Treatment of textile wastewater in the Fenton process in the presence of iron nanocompounds and Cu^{+2} ions

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Abstract Methods used to decompose pollutants in textile wastewater include oxidation/precipitation in the Fenton process. New research trends cover the application of iron nanocompounds in the reaction system. Iron nanocompounds exhibit catalytic activity which increases the effectiveness of oxidation processes. Also other metal nanocompounds or metal ions, in this number Cu^{+2}, are active in supporting pollutant decomposition in the Fenton processes. The aim of the study was to determine and optimize the efficiency of pollutant decomposition in textile wastewater by the Fenton method in the presence of iron oxide nanoparticles and Cu^{+2} ions and to compare it with the classical Fenton method. The Fenton process was optimized as a result of studies on the effect of compounds used in the treatment, doses of iron, nano-iron and Cu^{+2} ions, hydrogen peroxide and pH of the solution on the efficiency of decolorization and decomposition of pollutants. It was found that the efficiency of pollutant decomposition in which iron nanocompounds and Cu^{+2} ions were applied, was even twice as high as in the classical method. It was probably connected with the catalytic action of iron oxide nanoparticles and Cu^{+2} ions and higher concentration of hydroxyl radicals in the reaction system.

Keywords: textile wastewater, Fenton process, iron nanocompounds, Cu^{+2} ions

1. Introduction

Textile wastewater is difficult to treat. Its nuisance and hazardous environmental impact follows from intensive color, high content of chemical substances, the presence of suspensions, poor biodegradability and diversified pH. Methods used to decompose pollutants in wastewater include oxidation/precipitation in the Fenton process (Kos *et al*., 2010; Blanco *et al*., 2011; Wei *et al*., 2013). It consists in a non-selective and highly efficient oxidation of organic compounds by means of hydroxyl radicals formed in the chain reaction of hydrogen peroxide decomposition in the presence of bivalent iron salts, which is represented by the following mechanism:

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

High reactivity of hydroxyl radicals and their low selectivity enables oxidation of large groups of organic compounds occurring in the textile wastewater, in this number dyes and detergents. Due to this, textile wastewater can be significantly decolorized and a main load of organic pollutants can be removed.

The efficiency of oxidation with Fenton's reagent is the highest at pH ranging from 2 to 5 and for H_2O_2/Fe^{2+} molar ratio being about 1 : 1. The mechanism of this reagent cannot be considered well explained because of a variety of iron(II) and iron(III) complexes and numerous radical intermediate products and their consecutive reactions (Fu *et al*., 2010; Blanco *et al*., 2012). An important role is also played by Fe^{3+} ions occurring in the process which decompose H_2O_2 producing hydroperoxide radicals $HO_2^\cdot$:

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

Properties similar to those of iron ions in reactions (1) and (2) have also the ions of other metals, such as Cu, Co, Mn and Ti (Sawyer *et al*., 1996).

New trends in the research on pollutant oxidation processes by the Fenton method cover the application of iron nanocompounds in the reaction system (Bach *et al*., 2010; Garrido-Ramirez *et al*., 2010; Xu *et al*., 2012; Kos *et al*., 2014). Their presence has an effect on the oxidation reaction of chemical compounds present in the wastewater. Iron nanocompounds exhibit catalytic activity which increases the efficiency of oxidation processes. Also other metal nanocompounds or metal ions, in this number Cu^{+2}, are active in supporting pollutant decomposition in the Fenton processes (Zhang at al., 2008; Ambashta and Sillanpaa, 2011; Tian *et al*., 2011; Choi and Lee, 2012; An *et al*., 2013; Wu at al., 2013). The aim of the study was to determine and optimize the efficiency of pollutant decomposition in textile wastewater by the Fenton method in the presence of iron oxide nanoparticles and Cu^{+2} ions and to compare it with the classical Fenton method.

2. Methods

2.1. Materials

The tested material was textile wastewater generated during dyeing of cellulose fibers. The wastewater contained azo dyes, a cationic surfactant, acetic acid, sodium carbonate and sodium chloride. The wastewater had an intensive red color, its absorbance was 0.987 (436 nm), 3.418 (525 nm) and 0.053 (620 nm); COD was 211 mg O_2/dm^3, and initial pH was 10.4.

