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Textile Wastewater Treatment by the Fenton Method

Abstract
The aim of this study was to determine the efficiency of the decomposition of pollutants present in textile wastewater in the Fenton process. The main processing parameters, namely the optimum quantities of hydrogen peroxide and ferric salts added as well as the pH of a solution, were determined in textile wastewater formed during different technological operations. These data were used to verify the applicability of empirical formulae describing these values. It was found that the use of Fenton's reagent in the technology of textile wastewater treatment was an efficient method for the decomposition of pollutants and could be successfully applied as a preliminary stage prior to further biological treatment. To achieve the proper efficiency and economy of this solution, continuous control of the wastewater composition and quick optimisation of process conditions are required. It is necessary to check the reaction for a large amount of various types of wastewater and to find relevant relations which would enable quick optimisation of the process with respect to the changing input parameters of the wastewater subjected to treatment.

Key words: *textile wastewater, chemical oxidation, Fenton method, process efficiency.*

Introduction

Textile wastewater is difficult to treat with the use of classical physicochemical and biological methods, which is mainly due to their intensive colour, high content of surfactants and other organic and inorganic compounds, a significant toxicity and poor biological recovery. Therefore, for many years researches have been carried out to improve the efficiency of treatment methods, and new methods characterised by a high degree of pollutant removal, good efficiency and reasonable cost have been searched for [1 - 3].

Among the methods which enable a decrease in pollutant concentrations in wastewater, one of the simplest and cheapest is Fenton's reaction, which consists in the non-selective and highly efficient oxidation of organic compounds by means of hydroxyl radicals [4 - 7], which are formed in a chain process of hydrogen peroxide decomposition in the presence of bivalent iron salts, which is represented by the following mechanism:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO^\bullet \quad (1)$$

The process is a radical reaction during which significant quantities of hydroxyl radicals $HO^\bullet$, capable of the oxidation of even the most resistant pollutants, are generated [8 - 10]. The basic advantages of this method include the high efficiency of the oxidation reaction, low cost, easily available substrates and the simplicity of the procedure.

The efficiency of oxidation with Fenton's reagent is the highest at a pH ranging from 2 to 5 and for a molar ratio of H_2O_2 to Fe^{2+} of about 1 : 1. The mechanism of this reagent was tested thoroughly for many reactions of organic compounds and enzymatic reactions. However, it cannot be considered well explained because of the variety of iron(II) and iron(III) complexes as well as the numerous radical intermediate products and their consecutive reactions [11 - 13]. An important role is also played by Fe^{3+} ions occurring in the process, which decompose H_2O_2, producing hydroperoxide radicals $HO_2^\bullet$:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^\bullet \quad (2)$$

Properties similar to those of iron ions in reactions (1) and (2) also have the ions of other metals, such as Cu, Co, Mn and Ti [14].

The aim of our work was to determine the efficiency of the decomposition of pollutants present in textile wastewater in the Fenton process. Taking textile wastewater from different technological operations as an example, the main processing parameters, including the optimum amounts of hydrogen peroxide and ferric salts added, were determined. The data were used to check the applicability of empirical formulae identifying these values. The possibility of predicting the optimum amounts of substrates added in the process is very important for wastewater treatment plants in which the Fenton process is used, especially when the wastewater composition undergoes continual quantitative and qualitative changes, as is the case in textile wastewater.

Methods

The object of study was real textile wastewater of different concentration and composition: concentrated dyeing and washing wastewater, as well as averaged general process effluents and concentrated effluents from the nanofiltration process. The washing wastewater-1 tested came from the process of the preliminary washing of cotton fabric with a polyester core, in which a nonionic detergent was used for washing. Washing wastewater-2 was produced in the preliminary washing of polyester knitted fabrics, in which an anionic detergent was used for washing. The types of dyeing wastewater tested were formed during the dyeing of cotton knitted fabrics with reactive dyes. The general averaged process effluents were taken from a Łodź textile factory which processes cotton fabrics. The concentrated effluent tested was generated during the nanofiltration of wastewater from the dyeing of cotton fabrics. Physicochemical characteristics of the wastewater tested are given in ***Table 1***.

