DECOMPOSITION OF NON-IONIC SURFACTANT SYMPERONIC NP10 BY THE FENTON PROCESS IN THE PRESENCE OF IRON-OXIDE NANOPARTICLES

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ABSTRACT

Detergents belong to the class of chemical compounds whose consumption is still growing in the world. Getting to surface water they cause a decrease of water surface tension which contributes to foaming. Additionally, they are characterized by toxicity towards aquatic organisms.

Methods used to decompose surfactants include oxidation/precipitation in the Fenton process. New trends in the studies on the oxidation of pollutants by the Fenton method include the use of iron nanocompounds in the reaction system. The presence of nanoparticles affects the oxidation of many chemical compounds occurring in water and wastewater. In many cases, the use of iron nanocompounds has an influence on the increase of oxidation efficiency due to which hazardous chemical compounds occurring in water decompose faster and more effectively.

The aim of our studies was to determine and optimize the efficiency of decomposition of a non-ionic surfactant Symperonic NP10 by the Fenton method in the presence of iron-oxide nanoparticles and to compare it with the classical Fenton method. Surfactants, including Symperonic NP10, which contain an aromatic ring, have low susceptibility to biodegradation. The novelty of our study is to use iron-oxide nanoparticles as a catalyst in the homogeneous Fenton process.

The subject of our studies were water solutions of a nonionic detergent Symperonic NP10 used in textile industry. Water solutions of the surfactant were subjected to treatment by the classical Fenton method and to treatment in the presence of iron (II, III) oxide nanopowder. In samples before and after the treatment COD and TOC were determined. The effect of process conditions such as pH, ferrous sulfate, iron oxide nanopowder and H_2O_2 doses on the efficiency of detergent decomposition was determined. It was also checked to what extent the addition of iron oxide nanopowder could improve the decomposition rate and efficiency compared to the classical Fenton process.

In the nanoFenton process a 20-30% increase of the detergent decomposition was achieved in relation to the classical Fenton process. Iron oxide nanopowder catalyzed the process of detergent decomposition increasing its efficiency and the degree of mineralization. The efficiency of detergent oxidation reached 80%. It was probably connected with the catalytic action of iron oxide nanoparticles and higher concentration of hydroxyl radicals in the reaction system.

Keywords: non-ionic detergent, Symperonic NP10, Fenton process, iron nanocompounds

1. Introduction

Detergents belong to the class of chemical compounds whose consumption is still growing in the world. Getting to surface water they cause a decrease of water surface tension which contributes to foaming. Additionally, they are characterized by toxicity towards aquatic organisms. Methods used to decompose surfactants include oxidation/precipitation in the Fenton process (Perkowski *et al.*, 2006; Blanco *et al.*, 2012). New trends in the studies on the oxidation of pollutants by the Fenton method include the use of iron nanocompounds in the reaction system (Lin *et al.*, 2008; Garrido-Ramirez *et al.*, 2010; Xu *et al.*, 2012). The presence of nanoparticles affects the oxidation of many chemical compounds occurring in water and wastewater. In many cases, the use of iron nanocompounds has an influence on the increase of oxidation efficiency due to which hazardous chemical compounds occurring in water decompose faster and more effectively. The aim of our studies was to optimize the efficiency of decomposition of non-ionic surfactant Symperonic NP10 by the Fenton method in the presence of iron nanocompounds and to compare it with the classical Fenton method.

2. Methods

Subject of studies: The subject of studies were water solutions of a nonionic detergent Symperonic NP10 at the concentration of 0.1 g/dm^3 (0.15 mmol/dm^3). Its molecular structure is shown in Figure 1.

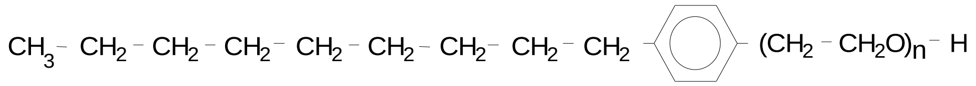

Figure 1: Molecular structure of a nonionic detergent Symperonic NP10.

