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Application of Fenton's Reagent in Detergent Separation in Highly Concentrated Water Solutions

Abstract

The concentrations of surfactants occurring in textile wastewater generated in washing processes reach from tens to several thousands of mg/dm³. A separate problem are the surfactants which remain on the walls of used packages. These remnants are eluted with water, and the concentration of detergents in sewage formed in this way is even higher than in washing baths, and can reach thousands of mg/dm³. The purpose of the study was to determine the degradability of selected detergents in highly concentrated water solutions exposed to Fenton's reagent. Experiments were made on 8 solutions of selected detergents and their mixtures. The authors investigated the effects of optimising Fenton's process, taking the Empicol and Slovafof solutions as examples. It was found that Fenton's process could be successfully used in concentrated water solutions of detergents. The degrees of reduction obtained are high, reaching 97% even at very high initial COD values (~ 35,000 mg O₂/dm³).

Key words: Fenton's reagent, detergents, concentrated water solutions.

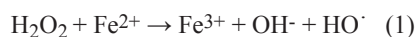
Introduction

Ionic and non-ionic surfactants occur in textile wastewater at concentrations ranging from dozens to even several thousands of mg/dm³. The presence of surfactants causes serious problems in the operation of wastewater treatment plants, and at high enough concentrations they hamper the processes of biological treatment. A characteristic feature of detergents is their low susceptibility to biodegradation, and often high toxicity. This particularly concerns non-ionic surfactants, which are classified as the so-called 'hard' detergents resistant to treatment processes. When surfactants reach surface water, they may cause disturbances even at very small concentrations, such as at 1 mg/dm³. The most important problems include reducing the surface tension of the water, and consequently a reduction of oxygen diffusion. This in turn leads to a decrease in the efficiency of self-purification processes. The organoleptic properties of the water also deteriorate. The presence of surfactants in a concentration exceeding 3 mg/dm³ in receiving water causes foaming, and has a disadvantageous effect on fish stocks.

Another problem is the surfactants left on the walls of used packages. These remnants are eluted with water, and the concentration of detergents in sewage formed in this way is even higher than in washing baths, and can reach thousands of mg/dm³. An efficient way to reduce the concentration of detergents present in sewage is to use Fenton's method, i.e. supporting coagulation with the use

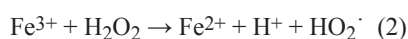
of ferrous salts by hydrogen peroxide. Hence, the aim of the study was to determine the degradability of selected detergents in water solutions and sewage exposed to the action of Fenton's reagent.

The term 'Fenton's reagent' refers to a water solution of hydrogen peroxide and ferrous salts, and is named after a chemist who in 1894 was the first to find that ferrous ions (Fe²⁺) strongly catalyse the process of hydrogen peroxide oxidation [1]. Reactive hydroxyl radicals are formed during the reaction of H₂O₂ with ferrous ions. This is illustrated by the following mechanism:



It is known from literature [2] that due to their very high oxidising potential, hydroxyl radicals destroy organic compounds in sewage which are unsusceptible to oxidation and biodegradation.

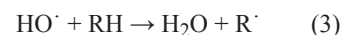
The oxidation efficiency of Fenton's reagent is the highest at pHs ranging from 2 to 5 and at a 1:1 molar ratio of H₂O₂ and Fe²⁺. The mechanism of this reagent's action was tested in detail for many reactions involving organic compounds and enzymes, although it cannot be considered as well-known, because of the variety of iron (II), iron (III) complexes and numerous radical intermediate products and their consecutive reactions. A significant role is played by Fe³⁺ ions which decompose H₂O₂ and produce HO₂[·] hydroperoxide radicals:



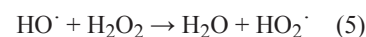
Properties similar to those of iron ions in reactions (1) and (2) are also shown by

the ions of other metals, such as Cu, Co, Mn and Ti.

In the solutions of H₂O₂ and ferric salts (II), organic compounds (RH) are oxidised in radical chain reactions. The main factor oxidising and propagating the reactions are HO[·] radicals:

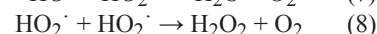
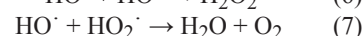
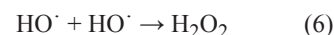


Hydroxyl HO[·] radicals also decompose H₂O₂, producing HO₂[·] radicals:

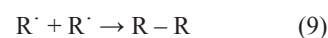


In the reactions of R[·] radicals with Fe³⁺ ions, carboniums R⁺, and with Fe²⁺ ions R⁻ carbanions, can be formed.