The Fenton reagent used in the experiments was composed of about 30% solution of hydrogen peroxide (analytically pure, PPH POCh, Gliwice) and iron(II) salt in the form of technical $FeSO_4 \cdot 7H_2O$. In the textile wastewater prior to processing, the reaction was corrected to pH = 3.5 by means of sulfuric acid solution added at a concentration of 1 mol/dm^3. Next, pollutants were subjected to oxidation by the Fenton method. A determined amount of solid ferrous sulfate was added to the solution and mixed until complete dissolution. Then a proper amount of hydrogen peroxide was added drop wise. First, the solution was mixed vigorously for 2 minutes, then slowly for the next 10 minutes and left for 24 hours. After this time the solution was neutralised with 10% NaOH to a pH of about 11. After a subsequent 24 hour period the solution was decanted and filtered. The sample tested was analysed: the COD was determined, and in some cases the content of anionic surfactants was specified. The experiments were carried out at room temperature. The dilution degree of the solution was included in the calculations.

Results

Effect of the hydrogen peroxide concentration

To determine the effect of the hydrogen peroxide concentration on the Fenton process, the concentration of ferrous sulfate was kept constant, while the amount of hydrogen peroxide was variable.

In the case of dyeing and washing-2 wastewater, the concentration of ferrous sulfate was 1.6 g/dm^3 of wastewater (5.76 mmol/dm^3), and the concentration of hydrogen peroxide was changed in the range of 5 to 80 cm^3/dm^3 of wastewater (0.058 – 0.93 mol/dm^3). In washing-1 wastewater and general averaged process effluents, these values were 2 g/dm^3 of wastewater (7.2 mmol/dm^3) for ferrous sulfate and from 20 to 80 cm^3/dm^3 of wastewater (0.23 – 2.33 mol/dm^3) for hydrogen peroxide. For concentrated effluent from the nanofiltration process, the concentration of ferrous sulfate was

Table 1. *Physicochemical parameters of the wastewater tested.*

No.	Wastewater type	COD, mg O_2/dm^3	Chlorides, mg/dm^3	pH	Anionic surfactants, mg/dm^3
1	dyeing	4170	2100	10.3	-
2	washing-1	2190	-	7.3	-
3	washing-2	350	-	7.2	30.0
4	general	1720	-	9.2	9.8
5	concentrated	4930	-	10.3	-

1 g/dm^3 of wastewater (3.6 mmol/dm^3), and that of hydrogen peroxide was from 20 to 200 cm^3/dm^3 of wastewater (0.23-2.33 mol/dm^3). ***Figure 1*** shows the effect of the hydrogen peroxide concentration on the Fenton process for the wastewater samples tested.

When investigating the effect of the amount of H_2O_2 added to different types of textile wastewater, practically identical relations were obtained. The efficiency of COD reduction grew up to a certain quantity of hydrogen peroxide added, , beyond which it was practically at a constant level. At a low initial value of COD (350 mg O_2/dm^3) in washing wastewater-2, a maximum reduction in this parameter was obtained fastest at small concentrations of H_2O_2 (5 cm^3/dm^3, i.e. 0.058 mol/dm^3). For other wastewater types with initial COD values from 1720 to 4920 mg O_2/dm^3 , the optimum amounts of H_2O_2 were similar, reaching about 40 cm^3/dm^3 of wastewater (0.466 mol/dm^3).

Significant differences were observed in the degrees of COD reduction obtained. The highest COD reduction, 90%, was achieved in washing wastewater-2, which had the smallest load, lowest initial COD and was easily degradable. Washing wastewater-1 and general process wastewater behaved in a similar way. In the first case COD reduction reached 90%, while in the second it was 87%. The initial values of COD in these types of wastewater were similar, amounting to 2190 and 1720 mg O_2/dm^3, respectively. Moreover, in the process wastewater in the whole range of hydrogen peroxide quantity, a 100% reduction in anionic surfactants was achieved.