2.2. Experimental procedure

Analytically pure ferrous sulfate $FeSO_4*7H_2O$, copper sulfate $CuSO_4*5H_2O$ and 30% hydrogen peroxide H_2O_2 (Chempur, Piekary Śląskie), iron (II, III) oxide nanopowder <50 nm (Sigma Aldrich) as well as H_2SO_4 and analytically pure NaOH (POCh, Gliwice) were used in the experiments. The pH values of wastewater were reduced to 4, 3.5, 3, 2.5 and 2 by means of 5N sulfuric acid solution. Next, samples were completed either exclusively with ferrous sulfate or jointly with ferrous sulfate and iron (II,III) oxide nanopowder or jointly with ferrous sulfate, iron (II,III) oxide nanopowder and copper sulfate in the solid state and the solution was stirred until complete dissolution. Then 30% solution of hydrogen peroxide was added drop-wise to the wastewater. Once H_2O_2 had been added, the wastewater was stirred vigorously for 2 minutes, and then slowly for the next 10 minutes. The wastewater was left for 24 hours. After that, the samples were neutralized with 10% solution of NaOH to pH about 11. After 24 hours, the wastewater was decanted and filtered.

2.3. Analytical control

After the treatment, the color of wastewater was determined on the basis of absorbance measurements by the spectrophotometric method at three wavelengths 436, 525 and 620 nm. The COD was also determined by Hach-Lange tests. The spectrum of the raw textile wastewater is shown in Figure 1.

Since the absorbance of wastewater at a wavelength of 525 nm was much higher than at other wavelengths, its changes were taken as the most representative in assessing changes of wastewater color. Spectrophotometric analysis was made with the use of JASCO V-630 apparatus (JASCO, Japan).

3. Results and discussion

The Fenton process was optimized due to studies of the effect of compound used in the treatment, dosage of nano-iron, Cu^{+2}, hydrogen peroxide and pH of the solution on the efficiency of decolorization and decomposition of pollutants.

3.1. The effect of doses of iron oxide nanopowder

Experiments started with the determination of the effect of the dose of iron oxide nanopowder on the efficiency of pollutant decomposition in the wastewater in the Fenton process with the use of Cu^{+2} ions. The wastewater was treated at the doses of iron oxide nanopowder from 0.01 to 0.04 g/dm^3, at the constant doses of ferrous sulfate (0.5 g/dm^3), copper sulfate (0.1 g/dm^3) and hydrogen peroxide (5 cm^3/dm^3). The experiments were carried out at pH=3.5. The wastewater decolorization and COD reduction are illustrated in Figure 2.

Irrespective of the dose of iron oxide nanopowder, the wastewater was very well decolorized with color reduction reaching from 99 to 99.8%. This resulted probably from the fact that at the applied treatment parameters the obtained decolorization degrees were high in general. The best results of decolorization reaching 99.8% were obtained at the dose of iron oxide nanopowder 0.02-0.03 g/dm^3. COD reduction in the solution was also increasing with an increase of iron oxide nanopowder dose from 62 to 68%. The iron nanocompounds catalyzed the process of pollutant decomposition in the Fenton process.

In the second series of experiments the applied doses of iron oxide nanopowder were increased 10-fold. The wastewater was treated at the doses of iron oxide nano-powder from 0.1 to 0.4 g/dm^3, at constant doses of ferrous sulfate (0.5 g/dm^3), copper sulfate (0.1 g/dm^3) and hydrogen peroxide (5 cm^3/dm^3). The wastewater decolorization and COD reduction are illustrated in Figure 3.

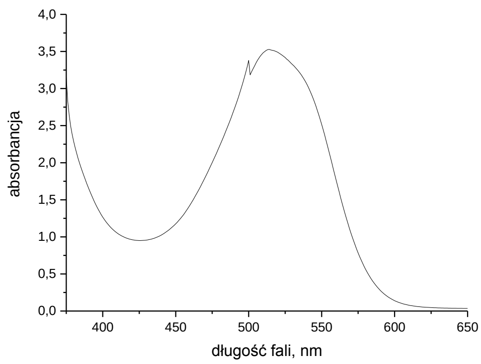

Figure 1. The spectrum of raw textile wastewater

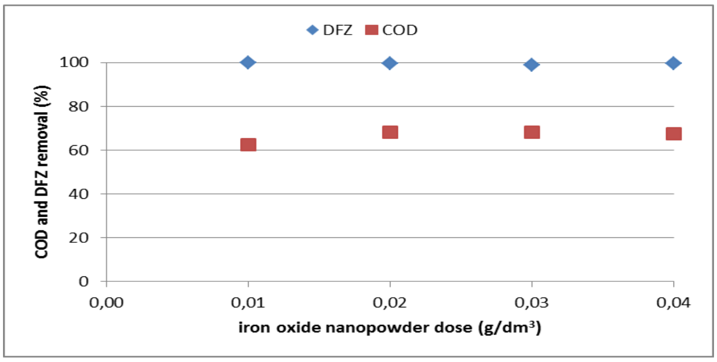

Figure 2. Changes in COD and color of the textile wastewater depending on the doses of iron oxide nanopowder.

