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Decomposition of a Nonionic Detergent by the Fenton Process in the Presence of Iron Nanocompounds

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Abstract
The aim of the research was to determine the efficiency of decomposition of a nonionic detergent Symperonic NP10 by the Fenton method in the presence of iron nanocompounds and to compare it with the classical Fenton method. Detergent water solutions were subjected to the classical purification method with the application of ferrous sulfate and then compared by using ferrous sulfate with the addition of iron (II, III) oxide nanopowder . The treatment process was optimised from studies on the effect of ferrous sulfate and iron (II, III) oxide nanopowder doses, hydrogen peroxide and pH of the solution on treatment efficiency. Iron oxide nanopowder application allowed to increase the efficiency of detergent decomposition.

Key words: *nonionic detergent, Fenton reaction, iron nanocompounds, detergent decomposition.*

Introduction

Surfactants comprise the group of chemical compounds most often applied both in industry and households. They are used as detergents and washing agents mainly in households. In industry, they are applied as wetting agents for casting moulds (metallurgy), in the production of pesticides (chemical industry), plastics and synthetic resins, dyes and varnishes, cellulose and paper, in food production, and additionally in photography, printing industry, cosmetics, pharmacology, medicine, plant protection and zootechnics.

Big amounts of surfactants are used in the textile industry in washing, dyeing and finishing processes. After wet processing they are practically removed to the post-process wastewater. An important group are non-ionic surfactants (NIS). Recently significant growth has been observed in the range of their applicability and production. NIS's are the products of the condensation of ethylene oxide with alkylphenols or long-chain alcohols. Surfactants, including non-ionic ones, which contain an aromatic ring, usually have low susceptibility to biodegradation.

In general, their negative influence is that in water they dissolve toxic substances that otherwise are hardly or completely insoluble. Through decreasing the surface tension of water they make it foam, which deteriorates the conditions for diffusing oxygen and reduces its concentration in water. This has a negative effect on the self-purification ability of water reservoirs and on the development of plant life. Thus surfactants are substances that are indirectly hazardous and for this reason they should be decomposed and removed from water and wastewater. Hence it is necessary to devise and develop efficient technologies to render them harmless.

One such technology is the Fenton method [1 - 6], belonging to the group of so-called advanced oxidation processes (AOPs) which take advantage of hydroxyl radicals that are characterised by a high oxidising potential and non-selective action. During the Fenton reaction organic compounds are oxidised by hydroxyl radicals formed in the chain process of hydrogen peroxide decomposition in the presence of divalent iron salts. This is a radical reaction which generates big amounts of hydroxyl radicals $HO^{\bullet}$ characterised by a high oxidising potential, due to which even the most resistant pollutants present in the wastewater can be decomposed.

Detergents, including nonionic ones, are well degradable in water solutions in all types of advanced oxidation processes, including the Fenton process, where besides oxidation coagulation caused by precipitation of iron (III) hydroxide also occurs. Using the Fenton process we can decrease the concentration of pollutants significantly, including detergents present in the textile wastewater [7 - 10].

The main advantages of the Fenton process include good efficiency of pollutant decomposition, simple technology and low costs. A certain problem is the sludge formed during coagulation, which requires separation and disposal in appropriate conditions. Hence it is important to minimise the amount of iron added to the purified solution. It is necessary to make an optimum choice correctly, on the one hand taking into account the yield and rate of oxidation, and on the other having in mind the quantity of iron hydroxide sludge being formed.

A novelty in the oxidation of pollutants is the process carried out in the presence of iron nanocompounds [11 - 13]. The presence of nanoparticles affects the course of oxidation of many compounds present in the water. Using iron nanocompounds, studies were carried out on the removal of trichloroethylene [14], phenol [15 - 17], dyes [18, 19], olefin [20], humic acids [21], antibiotics [22] and chlorophenols [23]. The investigations were performed with the use of iron nanocompounds in the form of Fe-Fe_2O_3 nanopowder, as well as Fe_3O_4 and zero-valent iron. In some cases, in order to improve the catalytic properties of iron nanocompounds, they are placed on organic nanocarriers (e.g. poly3,4-ethylene-dihydroxythiophene) or inorganic ones (e.g. hydroxyapatites). The studies showed an increased efficiency of the decomposition of most compounds tested as compared to the classical Fenton process.