In dyeing wastewater and concentrated effluent with an initial COD equal to 4170 and 4930 mg O_2/dm^3, respectively, the reduction in this parameter was remarkably lower, i.e. 27% and 64%, respectively. Despite a slightly lower initial COD, the dyeing wastewater appeared to be much less susceptible to oxidation in the Fenton process. The substances present in that wastewater, including reactive dyes, were difficult to degrade even when very big quantities of H_2O_2 were added.

Effect of iron ion concentration

The influence of iron II ion concentration on the efficiency of pollutant decomposition in textile wastewater was investigated at a constant initial hydrogen peroxide concentration with a changing amount of $FeSO_4 \cdot 7H_2O$ added. In the case of dyeing and washing wastewater-2,

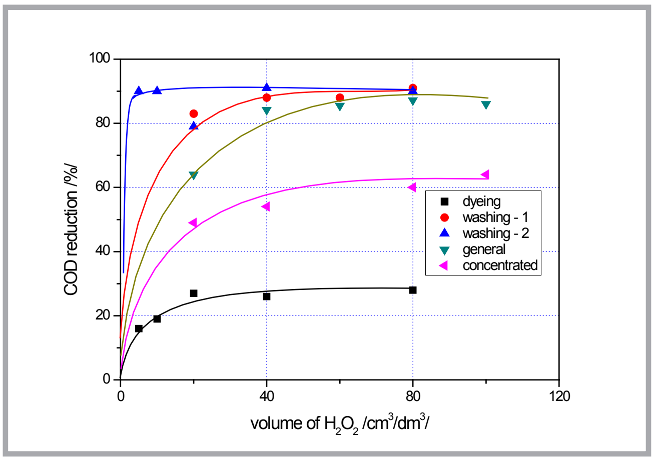

Figure 1. *Effect of the hydrogen peroxide added on the percent of COD reduction in textile wastewater: ■ – dyeing, ● – washing-1, ▲ – washing-2, ▼ – general ◄ – concentrated.*

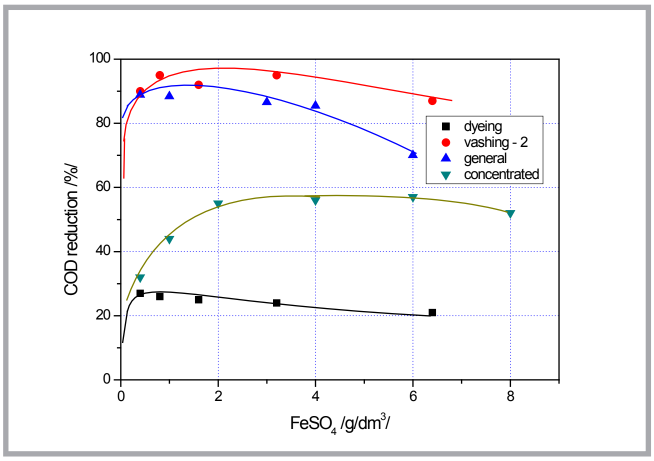

Figure 2. *Effect of $FeSO_4 \cdot 7H_2O$ addition on COD reduction in textile wastewater: ■ - dyeing, ▲ - washing-2, ▼ - general, ◄ - concentrated.*

