodegradation of soap in anaerobic digesters and on sludge amended soils, *Wat. Res.*, **33**, (1), 105, **1999**
6. KOZIOROWSKI B., J. KUCHARSKI, Technology of water, WNT Warsaw **1964** (in Polish)
7. SWIFF G., Abstracts of the international Symposium on Biodegradable Polymers, *Biodegradable Polymer Sci.*, Tokio 61, **1991**
8. KOWAL A.L., Technology of water, Arkady, Warsaw **1977** (in Polish)
9. LEDAKOWICZ S., PERKOWSKI J., Kinetics of destruction of non-ionic detergent TRITON-100 by ozonation, *Inż. Chem. Proc.* **19**, (11), 205, **1998** (in Polish)
10. LEDAKOWICZ S., OLEJNIK D., The use of advanced oxidation process (AOP) for the decomposition of Triton X-114 nonionic detergent, *Przem. Chem.* **80**, 10, **2001** (in Polish)
11. LIN S. H., LIN CH. M., LEN H. G., Operating characteristics and kinetic studies of surfactant wastewater treatment by Fenton oxidation, *Wat. Res.* **33**, (7), 1735, **1999**
12. LIN S.H., LO, Cho.C., Fenton process for treatment of desizing wastewater, *Wat. Res.* **31**, 2050, **1995**
13. SCOTT M. J., JONES M. N., The biodegradation of surfactants in the environment, *Biochim. Biophys. Acta* **23**, 1508(1-2), 235, **2000**
14. SZWACH J., BEKIERZ G., New views on interaction of surfactants on the natural environment, *Przem. Chem.*, **75**, 2, **1996** (in Polish)
15. SIWINSKI P., SZYMAŃSKI A., ŁUKASZEWSKI Z., Biodegradability of Detergent Powder Surfactants in The River Water Die-Away Test, *Polish J. Environ. Stud.*, **7**, (4), 251, **1998**
16. SZYMAŃSKI A., WYRWAS B., ŁUKASZEWSKI Z., Application of an indirect tensammetric method for the determination of non-ionic surfactants in surface water, *Anal. Chim. Acta*, **305**, 256, **1995**
17. BARTOSZ G., Other face of oxygen, PWN, Warsaw **1995** (in Polish)
18. KREMER M. L., Mechanism of the Fenton reaction. Evidence for a new intermediate, *Phys. Chem. Chem. Phys.*, **1**, 3595, **1999**
19. MALIK P.K., SAHA S.K., Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst, *Elsevier Science*, **31**, (3), 241, **2003**

20. DUTA K., MUKHOPADHYAY S., BHATTACHARJEE S., Chemical oxidation of methylene blue using a Fenton-like reaction, *J. Hazard Mater.*, **84**, 55, **2001**
21. HAGE J.H., LLOBET A., SAWYER D.T., Aromatic Hydroxylation by Fenton Reagents {Reactive Intermediate  $[L_x^+Fe^II OOH(BH^+)]$ }, not Free Hydroxyl Radical (HO·)}, *Bioorganic & Medicinal Chemistry*, **3**, (10), 1383, **1995**
22. KOWALSKA M., GACA J., Chlorides as the potential agents contributing to formation of chloroorganic compounds in oxidation of amines, *Polish J. Environ. Stud.*, **11**, (1), 41, **2002**
23. GACA J., KOWALSKA M., New method of 2,4,6-trichloroaniline synthesis, *Pol. J. Appl. Chem.*, **85**, 3, **2001**
24. GACA J., KOWALSKA M., Effect of peroxides on decomposition of surfactants, *Congress PTCh i SITPCh*, Lublin p.1038, **2003** (in Polish)
25. ASPLUND G., GRIMVALL A., Organohalogens in nature, more widespread than previously assumed, *Environ. Sci. Technol.*, **25**, 1346, **1991**.

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