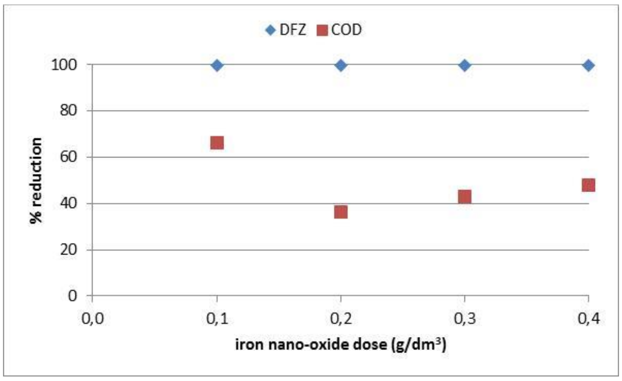

Figure 3. Changes in COD and color of textile wastewater depending on the doses of iron oxide nanopowder.

Table 1. Changes of COD and color in the textile wastewater depending on the doses of copper sulfate.

	Copper sulfate dose (g/dm^3)		
	0,1	0.2	0.3
COD (mgO$_2$/dm^3)	71	65	136
COD reduction (%)	66.3	69.2	35.5
Absorbance (525 nm)	0.009	0.004	0.008
Absorbance reduction (%)	99.7	99.9	99.8

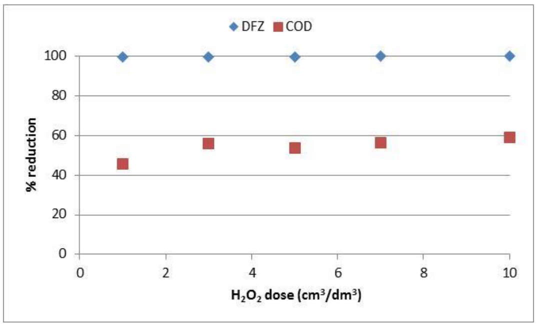

Figure 4. Changes in COD and color after the treatment depending on the doses of hydrogen peroxide.

An increased dose of iron oxide nanopowder did not improve the degree of wastewater decolorization causing at the same time a significant decrease of COD reduction to 36.5% at a dose of iron oxide nanopowder greater than 0.1 g/dm^3. Increased doses of iron oxide nanopowder had a definitely negative effect and badly affected pollutant decomposition in the wastewater.

3.2. The effect of copper sulfate doses

The wastewater was treated at the doses of copper sulfate from 0.1 to 0.3 g/dm^3, at constant doses of ferrous sulfate (0.5 g/dm^3), iron oxide nanopowder (0.1 g/dm^3) and hydrogen peroxide (5 cm^3/dm^3). The experiments were carried out at pH = 3.5. The decolorization of wastewater and COD reduction are illustrated in Table 1.

As a result of oxidizing treatment, the wastewater was almost completely decolorized irrespective of the applied dose of copper sulfate. On the other hand, the degree of COD reduction strongly depended on the copper sulfate dose and ranged from 66.3% to 35.5% at doses from 0.1 to 0.3 g/dm^3. A higher concentration of Cu^{+2} ions had a negative effect on the decomposition of pollutants in the wastewater significantly decreasing the reduction of COD.

3.3. The effect of hydrogen peroxide dose

The next series of experiments covered determination of the effect of hydrogen peroxide concentration on the decomposition of pollutants in the textile wastewater. From 1 to 10 cm^3/dm^3 of hydrogen peroxide was added to the wastewater. The applied dose of iron oxide nanopowder was 0.1 g/dm^3, dose of copper sulfate was 0.1 g/dm^3 and of ferrous sulfate 0.5 g/dm^3. pH of the solution – 3.5. Figure 4 shows the experimental results.

With increasing doses of hydrogen peroxide there was an increase in the degree of pollutant decomposition in the wastewater. The degree of wastewater decolorization increased from 97.9 to 100%, so at the highest doses of H_2O_2 the wastewater was completely decolorized. The dose of hydrogen peroxide also affected the degree of COD reduction which increased from about 65% at the lowest applied dose of H_2O_2 (1 cm^3/dm^3) to 70% at the highest dose (10 cm^3/dm^3). The degree of pollutant decomposition in the wastewater measured by COD was high already at the lowest dose of hydrogen peroxide and increased even more with increasing H_2O_2 dose although this increase was relatively small.

3.4. The effect of pH

An important parameter affecting the Fenton process is pH of the solution. Therefore, the effect of pH on the reaction carried out using iron oxide nanopowder and Cu^{+2} ions was tested. The dose of ferrous sulfate was 0.5 g/dm^3, iron oxide nanopowder 0.1 g/dm^3, copper sulfate 0.1 g/dm^3 and hydrogen peroxide 5 cm^3/dm^3. Figure 5 shows results of changes in COD reduction in the wastewater depending on the initial pH.