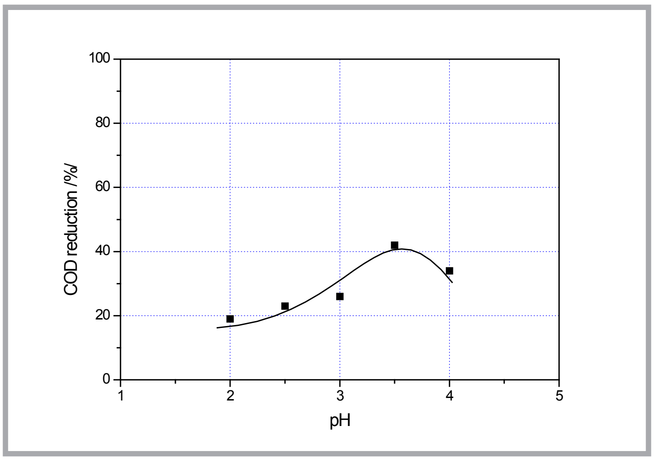

Figure 3. *Effect of pH on COD reduction in dyeing wastewater. The amount of H_2O_2 solution added was 20 cm^3/dm^3 (0.23 mol/dm^3) and ferrous sulfate - 1.6 g/dm^3 (5.76 $mmol/dm^3$).*

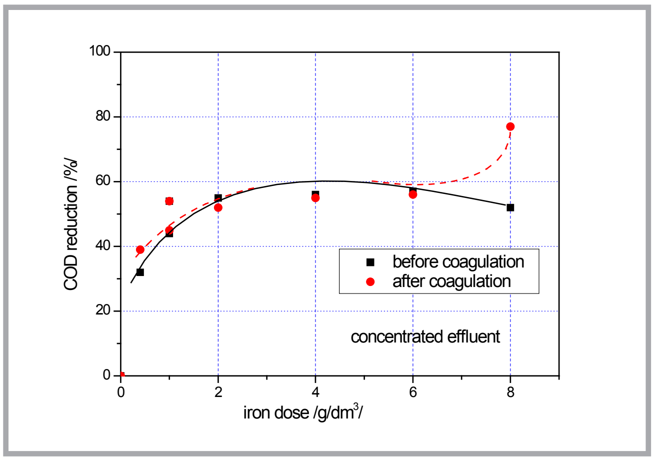

Figure 4. *Comparison of results of COD reduction in the concentrated effluent during the Fenton process prior to and after coagulation.*

the amount of hydrogen peroxide was 20 cm^3/dm^3 of wastewater (0.23 mol/dm^3), and ferrous sulfate was applied in the following quantities: 0.4, 0.8, 1.6, 3.2 and 6.4 g/dm^3 of wastewater, which corresponded to 1.44, 2.88, 5.76, 11.51 and 23.02 $mmol/dm^3$. For general process wastewater and concentrated effluent, the initial concentration of hydrogen peroxide was 40 cm^3/dm^3 of wastewater (0.466 mol/dm^3), and ferrous sulfate addition was 0.4, 1, 2, 3, 4, 6 and 8 g/dm^3 of wastewater (1.44, 3.6, 7.2, 10.8, 14.4, 21.6 and 28.8 $mmol/dm^3$). The effect of the quantity of ferrous sulfate on the Fenton process for the wastewater samples tested is shown in ***Figure 2***.

The dependence of COD reduction in wastewater on the amount of iron II added to the textile wastewater tested revealed a flat maximum in all cases. The addition of iron quantities exceeding optimal doses deteriorated COD reduction in the textile wastewater only slightly. In three cases the optimal amount of $FeSO_4 \cdot 7H_2O$ was about 1 g/dm^3 (3.6 $mmol/dm^3$), while for the concentrated effluent characterised by a high initial COD, this amount was higher, i.e. about 2 g/dm^3 (7.2 $mmol/dm^3$).

The type of wastewater was very important for the efficiency of oxidation processes by the Fenton method. The dyeing wastewater was poorly purified – 27% COD reduction: the concentrated effluent achieved a better result – 56%; the best effects were achieved for averaged wastewater – 89% and washing wastewater-2 – 95%. Exceeding the optimal iron quantity had the most disadvantageous effect on COD reduction in the general wastewater – a decrease of 18.3%. The smallest decrease was observed for the concentrated effluent and dyeing wastewater - 4% and 5%, respectively. In the case of process and washing wastewater -2, a 100% reduction in anionic surfactants was reported in all experiments.

