DECOMPOSITION OF AZO DYE DIRECT RED 23 IN THE FENTON PROCESS IN THE PRESENCE OF IRON OXIDE NANOPOWDER

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EXTENDED ABSTRACT

Decoloration problems are important both in the wastewater treatment technology and in water conditioning. Actually, nearly all branches of industry discharge dyestuff to sewage. The type and quantities of the dyestuff vary with the type of industrial plant, production volume and assortment, and applied technologies. Most dyestuff is discharged into sewage by companies that produce it and these which use it. A significant source of colored wastewater is textile industry.

The Fenton process is one of the methods to significantly reduce the concentration of pollutants in textile wastewater. It involves not selective and highly efficient oxidation of organic compounds with hydroxyl radicals produced in the chain decomposition of hydrogen peroxide with the participation of divalent iron salt. The process is a radical reaction which generates big quantities of HO• hydroxyl radicals that are capable of oxidizing even the most resistant pollutants present in the wastewater. Main advantages of the method include high oxidation efficiency, inexpensive and easily available substrates and simple procedure. Novelty in the oxidation of pollutants by the Fenton method is running it with the participation of iron nanocompounds. The presence of nanoparticles has an influence on the oxidation of many compounds present in water. With the use of iron nanocompounds, the removal of trichlorethylene, phenol, olefin, humic acids, antibiotics and chlorophenols was investigated.

The presence of nanoparticles affects also the oxidation of dyestuff in water solutions and industrial wastewater. However, there are relatively few references in the literature on this subject. The aim of our investigations was to determine the decomposition efficiency of azo dye Direct Red 23 by the Fenton method with the use of iron nanocompounds and to compare it with the classical Fenton method. The azo dyes belong to the group of hardly biodegradable xenobiotics whose efficient removal from wastewater is a necessity.

The subject of our studies was azo dye Direct Red 23 used in textile industry. Water solutions of the dye were subjected to treatment by the classical Fenton method and to treatment in the presence of iron(II, III) oxide nanopowder. In wastewater samples before and after the treatment, color was determined by DFZ parameter as well as COD and TOC. The Fenton process was optimized due to studies on the effect of compound used in the treatment, doses of iron and iron(II, III) oxide nanopowder, hydrogen peroxide and pH of the solution on decoloration efficiency. It was found that the efficiency of dye decomposition in the processes of treatment in which iron nanocompounds were applied, was higher than in the classical method.

Keywords: azo dye, Direct Red 23, Fenton process, iron nanocompounds
1. INTRODUCTION

Decoloration problems are important both in the wastewater treatment technology and in water conditioning. The type and quantities of the dyestuff vary with the type of industrial plant, production volume and assortment, and applied technologies. A significant source of colored wastewater is textile industry. The Fenton process is one of the methods to significantly reduce the concentration of pollutants in textile wastewater (Feng et al., 2010; Kos et al., 2010; Blanco et al., 2012). The process is a radical reaction which generates big quantities of HO• hydroxyl radicals that are capable of oxidizing even the most resistant pollutants present in the wastewater (Bianco et al., 2011; Li et al., 2012). Main advantages of the method include high oxidation efficiency, inexpensive and easily available substrates and simple procedure. Novelty in the oxidation of pollutants by the Fenton method is running it with the participation of iron nanocompounds. The presence of nanoparticles has an influence on the oxidation of many compounds present in water. With the use of iron nanocompounds, the removal of trichloroethylene (Choi et al., 2012), phenol (Zhang et al., 2008; Zelmanov et al., 2008; Prucek et al., 2009), olefins (Dutta et al., 2010), humic acids (Nie et al., 2010), antibiotics (Chen et al., 2012) and chlorophenols (Vinita et al., 2010; Ortiz de la Plata et al., 2012) was investigated. The presence of nanoparticles affects also the oxidation of dyestuff in water solutions and industrial wastewater (Lin et al., 2008; Shahwan et al., 2011). Additionally, some metal oxides, e.g. cobalt nano-oxide, reveal a supporting action (Zhang et al., 2009; Ambashta and Sillanpaa, 2011). The mechanism of pollutant decomposition in the Fenton process with the use of iron nanocompounds is as yet poorly recognized. Using iron nanocompounds in pollutant decomposition, investigations show an increase of the decomposition efficiency as compared to the Fenton process performed in a classical way. The aim of our investigations was to determine the decomposition efficiency of azo dye Direct Red 23 by the Fenton method with the use of iron nanocompounds and to compare it with the classical Fenton method. The azo dyes belong to the group of hardly biodegradable xenobiotics whose efficient removal from wastewater is a necessity.