The kinetic chain ends in the reactions between the radicals:



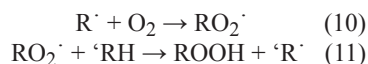
Non-ionic and ionic forms of the radicals contribute to the kinetic complexity of the mechanism of the chain reaction of oxidation of organic compounds with Fenton's reagent, as well as with other oxidants which generate HO[·] and HO₂[·] radicals. The mechanism should also include the recombination of R[·] radicals according to the network:



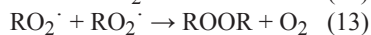
Even if only one R-H compound is oxidised, several R-type radicals are usually formed in the reacting solution. Parallel to R-R dimers, according to network (9), isomeric 'R-R', 'R'-R dimers and other

products of recombination of the radicals can be formed.

The concentration of oxygen formed in reactions (7) and (8) is usually low. However, in solutions saturated with oxygen, peroxide and hydroperoxide radicals are formed. In general, these reactions for RH compounds can be written as follows:



The kinetics of reaction (10) in water solutions have been studied for only a few compounds. The rate of these reactions is limited by diffusion ($k > 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). $R\cdot$ and $RO_2\cdot$ radicals quickly recombine, contributing to the termination of the chain reaction:



Reactions (12) and (13) are competitive to reactions (10) and (11) respectively, which makes kinetic studies difficult.

From these concise characteristics of reactions (1) to (13), we can see the complex mechanism of the oxidising action of Fenton's reagent. The $HO\cdot$ radicals play the most important role because they propagate the chain reaction of oxidation, and simultaneously in reaction (5) they produce $HO_2\cdot$ radicals which also take part in the propagation. The network of reactions (2) to (3) and (5) to (13) does not change significantly when $HO\cdot$ radicals are generated in different ways, for instance by ozone decomposition, or due to photolysis or radiolysis.

Oxidation with Fenton's reagent is justified, for instance, before carrying out further biological treatment of wastewater that contains compounds which are hardly biodegradable. Our preliminary studies on the treatment of model dyes and washing baths with the use of hydrogen peroxide and iron salts demonstrated a significant increase in treatment efficiency including the removal of dyes and surfactants [11].

A direct improvement in oxidation efficiency with the help of Fenton's reagent is impossible by simply raising the concentration of hydrogen peroxide and ferrous salts in the solution. In many cases, this leads to negative effects, decreasing the efficiency of formed hydroxyl radicals; this is related to the secondary reactions that reduce their concentrations in an unprofitable way.

Therefore, attention has recently increased to new kinds of Fenton's method involving ultraviolet and ionising radiation, called photo-Fenton and Fenton technology.

Aim of the study

The purpose of the study was to determine the degradability of selected detergents in highly concentrated water solutions under the influence of Fenton's reagent.

Analytical methods applied

Samples of the detergent solutions and their mixtures before and after treatment with Fenton's reagent were analysed in order to determine the following parameters:

1. chemical oxygen demand – COD, determinations made according to the Polish Standard PN-74/C-04578
2. biochemical oxygen demand – BOD₅, determinations made according to the Polish Standard PN-74/C-04578
3. content of anionic surfactants – AS, determinations made according to the Polish Standard PN-74/C-04550.
4. pH measurement
5. soluble substances – SS, determinations made according to the Polish Standard PN-78/C-04541
6. organic soluble substances – OSS, determinations made according to the Polish Standard PN-78/C-04541
7. total organic carbon – TOC
8. the content of iron ions in the solution by means of AAS (atomic adsorption spectrometry)

Reagents applied

All experiments were made using the following reagents:

- ferrous sulphate $FeSO_4 \times 7 H_2O$ (technical),
- hydrogen peroxide H_2O_2 in 35% water solution (technical),
- water solutions of NaOH and HCl at the concentration of c. 2 mol/dm³ were used to adjust the pH of the tested solutions.

Physicochemical properties of tested detergents

Eight detergents offered by Brenntag Polska Sp. z o.o. were analysed. Their characteristics are given below [2].