Effect of pH

Taking dyeing wastewater as an example, studies on the effect of pH upon the efficiency of the Fenton process were carried out. The following pH values were used: 2, 2.5, 3, 3.5 and 4, which were initial values. During the Fenton process, the solutions were acidified and, depending on the initial pH value and wastewater type, the acidity decreased from pH 0.5 to 1. The quantities of ferrous sulfate and hydrogen peroxide added were constant, amounting to 1.6 g/dm^3 (5.76 $mmol/dm^3$) and 20 dm^3/dm^3 of wastewater (0.23 mol/dm^3), respectively. Figure 3 shows the results of COD reduction.

As follows from the relations shown in Figure 3, the efficiency of the purification process had a maximum at pH = 3.5. Differences in the reduction efficiency were quite significant, reaching about 20%. Based on this result, one can state that the decomposition of pollutants present in dyeing wastewater depends, to a large extent, on the initial pH of the solution.

Coagulation

In order to verify the effect of coagulation on the final result of textile wastewater purification in the Fenton process, the COD of the solution was determined after oxidation but prior to neutralisation. A second series of analyses were performed after the neutralisation, decantation and filtration of the wastewater. Results obtained for the concentrated effluent, which was characterised by a high initial COD, are shown in ***Figure 4***.

Data obtained for the concentrated effluent from the nanofiltration process confirm that the process of coagulation with ferric hydroxide at a $FeSO_4 \cdot 7H_2O$ concentration up to 6 g/dm^3 (21.6 $mmol/dm^3$) does not affect the final COD reduction in the wastewater. Products formed in the oxidation process do not coagulate from the solution. Only an increase in the amount of iron and related decrease in oxidation efficiency make the coagulation process important. The COD reduction increases from 52% to 78%. In all probability non-oxidised initial pollutants and products of their decomposition amounting to about 25% of the initial COD are removed from the solution along with the deposit of ferric hydroxide.

Discussion

Tests made on textile wastewater showed that hydroxyl radicals produced in the Fenton process effectively decomposed pollutants present in it. The efficiency of the decomposition of organic compounds depended on the initial wastewater composition and initial concentration of pollutants. The types of wastewater tested had different characters (dyeing, washing and general process wastewater, & concentrated effluents after nanofiltration) and pollutant concentrations, which was demonstrated by the broad range of COD values - from 350 to 5000 mg O_2/dm^3. Among the solutions tested, it was found that pollutants present in washing wastewater decomposed most effectively. Despite the different compositions of these types of wastewater, in which one contained nonionic surfactants (washing-1) while the others had the anionic type (washing-2), whose COD values were 2200 and 350 mgO_2/dm^3, respectively, the reduction in COD obtained in optimum conditions was similar: in less concentrated wastewater (washing-2) it reached 95% at most, while in 6-times more concentrated wastewater (washing-1) it was 90%. It can be concluded that surfactants are very susceptible to oxidation in the Fenton process. Optimum doses of ferrous sulfate in the case of more concentrated wastewater were 4 times higher than for less concentrated wastewater, being 2 g (7.2 mmol/dm^3) and 0.5 g $FeSO_4$/dm^3 of wastewater (1.8 mmol/dm^3), respectively. Similarly, the amount of hydrogen peroxide required was 6 times higher, amounting to 30 cm^3/dm^3 (0.349 mol/dm^3), as compared to 5 cm^3/dm^3 (0.058 mol/dm^3).

Very good results of the wastewater treatment were also obtained in the case of general averaged process wastewater. The 86% COD reduction was only slightly worse than results achieved for washing wastewater. The optimum dose of ferrous sulfate was nearly 1 g of $FeSO_4 \cdot 7H_2O$/dm^3 of wastewater (3.6 mmol/dm^3), and that of hydrogen peroxide - around 40 cm^3/dm^3 (0.466 mol/dm^3).