2. METHODS

Subject of studies. The subject of our studies was water solutions of azo dye Direct Red 23 at the concentration of 0.1 g/l. The initial COD of the solution was 52 mg O2/l, TOC content was 16.1 mg/l. Molecular formula – C35H25N7Na2O10S2, molecular weight 813.72. Molecular structure is shown in Figure 1.

Experimental procedure. The pH values of water dye solutions were reduced to 4, 3.5, 3, 2.5 or 2 by means of 5N solution of sulfuric acid. Next, the samples were completed either exclusively with ferrous sulfate or jointly with ferrous sulfate and iron(II,III) oxide nanopowder (Sigma-Aldrich) in the solid state and the solution was stirred until complete dissolution. Then a 32% solution of hydrogen peroxide was added drop-wise to the solutions. Once H2O2 had been added, the wastewater 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 neutralized with a 10% solution of NaOH to pH about 11. After 24 hours, the purified water dye solutions were decanted and filtered.

Analytical control. In the samples before and after the treatment, color was determined by a spectrophotometric method. Absorbance was measured at the wavelength 505 nm. COD and TOC were also determined.

3. RESULTS

The investigation started with the determination of dye decomposition efficiency with the joint use of ferrous sulfate and iron nanocompounds. The solutions of dyes were treated with the use of total dose of iron compounds equal to 0.3 g/l, changing proportions between ferrous sulfate and iron oxide nanopowder at the constant dose of hydrogen peroxide equal to 3 ml/l. Experiments were carried out at two different values of pH, i.e. 2 and 3.5. Results are illustrated in Figures 2 and 3.

![Figure 2](image)

**Figure 2.** Changes in the spectrum of Direct Red 23 subjected to the Fenton process depending on the ratio of ferrous sulfate to iron oxide nanopowder doses; the applied dose of hydrogen peroxide was 3 ml/l; pH of the solution = 2.0.

Irrespective of the amount of iron nanocompounds in the total dose, the solution was decolorized (95% color reduction). The degree of COD reduction increased initially with an increase of the quantity of iron oxide nanopowder in the total dose. At the doses of nanopowders of iron oxide equal to 30 mg/l and ferrous sulfate 270 mg/l reached a maximum (35%), and next decreased to 15%. The amount of iron oxide in the total dose had a significant influence on treatment efficiency. Similar relationships were obtained in TOC determination. A maximum TOC reduction reaching 48% was obtained at the doses of iron oxide nanopowder of 30 mg/l and ferrous sulfate of 270 mg/l. Then the TOC reduction decreased to 35%.

Similar experiments were performed at pH = 3.5. Results are shown in Figures 4 and 5. Different ratios of iron compounds and nanocompounds used had no considerable effect on color reduction. In each case the wastewater was well decolorized. The degree of color reduction was about 10% lower than at pH=2 and reached about 85%. The degree of COD reduction increased initially from 35% to 44%, and next it was decreasing. An optimum dose of iron oxide nanopowder was 30 mg/l and of ferrous sulfate 270 mg/l. An
optimal, weight ratio of ferrous sulfate to iron oxide nanopowder was 9 : 1. The degrees of COD reduction were up to 20% higher in relation to those which were obtained at pH = 2. The TOC reduction was similar (around 15%) irrespective of the ratio of iron oxide nanopowder to ferrous sulfate in the total dose and around 20-25% lower than at pH=2. Lower values of TOC in relation to COD provided an evidence of incomplete mineralization of dye molecules.

![Figure 3](image1.png)

**Figure 3.** Changes of COD, TOC and color in Direct Red 23 solutions depending on the doses of ferrous sulfate and iron(II,III) oxide nanopowder; the applied hydrogen peroxide dose was 3 ml/l; pH of the solution = 2.0.