The aim of the research presented in this paper was to determine the efficiency of decomposition of nonionic detergent Symperonic NP10 in the Fenton process in the presence of iron nanocompounds as compared to the classical Fenton process. The detergent chosen for the tests is one of the components of laundry detergents used in the textile industry.

Symperonic NP-10 is a surfactant quite toxic for *Vibro fisheri* bacteria used in biotoxicity tests. Tests with a solution with a concentration of 100 mg/dm^3 showed that the inhibition value was 35% and the value of EC_{50} 29. The biodegradability of the solution measured by the BOD_5/COD ratio was low, ca. 0.06. These data indi-

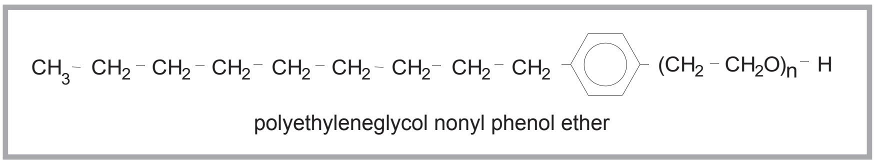

Figure 1. *Molecular structure of nonionic detergent Symperonic NP10.*

cate the need for the chemical decomposition of the detergent before subjecting the solution to biological treatment [24].

Methods

Subject of studies. The subject of our studies were water solutions of a nonionic detergent Symperonic NP10 at the concentration of 0.1 g/dm^3 (0.15 mmol/dm^3). Molecular formula – $C_{35}H_{68}O_{11}$, molecular weight 664 g/mol, density 1.059 g/cm^3. The molecular structure is shown in ***Figure 1***.

Analytically pure ferrous sulfate $FeSO_4 \times 7H_2O$ and 30% hydrogen peroxide H_2O_2 (Chempur, Piekary Śląskie, Poland), iron (II, III) oxide nanopowder <50 nm (Sigma Aldrich) as well as H_2SO_4 and analytically pure NaOH (POCh, Gliwice, Poland) were used in the experiments.

Experimental procedure. The pH values of water detergent solutions were reduced to 4, 3.5, 3, 2.5 or 2 by means of a 5 N 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 in a solid state and the solution was stirred. Then a 32% solution of hydrogen peroxide was added drop-wise to the solutions. Once H_2O_2 had been added, the solution was stirred vigorously for 2 minutes, and then slowly for the next 10 minutes. The solution was left for 24 hours. Next the samples were neutralised with a 10% solution of NaOH to a pH of about 11. After 24 hours, the purified water detergent solutions were decanted and filtered.

Analytical control. In the samples before and after treatment, the COD (Chemical Oxygen Demand) and TOC (Total Organic Carbon) were determined by Hach-Lange tests.

Results and discussion

The effect of process conditions such as iron oxide nanopowder dosage, hydrogen peroxide and pH of the solution on the efficiency of detergent decomposition was determined in the tests. 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.

Effect of ferrous oxide nanopowder dosage

The first step of the study was to determine the effect of iron oxide nanopowder dosage on the efficiency of Symperonic NP10 decomposition in the Fenton process. Experiments were performed using two dosages of ferrous sulfate equal to 0.2 g/dm^3 and 0.5 g/dm^3 and changing dosages of iron oxide nanopowder in the range from 0.015 to 0.1 g/dm^3. The initial detergent concentration was 100 mg/dm^3. A constant dosage of hydrogen peroxide equal to 5 cm^3/dm^3 was used. The weight ratio of iron oxide nanopowder to ferrous sulfide ranged from 1:13 to 1:2 at $FeSO_4 \times 7H_2O$, a dosage equal to 0.2 g/dm^3, and from 1:33 to 1:5 at $FeSO_4 \times 7H_2O$ 0.5 g/dm^3. The experiments were carried out at pH 3.5. The level of COD and TOC removal after processing was determined. ***Figures 2*** and ***3*** show results of the tests.