Experimental procedure: The pH values of water detergent solutions were reduced to 4, 3.5, 3, 2.5 or 2 by means of 5N solution of sulfuric acid. Next, the samples were completed either exclusively with ferrous sulfate or jointly with ferrous sulfate and iron (II,III) oxide nanopowder (Sigma-Aldrich) and the solution was stirred. Then 32% solution of H_2O_2 was added. The samples were stirred vigorously for 2 minutes, and then slowly for the next 10 minutes. The solution was left for 24 hours. Next, the samples were neutralized with 10% solution of NaOH to pH about 11. After 24 hours, the purified water detergent solutions were decanted and filtered.

Analytical control: In the samples before and after the treatment COD and TOC were determined by Hach-Lange tests.

3. Results

The effect of process conditions such as pH, ferrous sulfate, iron oxide nanopowder and H_2O_2 doses on the efficiency of detergent decomposition was determined. It was also checked to what extent the addition of iron oxide nanopowder could improve the decomposition rate and efficiency compared to the classical Fenton process.

The first step was to determine the effect of the dose of iron oxide nanopowder on the efficiency of Symperonic NP10 decomposition in the Fenton process. The experiments were made at pH 3.5 using doses of ferrous sulfate from 0.1 g/dm^3 to 0.75 g/dm^3 and changing the doses of iron oxide nanopowder in the range from 0.01 to 0.05 g/dm^3. Doses of H_2O_2 were 1, 3, 5 and 7 cm^3/dm^3. The removal of COD and TOC after processing was determined (Figures 2 and 3).

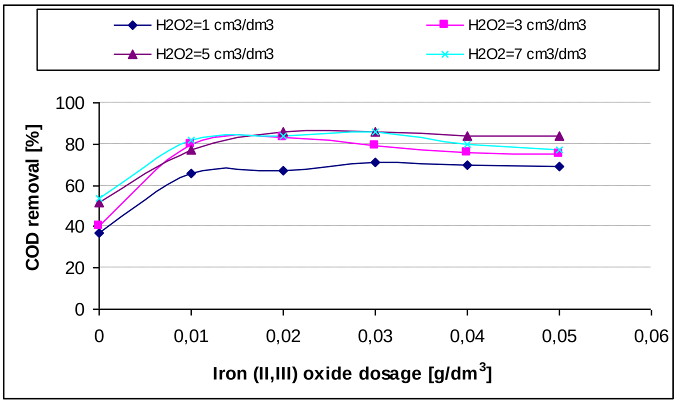

Figure 2: The effect of iron oxide nanopowder doses on COD changes in the Fenton process. $FeSO_4*7H_2O$ dose – 0.25 g/dm^3. Hydrogen peroxide doses: 1, 3, 5 and 7 cm^3/dm^3.

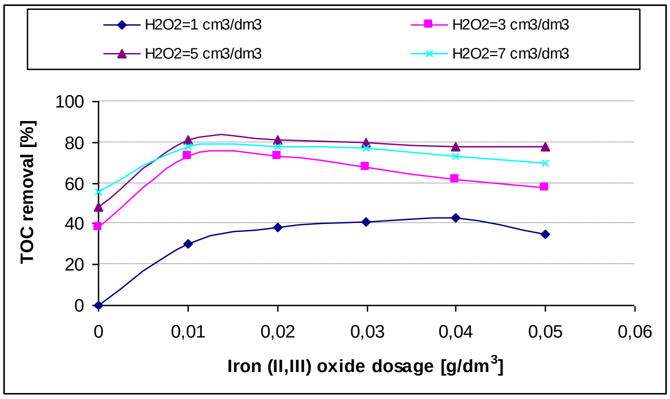

Figure 3: The effect of iron oxide nanopowder doses on TOC changes in the Fenton process. $FeSO_4*7H_2O$ dose – 0.25 g/dm^3. Hydrogen peroxide doses: 1, 3, 5 and 7 cm^3/dm^3.