![Figure 4](image2.png)

**Figure 4.** Changes in the spectrum of Direct Red 23 subjected to the Fenton process depending on the ratio of ferrous sulfate to iron oxide nanopowder; the applied hydrogen peroxide dose was 3 ml/l; pH of the solution = 3.5.
The next series of experiments covered determination of the effect of hydrogen peroxide concentration on the decomposition of dye particles (Figures 6 and 7).

The applied doses of hydrogen peroxide had an influence on color reduction. With an increase of $\text{H}_2\text{O}_2$ doses color reduction increased from around 80 to over 95%. COD reduction also depended on hydrogen peroxide doses. At the lowest dose equal to 1 ml/l it was 40%. Next, it increased rapidly reaching a maximum (73%) at 7 ml/l. Then, it
decreased to 63% at H$_2$O$_2$ dose of 10 ml/l. Very good relationship was obtained for TOC. The reduction of TOC increased from 10% (1 ml/l) to maximum 52% (7 ml/l), to decrease later to 47% (10 ml/l). The lowest TOC reduction in relation to COD was an evidence of the incomplete mineralization of dye molecules.

![Figure 7](image_url)

**Figure 7.** Changes in COD, TOC and color in the Direct Red 23 solutions depending on hydrogen peroxide dose. The applied dose of iron(II,III) oxide nanopowder was 30 mg/l and the dose of ferrous sulfate was 270 mg/l; pH of the solution = 3.5.

The next stage covered studies on the effect of pH on COD and TOC changes (Figure 8).

![Figure 8](image_url)

**Figure 8.** Changes of COD and TOC in Direct Red 23 solutions depending on pH of the solution. The applied dose of iron(II,III) oxide nanopowder was 30 mg/l, the dose of ferrous sulfate 270 mg/l, hydrogen peroxide dose – 3 ml/l.
In the case of COD at pH growing from 2 to 3, the reduction of this parameter increased from 35% to 65%. With an increase of pH, the reduction of TOC was growing gradually from 25% (pH = 2) to 35% (pH = 3), and next it decreased to 15% (pH = 4). The mineralization of dye molecules was most efficient at pH around 3. The best color reduction was obtained at lower pH values. This relation is in agreement with literature data for the classical Fenton process (Nowicki and Godala, 2002).

At the next stage of studies the effects of dye decomposition obtained in the classical Fenton process were compared with the results obtained in the process carried out in the presence of iron nanocompounds. Figure 9 shows results of the investigations. As follows from the obtained data, iron nanocompounds catalyzed the Fenton reaction thus increasing the efficiency of dye molecule decomposition and its mineralization as compared to the classical process. This was observed especially in the solution at pH=3.5, where in the process carried out in the presence of iron nanocompounds the degree of COD and TOC reduction was much higher than in the classical Fenton process (Figure 9B).

![Figure 9](image)

**Figure 9.** Changes of COD and TOC in Direct Red 23 solutions in the Fenton process compared with nanoFenton process. The Fenton process: pH=2.0; FeSO₄ – 0.27 g/l, H₂O₂ – 3 ml/l. NanoFenton process: pH=2.0; FeSO₄ – 0.27 g/l, iron oxide nanopowder – 0.03 g/l; H₂O₂ – 3 ml/l. Fenton process: pH=3.5; FeSO₄ – 0.27 g/l, H₂O₂ – 3 ml/l. NanoFenton process: pH=3.5; FeSO₄ – 0.27 g/l, iron oxide nanopowder – 0.03 g/l; H₂O₂ – 3 ml/l.

4. CONCLUSIONS

When the Fenton process was carried out in the presence of iron oxide nanopowder, the efficiency of decomposition of Direct Red 23 dye was higher than in the classical Fenton process. Results of dye decomposition depended on the ratio of nanocompounds to the quantity of ferrous sulfide, on the doses of reagents, including hydrogen peroxide, and on pH of the solution. The best results of decomposition were obtained at pH=3.5. Iron oxide nanopowder catalyzed the process of dye decomposition increasing its efficiency and the degree of mineralization. This was evident in the case of COD and TOC, while less distinct with respect to decoloration of the solution. Further studies on this subject we intend to carry out, will cover also the determination of reaction kinetics which should help us to understand the mechanism of oxidation processes.
REFERENCES


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