High COD removal was obtained, its value depending on both the dosage of ferrous sulfate and iron oxide nanopowder. Better COD removal was achieved at a higher dose of ferrous sulfate (***Figure 2***), depending on the dosage of iron oxide nanopowder; however, the values of COD removal obtained were similar, ranging from 83 to 87%. At a 2.5-times smaller dosage of ferrous sulfate, less COD removal was obtained, the value of which depending to a similar extent on the dosage of iron oxide nanopowder (***Figure 2***). With an increasing dosage of iron oxide nanopowder the COD removal increased from 69 to 74%.

While analysing the values of TOC obtained it was found that also in this case they depended on both the dosage of ferrous sulfate and iron oxide nanopowder dosages. At a higher initial dosage of ferrous sulfate (0.5 g/dm^3), TOC removal was more dependent on the dosage of iron oxide nanopowder than the COD removal (***Figure 3***, see page 113). The removal of TOC increased from 64 to 75% with an increase in the iron oxide nanopowder dosage. At the dosage of ferrous sulfate of 0.2 g/dm^3 it changed only slightly, i.e. 56 - 59%.

In summary, in the experimental conditions the degree of detergent oxidation was high, reaching 75%. However, low-molecular oxidation products, such as formic and acetic acid, less susceptible to Fenton's reagent, probably still remained in the solution [4, 6]. The TOC removal was about 10 - 20% smaller than the COD removal, which confirmed that organic products of Symperonic NP10 oxidation remained in the solution.

Effect of hydrogen peroxide dosage

The next series of experiments covered the determination of the effect of hydrogen peroxide concentration on the decomposition of detergent molecules. From 1 to 10 cm^3/dm^3 of hydrogen peroxide (32.7 to 327 mmol H_2O_2/dm^3, respectively) was added to the detergent solution. The dosages applied were as follows: 0.2 g/dm^3 ferrous sulfate and 0.075 g/dm^3 iron oxide nanopowder, as well as 0.5 g/dm^3 ferrous sulfate and 0.1 g/dm^3 iron oxide nanopowder, pH of the solution – 3.5. ***Figures 4*** and ***5*** show results of the experiments.

In the case of a lower dosage of ferrous sulfate – 0.2 g/dm^3 and iron oxide nanopowder – 0.075 g/dm^3, the removal of COD in the test range of hydrogen peroxide added first increased from 73% to 81% (H_2O_2 dosages from 1 to 5 cm^3/dm^3), and in the case of an H_2O_2 dosage from 5 to 10 cm^3/dm^3 it was at a similar level and did not exceed 83% (***Figure 4***). In the case of TOC the dependence was analogous. With an increase in the dosages of hydrogen peroxide applied the TOC removal was getting slower and tended to reach a plateau. With an increase in the hydrogen peroxide dosage in the test range from 1 to 10 cm^3/dm^3 the TOC removal increased from 51 to 74%. The resulting COD removal was about 10% higher than that of TOC.

In the case of a ferrous sulfate dosage of 0.5 g/dm^3 and an iron oxide nanopowder dosage of 0.1 g/dm^3, COD removal at hydrogen peroxide dosages from 1 to 3 cm^3/dm^3 increased from 70% to 84%. Next in the range of H_2O_2 dosages from 3 to 10 cm^3/dm^3 it was at a similar level, not exceeding 87% (***Figure 4***). A similar relationship was obtained for TOC. At a hydrogen peroxide dosage from 1 to