Empilan 2502 – diethanolamide of fatty acids of coconut oil (c. 80% solution). Chemical formula $R-CON-(CH_2CH_2OH)_2$ where $R = C_{12}-C_{18}$. Density – 1030 kg/m³ at 20 °C, physical state – liquid, boiling point > 100 °C, viscosity 1040 mPa s at 20 °C, soluble in ethanol, pH ~ 10.5.

Empigen BS/FA – cocoamidopropylbetaine (30% solution), C₁₂-C₁₈ alkylamidopropylbetaine. Density – 1000 kg/m³ at 20 °C, molecular mass – 350, physical state – liquid, boiling point c. 100 °C, melting point < 0, viscosity < 50 mPa s at 20 °C, pH ~ 5.

Trilon B – tetrasodium versenate. Chemical formula: $(NaOOCCH_2)_2NCH_2CH_2N(CH_2COONa)_2$. Bulk density – 650 kg/m³, molecular mass – 380, physical state – solid, melting point c. 400 °C, soluble in polar liquids, solubility in water c. 580 g/l at 20 °C, pH = 11 (10 g/l solution).

Empimin KSN 70/X – sodium salt of fatty alcohol sulphate C₁₃-C₁₅ oxyethylated with 3 moles of EO (70% solution). Density – 1100 kg/m³ at 20 °C, molecular mass – 441, physical state – paste, boiling point c. 100 °C, viscosity 3000 mPa s at 25 °C, pH = 7 to 9.

ABS acid – alkylbenzenesulphonic acid. Density – 1060 kg/m³ at 20 °C, physical state – viscous liquid, melting point < -5 °C, soluble in alkaline liquids and water pH ~ 1.0 (30 g/l solution).

Empicol ESB 70/25 – sodium lauryl sulphate oxyethylenated with 2 moles of EO 25% solution, oxyethylenated alkylsodium sulphate (C₁₀-C₁₆). Chemical formula $CH_3-(CH_2)_n-(O-CH_2-CH_2)_p-OSO_3Na$ where $n = 9-15$, $p = 2$. Density – 1050 kg/m³ at 20 °C, molecular mass – 384, physical state – viscous liquid, boiling point c. 100 °C, soluble in alcohols, pH = 8.0 to 8.5 (10% solution).

Slovafol 909 – oxyethylenated with 9 moles of ethylene nonylphenol oxide. Chemical formula: $C_9H_{19}-C_6H_4-O-(CH_2-CH_2-O)_9-H$. Density – 1055 kg/m³ at 25 °C, molecular mass – c. 616, physical state at 20 °C – liquid, boiling point > 250 °C, melting point c. 8 °C, viscosity 240 mPa s at 25 °C, soluble in ethanol, acetone and water, pH = 6 to 7.

ABS Na paste – alkylbenzene sodium sulfonate. Chemical formula: $RC_6H_4SO_3Na$

R = C₁₀H₂₁ - C₁₃H₂₇. Molecular mass 342 to 348. Physical state – paste, soluble in water without any limitation, pH = 7 to 9.5. Density – 1060 kg/m³ at 20 °C.

Characteristics of initial solutions

Water solutions of 8 selected detergents and two binary mixtures (1:1 ratio) were analysed in order to establish their initial characteristics by determining generally applied parameters for wastewater treatment. The initial concentration in all cases was 1.5% wt. The results are given in Table 1.

Experimental procedure

A 0.5 dm³ sample of detergent solution at the concentration of 1.5% wt in relation to a commercial preparation was placed in a 1.5 dm³ beaker; next, the pH was measured. Depending on the initial value, either NaOH or HCl solution was added to bring the pH to about 2. Then, ferric sulphate II FeSO₄ × 7 H₂O was added to the solution.

After adding iron II salt to the solution, it was mixed until the salt was completely dissolved, and then 35% hydrogen peroxide solution was added in the determined amount. The solution was constantly mixed, and the rate of droplet instillation was adjusted so as not to cause foaming. With large amounts of peroxide, the time needed for the instillation ranged from three to four hours. During the reaction, the solution was heated up to 50-56 °C. After the process of droplet instillation was completed, the solution continued to be mixed. It was found that the optimum time for additional mixing was about 4 hours. This ensured the complete decomposition of hydrogen peroxide (there were no problems with BOD₅ analysis) and the cooling of the mixture.

After oxidation and cooling, the solution was neutralised by adding NaOH solution to the value of pH = 10 to 11. In the case of Slovafof, pH of the solution after coagulation was around 12.4.