In the case of concentrated effluents, the results of treatment were quite satisfactory, namely a 64% COD reduction. It is worth noting that the concentrated effluent was extremely concentrated, its initial COD reaching 5000 mg O_2/dm^3. The optimum dose of ferrous sulfate determined was around 4 g of $FeSO_4 \cdot 7H_2O$/dm^3 of wastewater (14.4 mmol/dm^3), and that of hydrogen peroxide - about 60 cm^3/dm^3 (0.699 mol/dm^3).

The poorest treatment results were found for dyeing wastewater. At optimum concentrations of iron and hydrogen peroxide, a 27% COD reduction was obtained. The concentrations were 20 cm^3/dm^3 (0.233 mol/dm^3) for H_2O_2 and 0.5 g/dm^3 (1.8 mmol/dm^3) for $FeSO_4 \cdot 7H_2O$.

The optimum concentrations of hydrogen peroxide and iron determined for the textile wastewater tested were compared to the data calculated from formulae used in wastewater treatment technology.

Table 2. *Comparison of the optimum concentrations of iron and hydrogen peroxide required in the Fenton process for selected types of textile wastewater.*

	Wastewater type	Experimental value		Calculated value	
		cm^3/dm^3	mol/dm^3	cm^3/dm^3	mol/dm^3
Hydrogen peroxide - H_2O_2	dyeing	20	0.233	56.5	0.658
	washing-1	30	0.349	29.6	0.345
	washing-2	5	0.058	4.7	0.055
	general	40	0.466	23.3	0.271
	concentrated	60	0.699	66.7	0.777
		g/dm^3	mol/dm^3	g/dm^3	mol/dm^3
Ferric sulfate – $FeSO_4$□$7H_2O$	dyeing	0.5	0.0018	42.5	0.152
	washing-2	2	0.0072	3.5	0.0126
	general	1	0.0036	17.5	0.063
	concentrated	4	0.0144	50.3	0.181

$$V_{H_2O_2} \text{ in dm}^3 = 1.354 \cdot 10^{-5} \cdot V_{sample} \text{ in dm}^3 \cdot \text{COD in mg } O_2/\text{dm}^3 \quad (3)$$

$$V_{FeCl_2} \text{ in dm}^3 = 1.354 \cdot 10^{-5} \cdot V_{sample} \text{ in dm}^3 \cdot \text{COD in mg } O_2/\text{dm}^3 \quad (4)$$

Formula (3) enables the calculation of the optimum volume of 30% H_2O_2 solution depending on the initial value of COD of the wastewater and its quantity. Formula (4) is used to calculate the volume of 33% solution of $FeCl_2$ which should be used in the Fenton process.

The volume of $FeCl_2$ determined from formula (2) was converted into the mass of $FeSO_4 \cdot 7H_2O$ used in our experiments and into the value of molar concentration. The results of calculations and experimental data are given in ***Table 2***.

It is worth noting that the formulae provide a simple, proportional relation between the optimum quantity of components of the Fenton reagent and the initial COD of the solution. They do not cover specific features of wastewater, mainly the susceptibility to oxidation of components present in it. They work quite well in the case of solutions of various detergents and wastewater which contain them [15]. The results obtained confirm this observation with respect to the washing wastewater tested in the experiments. The doses of hydrogen peroxide calculated and experimentally determined are identical. Also the quantity of iron is similar and within the determination error. In other cases there are significant differences, especially for wastewater with a high initial COD.

In the case of dyeing wastewater and concentrated effluent, the use of large amounts of iron exceeding 40 g of $FeSO_4 \cdot 7H_2O$ per litre of wastewater is absolutely economically unjustified. In the treatment processes the effect of coagulation can dominate. Pollutants contained in the wastewater, despite the lack of oxidation and mineralisation, can be removed from the solution with a deposit of ferric hydroxide.