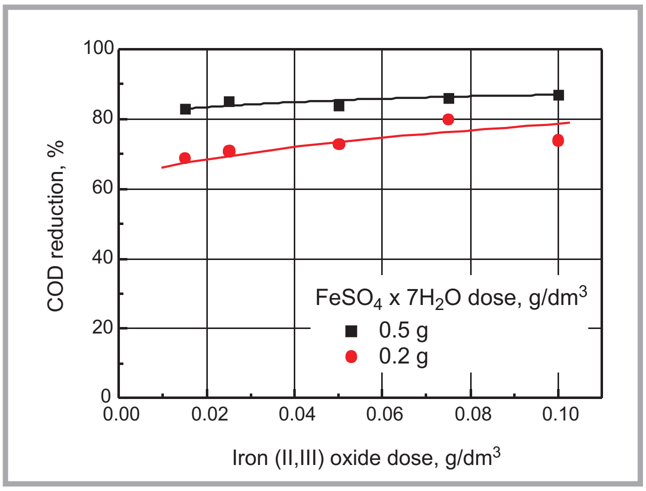

__Figure 2.__ Effect of iron oxide nanopowder dosage on COD changes in Symperonic NP10 solution at a concentration of 100 mg/dm^3 in the Fenton process. $FeSO_4 \times 7H_2O$ dosages – 0.2 g/dm^3 and 0.5 g/dm^3, the amount of hydrogen peroxide solution added – 5 cm^3/dm^3, pH = 3.5.

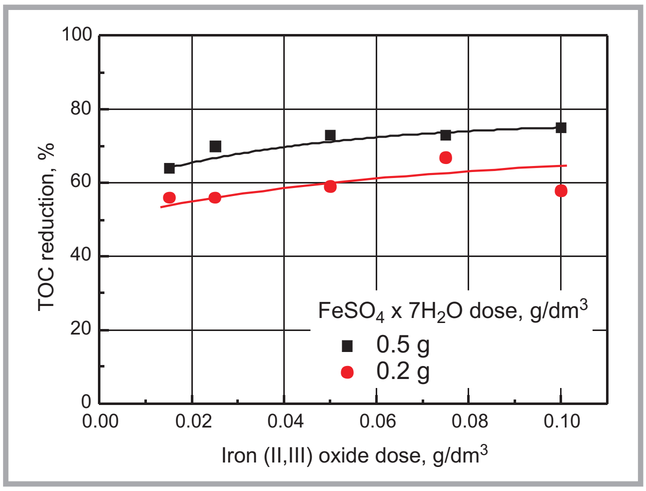

__Figure 3.__ Effect of iron oxide nanopowder dosage on TOC changes in Symperonic NP10 solution at a concentration of 100 mg/dm^3 in the Fenton process. Dosages of $FeSO_4 \times 7H_2O$ – 0.2 g/dm^3 and 0.5 g/dm^3, hydrogen peroxide solution added – 5 cm^3/dm^3, pH = 3.5.

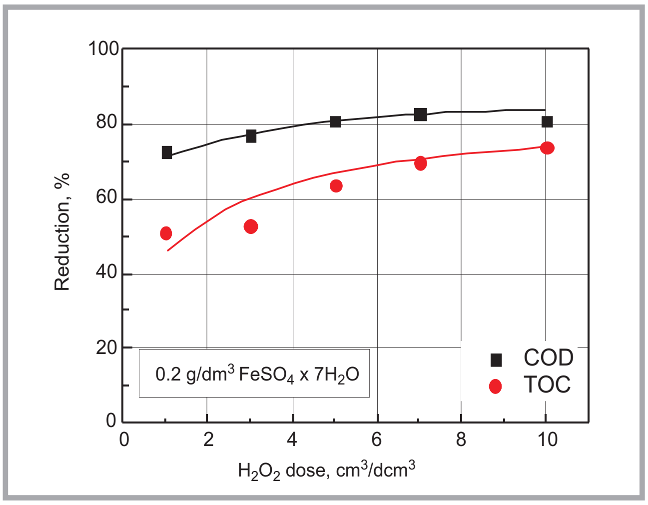

__Figure 4.__ Effect of hydrogen peroxide dosage on the changes of COD and TOC in Symperonic NP10 solution at a concentration of 100 mg/dm^3 in the Fenton process. $FeSO_4 \times 7H_2O$ dosage – 0.2 g/dm^3, iron oxide nanopowder dosage – 0.075 g/dm^3, pH = 3.5.