Applicability of Fenton's reagent in the solutions of detergents and their mixtures

Experiments were made on 8 solutions of selected detergents and their mixtures.

Table 1. Physicochemical characteristics of initial water solutions of selected detergents.

Detergent	COD, mg O ₂ /dm ³	BOD ₅ , mg O ₂ /dm ³	pH	AS, mg/dm ³	SS, mg/dm ³	OSS, mg/dm ³	TOC, mg C/dm ³
Slovafof	32600	3200	6.5	-	2470	360	11720
Empilan	35500	2400	9.4	7300	3620	460	11780
Empicol	7020	1270	6.8	1460	1460	790	1280
Empigen	8500	600	6.1	-	3180	880	1572
ABS acid	36500	400	1.5	18900	5160	600	11530
Empimin	21500	1400	7.3	19000	3160	1910	8740
Trilon B	3950	80	11.6	-	6620	3720	
ABS paste	10900	1100	7.8	4500	4710	1130	
Empilan +Slovafof	21500	400	8.1	3800	5540	380	11657
Empilan + Empicol	24250	1000	8.3	2280	2820	900	6797

Table 2. Characteristics of selected detergent solutions treated with Fenton's reagent.

Detergent	COD mg O ₂ /dm ³	COD reduction %	BOD ₅ mg O ₂ /dm ³	AS mg/dm ³	SS mg/dm ³	OSS mg/dm ³	Fe mg/dm ³	TOC mg/dm ³
Slovafof	4280	87.0	340	-	8140	8090	0.006	528
Empilan	3097	91.5	780	15.2	8912	7097	0.035	551
Empicol	813	89.5	340	22.8	3700	3600	0.026	412
Empigen	1219	85.9	420	-	4002	3813	0.029	-
ABS acid	1355	96.0	80	18.3	9950	9925	0.050	-
Empimin	580	97.0	380	11.3	7194	7102	0.106	-
Trilon B	1298	66.5	520	-	1967	1785	0.041	925
ABS paste	871	90.0	390	16.7	3895	3789	0.054	598
Empilan +Slovafof	8779	74.5	575	15.2	6561	6446	0.017	657
Empilan +Empicol	896	95.6	320	5.2	7144	7097	0.145	458

The amounts of iron II and hydrogen peroxide were selected on the basis of the initial values of COD of the tested solutions (Table 1). Calculations were made using the formulae applied in the technology of this process. They give the amount of 33% ferrous chloride solution and 35% volume of hydrogen peroxide solution [3].

$$V_{\text{FeCl}_2} = 1.069 \cdot 10^{-5} \cdot V_{\text{sample}} \cdot \text{COD} \quad (\text{I})$$

$$V_{\text{H}_2\text{O}_2} = 1.354 \cdot 10^{-5} \cdot V_{\text{sample}} \cdot \text{COD} \quad (\text{II})$$

The first formula determines the volume of the solution of ferrous chloride II, and hydrated ferric sulphate II in the solid form was used in the experiments, and so the relevant calculations were made. Fenton's process covering the solutions of 8 detergents and their two mixtures was performed according to the presented description. The results are given in Table 2 (the final value of COD is given in reference to the final solution obtained by dilution with H₂O₂ solution). The real COD reduction is naturally lower, and ranges from 63 to 82%.

Optimisation of Fenton's process taking the Empicol and Slovafof solutions as examples

Taking the Slovafof solution as an example, an attempt was made to optimise the process time. The first stage of the process covers the drop-wise addition of peroxide solution to the reaction medium and its time depends on the volume of H₂O₂ added. The strong foaming of the solution and the abrupt thermal effect require the slow addition of drops. Practically, it is most advantageous to carry out this part of the process for about 3 hours, as is confirmed by the results. When the reaction was carried out for 1 hour, the COD was equal to 6,955 mg O₂/dm³. When the reaction was prolonged to 3 hours, it decreased to 3,300 mg O₂/dm³. After the next 5 hours of mixing, the COD was 3,220 mg O₂/dm³. The experiment was made for 200 cm³ of detergent solution, adding 20 cm³ of 33% FeCl₂ solution and 20 cm³ solution of H₂O₂.