The degree of pollutant reduction in the wastewater strongly depended on pH of the solution. The lowest, only 6% COD reduction was obtained at pH = 2. With an increasing pH there was a gradual increase of COD reduction, which at pH = 3.5 reached a maximum value of 58% to decrease finally to 37% at pH = 4. The data obtained are in accordance with literature data for the classical Fenton process. For most of the tested compounds the optimum pH value in the classical Fenton process is about 3 (Nowicki and Godala, 2002). A decrease of the oxidation efficiency at higher pH values is caused by the precipitation of iron in the form of hydroxide. It is not recommended either to use too low pH values since OH radicals can react with H^+ ions which leads to a decrease of their concentration in the solution and reduction of oxidation efficiency of organic compounds.

3.5. Comparison of the classical Fenton process with process carried out with the use of iron oxide nanopowder and Cu^{+2} ions

At a next stage of the study the effects of pollutant decomposition obtained in the classical Fenton process were compared with the results obtained in the process carried out in the presence of iron nanocompounds and Cu^{+2} ions. Figure 6 show results of the investigations.

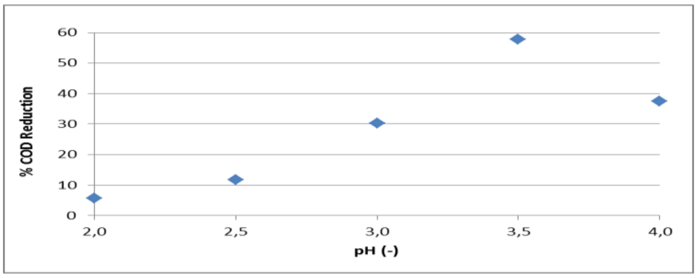

Figure 5. Changes of COD in textile wastewater depending on pH of the solution.

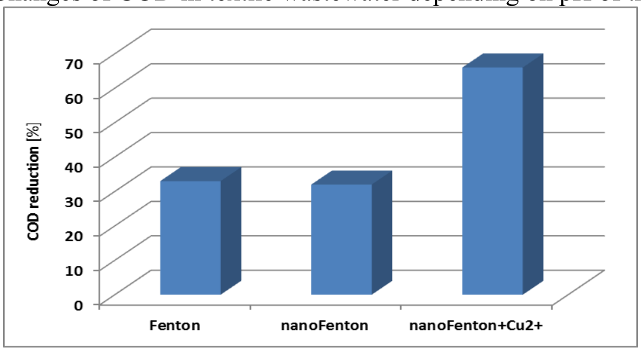

Figure 6. Changes in COD of textile wastewater in the Fenton process compared to the nanoFenton process and nanoFenton process with the use of Cu^{+2} ions. Fenton process: pH=3.5; $FeSO_4 \times H_2O$ dose – 0.5 g/dm^3, H_2O_2 dose – 5 cm^3/dm^3. nanoFenton process: pH=3.5; $FeSO_4 \times 7H_2O$ dose – 0.5 g/dm^3, H_2O_2 dose – 5 cm^3/dm^3, iron oxide nanopowder dose – 0.1 g/dm^3. nanoFenton + Cu^{+2} ions: pH=3.5; $FeSO_4 \times 7H_2O$ dose – 0.5 g/dm^3, H_2O_2 dose – 5 cm^3/dm^3, iron oxide nanopowder dose – 0.1 g/dm^3, copper sulfate dose – 0.1 g/dm^3

It follows from the obtained data that Cu^{+2} ions catalyzed the Fenton reaction increasing the efficiency of pollutant decomposition in textile wastewater as compared to the classical process. The resultant degree of COD reduction in the process conducted in the presence of iron oxide nanopowder and Cu^{2+} ions was twice as high as in the process carried out in the presence of iron oxide nanopowder and in the classical Fenton process.

4. Conclusions

As a result of the application of Cu^{+2} ions and iron oxide nanopowder in the Fenton process the effect of decomposition of pollutants in textile wastewater increased twice as compared to the classical process. Also a high level of wastewater decolorization reaching 100% was maintained. Cu^{+2} ions catalyzed the process of pollutant decomposition improving its efficiency and increasing the mineralization of pollutants. The results of treatment depended on the amount of iron oxide nanopowder and Cu^{+2} ions, the doses of hydrogen peroxide, and pH of the solution. The oxidation process was most efficient at pH 3.5. Optimum doses of iron oxide nanopowder and copper sullfate were about 0.1 g/dm^3.

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