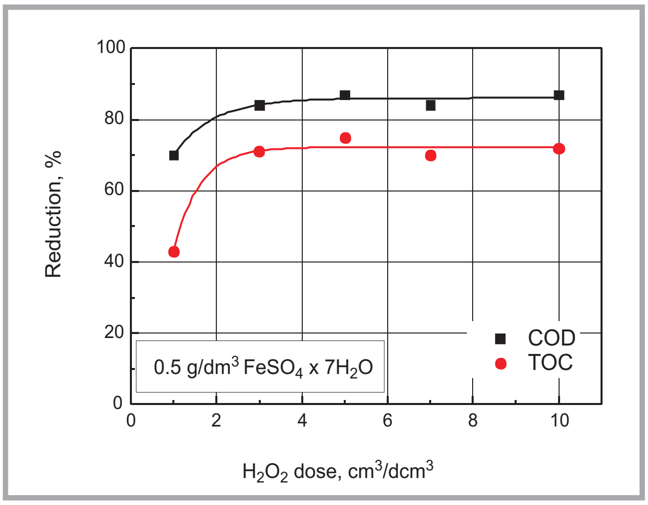

__Figure 5.__ Effect of hydrogen peroxide dosage on the changes of COD and TOC in Symperonic NP10 solution at a concentration of 100 mg/dm^3 in the Fenton process. $FeSO_4 \times 7H_2O$ dosage – 0.5 g/dm^3, iron oxide nanopowder dosage – 0.1 g/dm^3, pH = 3.5.

3 cm^3/dm^3 the TOC removal increased significantly from 43% to 71%, next at H_2O_2 dosages up to 10 cm^3/dm^3 it was at a similar level, not exceeding 75%.

As in previous cases, the TOC removal was lower than the COD. The detergent oxidation was much more efficient than its mineralisation. Low-molecular organic compounds with a high degree of oxidation remained in the solution. It was useless to apply hydrogen peroxide dosages exceeding 3 cm^3/dm^3 because this did not increase the efficiency of detergent decomposition.

The relationships obtained are consistent with the data described in literature for nonionic detergents in the classical Fenton process [8]. It follows from the Fenton reaction mechanism that when using big dosages of hydrogen peroxide, beyond a certain limit, the oxidation rate does not increase, and may even be lowered. A too high concentration of hydroxyl radicals promotes recombination reactions and increases the probability of competing reactions which do not lead to detergent oxidation [25]. As can be seen, a similar mechanism occurs in the Fenton process conducted with the use of iron oxide nanopowder.

At a dosage of hydrogen peroxide equal to 10 cm^3/dm^3, the level of COD reduction was comparable to that obtained in the Fenton process carried out at dosages of ferrous sulfate – 0.5 g/dm^3, iron oxide nanopowder – 0.1 g/dm^3 and H_2O_2 – 3 cm^3/dm^3. Thus, increasing the dosage of hydrogen peroxide three times, the dosage of ferrous sulfate can be reduced by 2.5 times and that of iron oxide nanoparticles by 25%, obtaining a comparable level of detergent mineralisation.

Effect of solution pH

An important parameter of the Fenton process is the pH of the solution. Therefore it was decided to check its effect on the reaction carried out with the use of iron oxide nanoparticles. Tests were conducted for a Symperonic NP10 concentration equal to 0.1 g/dm^3. The dosage of ferrous sulfate was 0.2 g/dm^3, iron oxide nanopowder – 0.075 g/dm^3, and hydrogen peroxide 5 cm^3/dm^3. Results of changes in the percentage of COD and TOC removal in the detergent solution

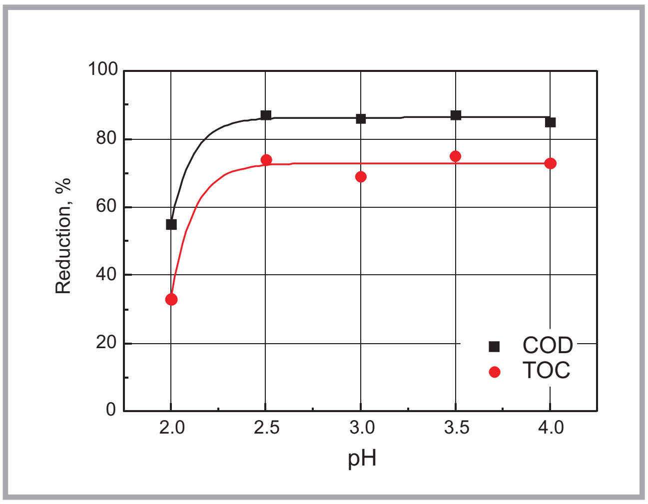

Figure 6. Effect of pH on COD and TOC changes in the Symperonic NP10 solution in the Fenton process. Dosage of ferrous sulfate – 0.2 g/dm³, iron oxide nanoparticles – 0.075 g/dm³, oxygen peroxide – 5 cm³/dm³.