High COD removal was obtained. Better COD removal (up to 87%) was achieved at higher doses of H_2O_2. It depended on the dose of iron oxide nanopowder, however, the obtained values of COD removal were similar. While analyzing the values of TOC it was found that the obtained relations were as in the case of COD. At smaller H_2O_2 doses the TOC reduction was by 20-25% lower than for COD, while at higher doses of H_2O_2 it was lower by only 5 to 10%. So, mineralization of detergent particles was promoted by a higher concentration of hydrogen peroxide in the system.

In the next series of experiments the effect of H_2O_2 concentration on the decomposition of detergent molecules was determined (Figures 4 and 5).

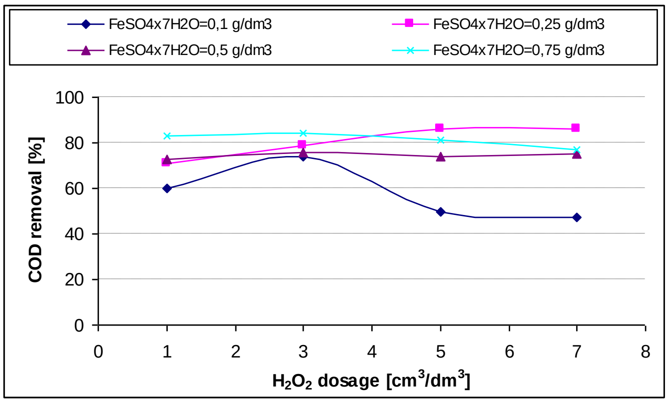

Figure 4: The effect of hydrogen peroxide dose on COD changes in the Fenton process. $FeSO_4*7H_2O$ doses: 0.1, 0.25, 0.5, 0.75 g/dm^3. Iron oxide nanopowder dose – 0.03 g/dm^3.

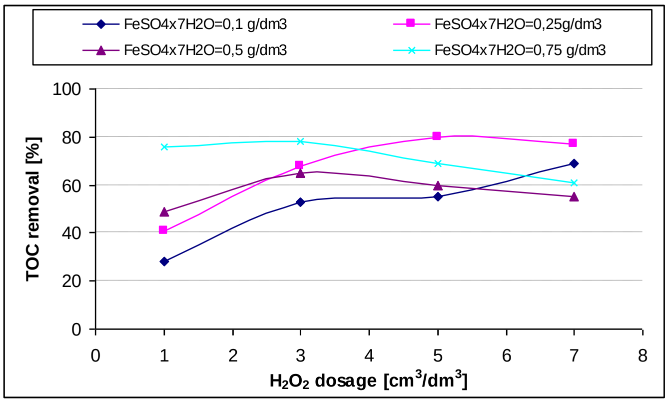

Figure 5: The effect of hydrogen peroxide dose on TOC changes in the Fenton process. $FeSO_4*7H_2O$ doses: 0.1, 0.25, 0.5, 0.75 g/dm^3. Iron oxide nanopowder dose – 0.03 g/dm^3.

The obtained values of COD and TOC reduction depended strongly on H_2O_2 doses. That was particularly evident at lower doses of ferrous sulfate. With an increase of H_2O_2 dose the reduction of COD and TOC also increased. At higher doses of ferrous sulfate it was pointless to use H_2O_2 doses higher than 3 cm^3/dm^3.

Changes in COD and TOC removal depending on the initial pH are shown in Table 1. The highest COD and TOC reduction was observed at pH=3.5.