The results presented show that for selected types of textile wastewater, the optimum molar ratio of iron to hydrogen peroxide $Fe^{2+} : H_2O_2$ is within a very broad range - from 1 : 8 (for washing wastewater-2) through 1 : 48 (concentrated effluent) to 1 : 129 (dyeing and general wastewater). Formulae (3) and (4), presented above, assume a constant value of this ratio irrespective of the type of wastewater and its composition, being $Fe^{2+} : H_2O_2 = 1 : 4.3$. In the literature these data are extended also taking into account the concentration of the compound being oxidised. For instance, in phenol oxidation the optimum ratio of phenol : $Fe^{2+} : H_2O_2 = 1 : 1 : 3$, while for a mixture of toluene, p-toluene, aniline and p-naphthalene, from 1.0 to 2.3 mol of H_2O_2 per one mol of decomposed aromatic compound is required [16, 17]. In the case of wastewater, these data should be referred to their initial COD to either calculate weight ratios with respect to mg O_2, or molar ratios related to the moles of molecular oxygen required for wastewater oxidation. It follows from the data obtained that the number of moles of hydrogen peroxide per one unit of COD reduction expressed in moles is 1.8 for dyeing wastewater, 4.5 for concentrated effluent, 5.3 for washing wastewater-2 and 8.7 for general effluents. These data should be referred, however, not to the initial COD of the wastewater but to its real reduction achieved, in which case these values are increased to 5.6 for washing wastewater-2, 6.6 for dyeing wastewater, 7.0 for concentrated effluent and 10.1 for general wastewater. Theoretical data determined from formulae (3) and (4) are COD : H_2O_2 : Fe^{2+} = 1 : 5 : 1.16.

Generally, it is assumed that the minimum concentration of iron ions enabling a Fenton reaction is 3 to 15 mg Fe^{2+}/dm^3. A typical weight ratio for a mixture of organic compounds ranges from 10 to 50. Increasing the Fe^{2+} concentration above 50% in relation to the concentration of hydrogen peroxide is not recommended because then iron becomes a scavenger of hydroxyl radicals.

An important parameter of wastewater treatment by the Fenton method is the pH of the solution. The process should proceed in a mildly acidic environment. The tests performed on textile wastewater confirmed that relation. The most advantageous value of pH appeared in the narrow range of pH = 3.5. Both lower and higher values of pH definitely diminish the reduction in COD. A mere difference of half a unit of pH above and below the optimum value causes a worsening of COD reduction by 8 to 12%. This result is in agreement with literature data, which provide us with the information that it is most beneficial to carry out the Fenton process in an acidic environment at a pH range from 3.5 to 5 [18]. However, there are cases when this range is different, e.g. 5 – 6 or 2 – 4 [19]. With respect to the decoloration process of certain dyes, the process rate is optimal in very broad ranges of pH - from 3 to 9. It is suspected that when a higher pH (> 5) is used, H_2O_2 is probably decomposed on fluffs of ferric hydroxide III, which causes that an appropriate amount of hydroxyl radicals cannot be formed. On the other hand, below pH = 3, in a reaction environment, an excess of Fe^{3+} ions is formed which not only induces a quick decomposition of H_2O_2 but also enhances competitive reactions, leading to the elimination of HO radicals, which is the main component oxidising organic compounds present in the wastewater.

Concluding remarks

The application of Fenton's reagent in textile wastewater treatment technology is an efficient method for the decomposition of pollutants present in it and can be used successfully as a preliminary stage preceding its further biological treatment. Due to their specific properties, including above all quick changes in the quantitative and qualitative composition, textile wastewater requires very elastic treatment technologies. One of such solutions can be a two-stage process which uses the Fenton reaction and biological methods. To obtain the relevant efficiency and economy of such a solution, it is required to continuously control the wastewater composition and to quickly optimise process conditions. Hence, it appears necessary to check the reaction with respect to big amounts of various types of wastewater and to find proper relations which would enable quick optimisation of the process with respect to the changing input parameters of the wastewater subjected to treatment.

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