The next stage covered the optimisation of the amounts of added iron and hydrogen peroxide. The experiments were made using solutions of two detergents,

namely Empicol ESB 70/25 and Slovafof 909. The amount of iron changed in the range from 70 to 1 gram for Empicol solutions, and from 122 to 1 gram for Slovafof solutions. In the case of hydrogen peroxide solutions, these amounts ranged from 47 to 400 cm³ for Empicol, and from 125 to 400 cm³ for Slovafof. The results are given in Table 3.

Attempts were also made at additional purification of the Slovafof solution. The solution was treated with Fenton's reagent and subjected to repeated purification. After removing the ferric hydroxide from the solution, the COD was 2800 mg O₂/dm³. The experiment was made for 200 cm³ solution with the addition of 20 cm³ 33% solution of FeCl₂ and 20 cm³ solution of H₂O₂. After this treatment, the COD dropped to 1660 mg O₂/dm³. (It should be remembered that the solution was diluted from 200 to 240 cm³.) In the second trial, the solution was ozonated for 5 hours, and the final value of the COD reached 1500 mg O₂/dm³.

For comparison, the Slovafof and Empicol solutions were subjected to coagulation, adding 17.5 g FeSO₄ × 7 H₂O to 1 dm³ detergent solution. The solutions were not acidified, and they were alkalinised with NaOH.

Results and discussion

Water solutions of eight selected detergents and two detergent mixtures at the concentration of 1.5% wt were preliminarily analysed in order to determine their physicochemical parameters which characterised them as industrial wastewater. The results are given in Table 1.

In all cases, high and very high values of chemical oxygen demand were observed. They ranged from 4000 to 37000 mg O₂/dm³. The Empicol solution had the smallest COD value, while the ABS acid had the highest. The reaction of the solutions was also different, from strongly acidic (ABS acid) to alkaline (Trilon B). The biochemical oxygen demand ranged from 80 to 3200 mg O₂/dm³. The biodegradability of the solutions illustrated by the BOD₅/COD ratio was low in all cases, from 1 to 9%. Only the Empicol solution was characterised by higher degradability, reaching 18%. Seven solutions of the ten tested contained anionic surfactants (AS). As expected, the determinations made according to the analytical methods given in the Polish Standard diverge,

Table 3. Characteristics of water solutions of Empicol and Slovafof treated with Fenton's reagent; a) 2 cm³ HCl + 200 cm³ H₂O, H₂O₂ was added drop-wise for 3 h and 5 h mixing, b) subjected only to coagulation without preliminary acidification.

Detergent	FeSO ₄ g	H ₂ O ₂ cm ³	COD mg O ₂ /dm ³	BOD ₅ mg O ₂ /dm ³	AS mg/dm ³	SS mg/dm ³	OSS mg/dm ³
Empicol a)	0	0	7020	1270	1460	1460	790
	27	47	820	340	15.2		
	70	250	280	56	9.2	41500	41150
	17.5	62	1260	480	76	23000	22210
	17.5	250	310	<10	11.3	19180	18650
	17.5	400	150	<10	0.0	15090	14840
	10	250	480	108	19.0	11650	11410
	5	250	510	130	18.5	6510	
	2.5	250	690	265	0.0	5120	4500
	1	250	850	260	9.3	3920	3220
b)	17.5	0	5900	700		19760	
Slovafof a)	0	0	32600	3200	-	2470	360
	122	210	4280	340	-		
	70	250	1210	107	-	43550	42530
	35	125	8770	40	-	51770	47720
	35	250	912	110	-	30850	29820
	35	400	760	16	-	26170	25420
	20	250	1142	260	-	21980	21390
	10	250	1258	230	-	18400	17900
	5	250	1336	185	-	9890	9820
	2.5	250	1030	285	-	7300	6690
1	250	1370	275	-	4910		
b)	17.5	0	25750	1800		21700	

sometimes significantly, from the values resulting from the solution concentration. The lowest value was obtained for Empicol. However, it should be kept in mind that the commercial preparation is a 25% solution of the active substance. The solutions of Slovafof, Empigen and Trilon B did not contain any anionic surfactants.

The amounts of FeCl₂ and H₂O₂ necessary to obtain proper pollutant reduction using Fenton's method were determined from the formulae used in wastewater treatment technology. Since the work is technological in nature, technical reagents were used in all experiments, namely copperas (FeSO₄ × 7 H₂O) and hydrogen peroxide (35% solution), which were recalculated and are given in Table 2. To avoid too high a dilution of the solution, which would result in obtaining an unreal COD decrease, the copperas was introduced to the solution in solid form prior to the reaction.