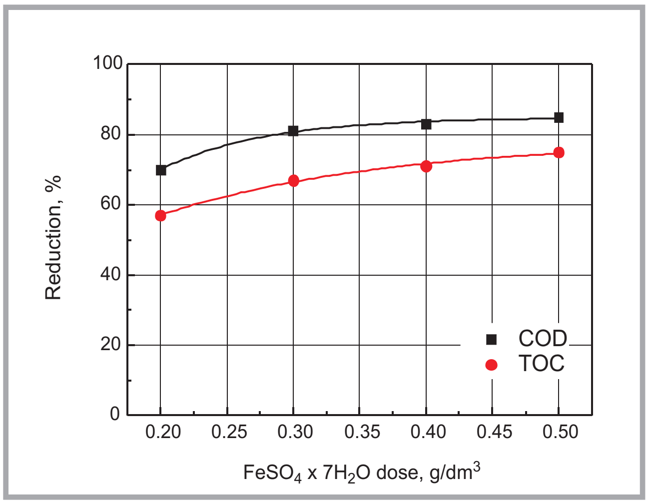

Figure 7. Effect of ferrous sulfate dosage on the changes in COD and TOC in the solution of Symperonic NP10 during the Fenton process. Hydrogen peroxide dosage – 5 cm³/dm³, pH of the solution – 3.5.

depending on the initial pH are shown in ***Figure 6***.

The tests showed that there was no dependence of COD and TOC removal on pH ranging from 2.5 to 4.0. The removal was 86% for COD and 74% for TOC. At pH 2.0 the removal of COD and TOC was significantly lower, reaching 55% and 33%, respectively.

According to the literature, for most of the compounds tested, the optimal pH value in the classical Fenton process is about 3 [25]. A decrease in the oxidation efficiency at higher pH values is caused by the precipitation of a part of iron in the form of hydroxide. The use of too low pH values is not recommended either, because ·OH radicals can react with H^+ ions, leading to a decrease in their concentration in the solution and a drop in the oxidation efficiency of organic compounds.

Comparison of the classical Fenton process with that carried out with the use of iron oxide nanopowder

It is important to compare the results of Symperonic NP10 decomposition obtained in the classical Fenton process with those attained in the process carried out in the presence of iron nanocompounds. For this reason experiments on the detergent decomposition in the classical Fenton process were carried out in a solution of 0.1 g/dm³ concentration using a hydrogen peroxide dosage of 5 cm³/dm³ at pH 3.5. The dosages of $FeSO_4 \times 7H_2O$ ranged from 0.2 to 0.5 g/dm³. ***Figure 7*** shows COD and TOC removal in the solution.

As follows from the data obtained, the COD removal increased with a ferrous sulfate dosage increase from 70% at 0.2 g/dm³ to 85% at a dosage of 0.5 g/dm³. Similarly the TOC removal increased from 57% to 75%.

Figure 8 shows changes in COD and TOC removal in solutions of Symperonic NP10 during the Fenton process as compared to the nanoFenton process. The Fenton process was carried out using ferrous sulfate dosages equal to 0.5 and 0.2 g/dm³ at a dosage of hydrogen peroxide of 5 cm³/dm³ and pH = 3.5. The nanoFenton process was conducted using the same process parameters as in the Fenton process and additionally iron oxide nanoparticles in the amount of 0.1 and 0.075 g/dm³.