Table 1: The effect of pH on COD and TOC removal in the nanoFenton process: ($FeSO_4$*$7H_2O$ dose – 0.5 g/dm^3, H_2O_2 dose – 3 cm^3/dm^3, iron oxide nanopowder dose – 0.05 g/dm^3).

pH	2.0	2.5	3.0	3.5	4.0
COD removal (%)	55	87	87	86	85
TOC removal (%)	33	74	75	69	73

It is important to compare the results of Symperonic NP10 decomposition obtained in the classical Fenton process with the results attained in the presence of iron nanocompounds (Figure 6). As follows from the obtained data, iron nanocompounds catalyzed the Fenton reaction increasing in this way the efficiency of detergent molecule decomposition and its mineralization as compared to the classical process.

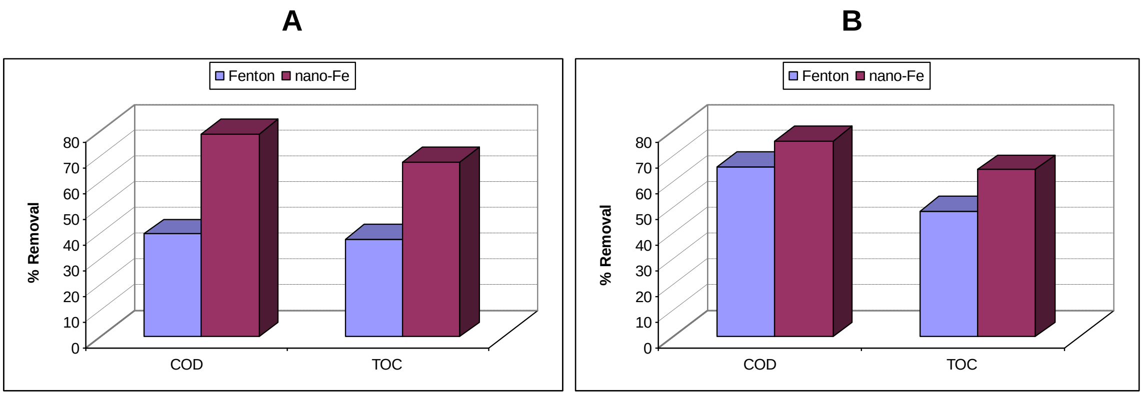

Figure 6: Changes of COD and TOC in Symperonic NP10 solution in the Fenton process compared to the nanoFenton process, pH=3.5, H_2O_2 dose – 3 cm^3/dm^3; A - Fenton process: $FeSO_4$ dose – 0.25 g/dm^3; nanoFenton process: $FeSO_4$ dose – 0.25 g/dm^3, iron oxide nanopowder dose – 0.03 g/dm^3; B - Fenton process: $FeSO_4$ dose – 0.5 g/dm^3; nanoFenton process: $FeSO_4$ dose – 0.5 g/dm^3, iron oxide nanopowder dose – 0.03 g/dm^3.

4. Conclusions

The novelty of our study was the use of iron-oxide nanoparticles as a catalyst in the homogeneous Fenton process. In the nanoFenton process a 20-30% increase of the detergent decomposition was achieved in relation to the classical Fenton process. Iron oxide nanopowder catalyzed the process of detergent decomposition increasing its efficiency and the degree of mineralization. It was probably connected with the catalytic action of iron oxide nanoparticles and higher concentration of hydroxyl radicals in the reaction system. The decomposition of Symperonic NP10 was an efficient process. The efficiency of detergent oxidation reached 80%. The best results of decomposition were obtained at pH=3.5. The optimum doses of iron oxide nanopowder ranged from 0.02 to 0.03 g/dm^3. The values of COD and TOC depended strongly on hydrogen peroxide dosage. With an increase of hydrogen peroxide dosage the removal of COD and TOC also increased. The TOC removal was by about 5-25% smaller than the COD removal which showed that organic products of Symperonic NP10 oxidation remained in the solution. The detergent oxidation was more efficient than its mineralization.

ACKNOWLEDGEMENTS

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