The experiments demonstrated the strong oxidising action of Fenton's reagent. The results of COD reduction ranged from 65 to 97%, as shown in Table 3. The COD of solutions before iron coagulation (for the acidic solution, after completing the reaction) and after the coagulation revealed in the majority of cases either

none or only a slight effect of organic pollutant sorption by ferric hydroxide Fe(OH)₃. Only in the case of Slovafof and Empilan or their mixtures, was there any evident sorption, which is documented by significant changes in COD.

Due to oxidation of the tested detergents, the values of BOD₅ usually decreased (an increase was observed for Trilon B). Biodegradability measured by the BOD₅/COD ratio for the tested solutions improved significantly, from several to tens of times. This is a very important fact, because despite the very profound destruction of the initial solution, the products of detergent decomposition do appear to be biodegradable. This offers a more optimistic view of the possibility of biologically treating this wastewater type.

The next stage of research was the optimisation of the amount of iron II and hydrogen peroxide. For these experiments, solutions of Empicol and Slovafof were selected. To check whether it was possible to reduce the concentration of iron II, the experiments were performed at a constant amount of hydrogen peroxide, ranging from 250 cm³ to 500 cm³ of detergent solution. The maximum amount of iron (added in the form of FeSO₄ × 7 H₂O) was 70 g, while the minimum was 1 g. From the results presented in Ta-

ble 5, we may conclude that the amount of iron has no important effect on the final COD reduction. All the levels of reduction reached so far were above 90%, even with a minimum amount of iron. However, it should be kept in mind that for the added amount of $\text{FeSO}_4 \times 7 \text{H}_2\text{O}$ (to 0.5 dm³ solution) reaching 10 g or less, the process becomes unstable. In the initial period, it practically does not occur at all. Only at a high concentration of hydrogen peroxide (at least 150 cm³ H₂O₂ added per 0.5 dm³ detergent solution) does the reaction gain speed to reach a turbulent course. The reaction mixture is heated up rapidly, and can even reach boiling point. When 1 g of $\text{FeSO}_4 \times 7 \text{H}_2\text{O}$ to 0.5 dm³ detergent solution was used, the mixture had to be heated up to initiate the reaction. After reaching about 60-70 °C, a violent reaction was observed which could result in the evaporation of around one-third of the solution. At the initial stage, a strong foaming occurred which was able to cause the boil-over of the solution in the reactor. It was thus necessary to cool down the reaction mixture. Hence, the process of oxidation should be carried out very carefully for these iron concentrations. For higher concentrations of iron II (above 10 g $\text{FeSO}_4 \times 7 \text{H}_2\text{O}$ per 0.5 dm³ solution), the process run is stable. At the initial phase (0.5 – 1 hour), the reaction mixture slowly heats up to about 60 °C. At this time, significant foaming appears. After this period the mixture stops foaming, and slowly changes colour to dark yellow or brown. At high iron concentrations, a brown deposit is precipitated. At low iron concentrations, the solution was bright yellow, and a small amount of deposit was also precipitated; in this case, however, it was white. The effects discussed were observed in the case of both Empicol and Slovafol solutions.

These experiments, the aim of which was to determine the effects of hydrogen peroxide concentration, were performed for one value of iron II concentration. 17.5 g $\text{FeSO}_4 \times 7 \text{H}_2\text{O}$ per 0.5 dm³ Empicol solution and 35 g $\text{FeSO}_4 \times 7 \text{H}_2\text{O}$ for Slovafol was used. The amount of hydrogen peroxide ranged from 62 cm³ to 400 cm³ for Empicol, and from 125 cm³ to 400 cm³ for Slovafol. The results are given in Tables 5 and 6, respectively.

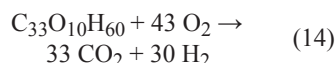
In the case of the Empicol solutions tested, no practical differences were obtained in the final values of COD for

250 and 400 cm³ of the added hydrogen peroxide. Taking the various dilutions of the reaction mixture into account, the real reduction of pollutants is even slightly worse for 400 cm³ H₂O₂. Similar results were obtained for Slovafol solutions characterised by an initial COD value which was greater by more than 4 times. A slight increase in pollutant reduction, by about 0.3%, cannot in any way explain the increase by almost two times in the amount of hydrogen peroxide used.