As follows from the relationships shown in ***Figure 8.A***, at a higher dosage of ferrous sulfate (0.5 g/dm³) and iron oxide nanopowder of 0.1 g/dm³ in the nanoFenton process the COD removal was several percent higher than in the classical Fenton process, while the removal of TOC was the same. At a lower dose of ferrous sulfate (0.2 g/dm³) and iron oxide nanopowder dosage equal to 0.075 g/dm³ in the nanoFenton process both the removal of COD and TOC was about 10%

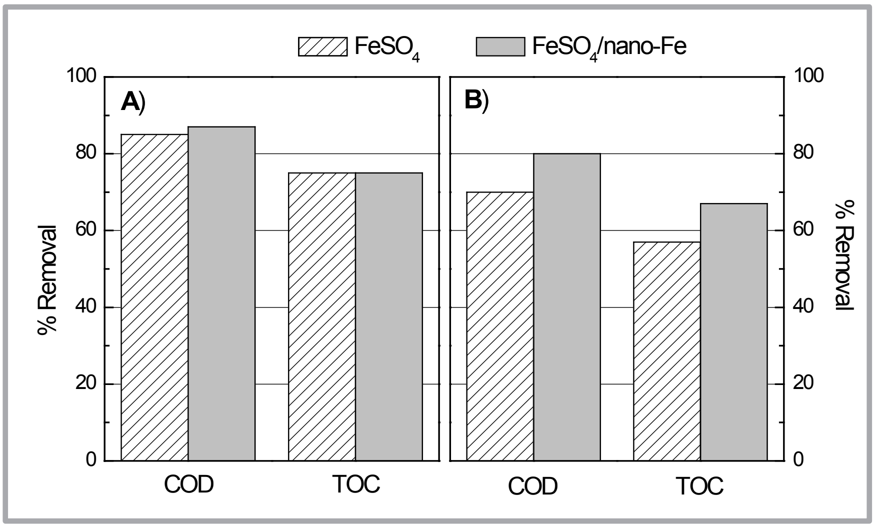

Figure 8. Changes in COD and TOC in Symperonic NP10 solution in the Fenton process compared to the nanoFenton process. A: Fenton process: pH=3.5, $FeSO_4$ dosage – 0.5 g/dm³, H_2O_2 dosage – 5 cm³/dm³, nanoFenton process: pH=3.5, $FeSO_4$ dosage – 0.5 g/dm³, iron oxide nanopowder dosage – 0.1 g/dm³, H_2O_2 dosage – 5 cm³/dm³, B: Fenton process: pH = 3.5, $FeSO_4$ dosage – 0.2 g/dm³, H_2O_2 dosage – 5 cm³/dm³; nanoFenton process: pH=3.5, $FeSO_4$ dosage – 0.2 g/dm³, iron oxide nanopowder dosage – 0.075 g/dm³; H_2O_2 dosage – 5 cm³/dm³.

higher than in the classical Fenton process (***Figure 8.B***). As follows from the relationships obtained, in experimental conditions the addition of iron oxide nanocompound had no significant effect on the conversion degree of Symperonic NP10. An advantageous result of this addition was more evident at a lower dose of ferrous sulfate.

Conclusions

The decomposition of Symperonic NP10 was an efficient process. A major drawback of the Fenton process, however, is the formation of hydrated sludge of iron (III) hydroxide, which must be rendered harmless. The sludge formed can contain a big load of various types of organic compounds generated in the process of detergent oxidation. Therefore it is important to minimise the amount of iron (II) used in the Fenton process, while not reducing its yield and efficiency. An advantageous solution can be the use of iron nanocompounds as they can improve the efficiency of oxidation and reduce the amount of iron ions required in the process, and thus contribute to a reduction in the amount of sludge formed. After completion of the process iron nanocompounds were transferred into the sludge.

The use of iron oxide nanopowder in the decomposition of Symperonic NP10 did not cause a significant increase in the oxidation efficiency, which was up to 10%. However, it is very interesting that the highest increase in the efficiency of Fenton process carried out in the presence of iron oxide nanopowder was obtained at the lowest dose of ferrous sulfate. Therefore it is planned to continue studies on the process optimisation which will cover the extension of the doses of iron oxide nanopowder applied, and also analysis of the amount of coagulation sludge being formed.

The nanoFenton process is very poorly acknowledged as regards its theory. Therefore the mechanism of action of iron nanoparticles on the formation of hydroxyl radicals and their reactions will be studied.

Acknowledgements

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