Finally, it was found that a factor of great importance for the process of oxidation of the detergent solutions tested was the amount of hydrogen peroxide used.

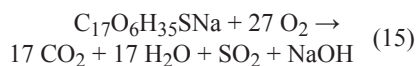
On the basis of the producer's data, in reference to the formulae of the applied detergents, we can state as follows:

For Slovafol:



The theoretical value of COD in the 1.5% wt. solution determined on the basis of the above reaction was 33,500 mg O₂/dm³ (experimental 32,600 mg O₂/dm³).

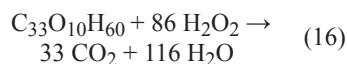
For Empicol:



The theoretical value of COD in the 1.5% wt. solution determined on the basis of the above reaction is 8,307 mg O₂/dm³ (experimental value 7,200 mg O₂/dm³).

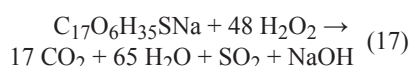
Since the theoretical values of COD are in good agreement with the experimental results, the given detergent composition should be assumed to be true, and the following equations for their oxidation with hydrogen peroxide can be written:

For Slovafol:



The theoretical quantity of hydrogen peroxide (in the form of a 30% solution), as determined on the basis of the above reaction which is required to oxidise 7.5 g detergent, is about 117 g.

For Empicol:



The theoretical amount of hydrogen peroxide (in the form of a 30% solution), as

determined on the basis of the above reaction which is required to oxidise 7.5 g detergent, is about 26 g.

The amount of hydrogen peroxide calculated from formula (II) was 210 cm³ for Slovafol and 47 cm³ for Empicol, i.e. about twice as much as theoretical values.

In order to better optimise the reaction, the oxidation of Empicol should be checked for about 50 cm³ hydrogen peroxide and low iron concentrations. The applied amount of 250 cm³, i.e. 5 times higher, can appear unnecessary in reference to this detergent.

It should be stated, however, that the increase of H₂O₂ enabled a decrease in the final COD value of more than five times. The experiments with coagulation in reference to both tested solutions revealed a slight decrease in the basic parameters. The COD reduction did not exceed 20%, and the changes in BOD₅ were similar within the limit of error.

A detailed economic analysis can provide an answer to the question of to what extent of decomposition (measured by COD decrease) it is profitable to increase the amount of hydrogen peroxide.

Neither for Empicol nor for Slovafol solution could the final values of COD be less than 100 mg O₂/dm³. Even when the solution was treated again with Fenton's reagent or subjected to ozonation, no significant decrease in the COD was observed. It seems that in the solution the products of decomposition which were obtained in the solution would be difficult to oxidise any further. Taking into account the biodegradability of the solutions being oxidised, good effects can be expected during their biological treatment.

The very high values of SS and OSS obtained in the samples containing Slovafol and Empicol after Fenton's process were mainly the effect of the reagents used in the experiments and their purity. This impact was due to the application of hydrochloric acid and sodium base (a slight increase), but it was also related to the iron (in the form of technical ferrous sulphate FeSO_4) which was added to the reaction medium.

Final conclusions

- Fenton's process can be successfully used in concentrated water solutions of detergents.
- The degrees of reduction obtained are high, reaching 97% even at very high initial COD values (~ 35,000 mg O₂/dm³).
- A factor determining the efficiency of Fenton's process with respect to the tested detergent solutions is the amount of hydrogen peroxide used.
- The process of oxidation can occur even at very small Fe²⁺ concentrations (part of gram of FeSO₄ × 7 H₂O per 0.5 dm³ solution), although the process is then not very stable, and requires a rise in temperature.
- Small amounts of Fe²⁺ in the solution contribute to the formation of small quantities of coagulation deposits after neutralisation. The hydrated deposits of ferric hydroxide Fe(OH)₃ are the main problem in the industrial application of Fenton's process.
- The economy of the process of oxidation with Fenton's reagent in relation to the detergent solutions tested is extremely advantageous. No other version of the advanced oxidation is as competitive in this case. Simple technology, low investment and operation costs (cheap reagents) offer an optimistic perspective for its industrial application. The only disadvantage is the formation of a deposit, which however can be greatly reduced. Hydrated deposits of ferric hydroxide can be utilised in many ways, particularly in small amounts, and do not contain adsorbed organic compounds in large quantities.



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