

Discoloration of Azo Dye Acid Red 18 by Fenton Reagent in the Presence of Iron Powder

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Received: 16 July, 2002

Accepted: 14 October, 2002

Abstract

The examined H_2O_2/Fe^0 process was found to be very efficient for discoloration of simulated wastewater containing 100 mg/dm^3 commercial azo dye Acid Red 18. The optimal doses of H_2O_2 and Fe^0 were 60 and 50 mg/dm^3 , respectively at pH 3 and 15 minutes reaction time. Under the described conditions total visual discoloration was achieved. A very important factor was reaction time. Generally, the smaller dose of iron powder, the greater reaction time needed for visual discoloration. A strict linear correlation was observed between Fe^0 amount in the range of $10\text{--}600\text{ mg/dm}^3$ and final pH. This suggests that the H_2O_2/Fe^0 process has undoubted advantages in comparison with the classical Fenton reaction, because using excessive amounts of the iron powder could reach higher final pH in the H_2O_2/Fe^0 process. Thus, smaller doses of base will be required for final neutralization of wastewater. It was also found that the dissolution time of iron powder at acidic conditions (before H_2O_2 was added) is an important parameter that influences the rate of discoloration. As the time of iron powder dissolution increases, the time needed for visual discoloration decreases.

Keywords: Fenton reagent, iron powder, azo dye, Acid Red 18

Introduction

The Fenton reaction [1, 2] is a catalytic process for the generation of hydroxyl radicals from hydrogen peroxide and is based on an electron transfer between H_2O_2 and iron ions acting as homogeneous catalyst. These radicals are a very strong oxidizing agent capable of reacting with a wide variety of organic compounds under ambient conditions. The advantage of the Fenton reagent is that no energy input is necessary to activate hydrogen peroxide [2]. Therefore, this method offers a cost-effective source of hydroxyl radicals, using easy-to-handle reagents. The Fenton reagent has been found to be effective in treating various industrial wastewater components including aro-

matic amines [3], a wide variety of dyes [4, 5], and many other substances, e.g. pesticides [6, 7] and surfactants [8, 9]. Therefore, the Fenton reagent has been applied to treat a variety of wastes such as those associated with the textile and chemical industries.

Azo dyes constitute the largest class of dyes used in industry [5]. More than two thousand azo dyes are known and over half of the commercial dyestuffs are azo dyes. Azo dyes are broadly used in the textile industry, and also widely employed to color solvents, inks, paints, varnishes, paper, plastic, rubber, foods, drugs, and cosmetics [10]. Azo dyes are resistant to aerobic biodegradation, since the conventional treatment (e.g. activated sludge) of wastewater contaminated with these dyes could not remove most azo dyes effectively [5, 11]. The resulting dye effluent may contain some components or moieties

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that could be toxic, carcinogenic or mutagenic to aquatic life [12]. Therefore, the degradation of azo dyes under alternative advanced oxidation technologies, as for example the Fenton reagent has to be explored.

Beside the classical Fenton's reaction (H_2O_2 /ferrous salt), recent studies have focused especially on investigation of the Fenton process with alternative iron sources. A number of researchers have investigated the application of metal oxides and supported metal oxides, especially those of iron, as catalytic materials for the oxidation of organic compounds in batch and fixed bed continuous flow treatment systems [13, 14]. They generally observed a greatly accelerated decomposition of hydrogen peroxide but variable amounts of contaminant loss. Watts et al. [15, 16] examined the efficiency of iron minerals toward catalyzed degradation of chlorobenzenes by hydrogen peroxide and noted considerable differences in reactivity with different types of iron oxides. The Fenton reactions were also observed with an iron-containing zeolite [17]. Valentine and Wang [18] examined the Fenton reaction in the presence of three iron oxides: ferrihydrite, a semicrystalline iron oxide and crystalline goethite. The catalytic activity of iron oxides toward quinoline oxidation was highest for goethite, much less for the semicrystalline material, and essentially negligible in the presence of ferrihydrite.

Lücking et al. [2] tested iron powder, graphite and activated carbon for their catalytic properties for the oxidation of 4-chlorophenol in aqueous solution with hydrogen peroxide. They concluded that iron powder could be used to replace iron salts as a catalyst for the Fenton reaction.

The disadvantage of Fenton's reagent is that the homogeneous catalyst, added as iron salt, cannot be retained in the process, thus causing additional water pollution [2]. In order to eliminate this disadvantage, discoloration of azo dye Acid Red 18 by the Fenton reagent in the presence of iron powder as a source of iron ions was examined in this paper. The effects of experimental factors such as H_2O_2 concentration, Fe^0 dosage, and pH on discoloration efficiency were tested.

Materials and Methods

Dye Wastewater

The simulated dye wastewater was prepared by dilution of commercial dye Acid Red 18 (BORUTA-KOLOR Sp. z o.o., Poland) with water. The dye was of high purity and used without further purification. Concentration of dye was 100 mg/dm^3 . The wastewater was characterized by an intensive red-ponceau color, high clarity and $\text{COD} = 94 \text{ mg/dm}^3$. The structure of Acid Red 18 is shown in Figure 1.

Experimental Procedure

The experiments were performed in glass reactors with a magnetic stirrer. The dye wastewater was put into reactors of 0.25 dm^3 volume, and then acidified with H_2SO_4 to the

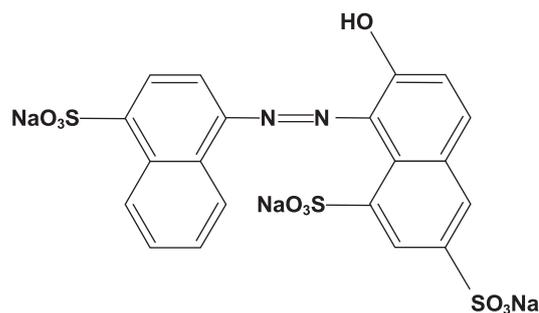


Fig. 1. Structure of the azo dye Acid Red 18.

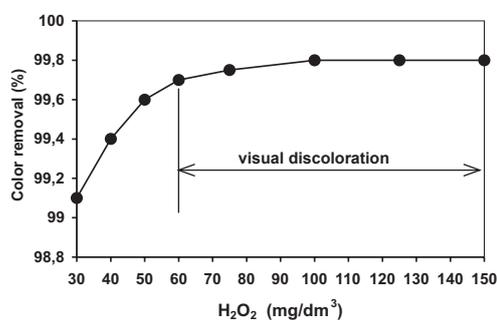


Fig. 2. Effect of H_2O_2 dosage on color removal by $\text{H}_2\text{O}_2/\text{Fe}^0$ process ($\text{Fe}^0 = 1 \text{ g/dm}^3$; 3.5 pH).

selected values, as a Fenton reaction is effective in acidic pH range. After that, under vigorous stirring, the various doses of zero-valent iron powder ($< 100 \mu\text{m}$, International Enzymes Ltd.) and 30% H_2O_2 were added to the flasks. After 15 minutes the samples were alkalinized with 0.1 N NaOH up to pH 9 in order to prevent further generation of hydroxyl radicals. Then, the samples were centrifuged at 3000 rpm (2.5 min) and analyzed at the maximum adsorption wavelengths of 510 nm, using a CARL ZEISS TECHNOLOGY UV-VIS Spectrophotometer.

Results and Discussion

Effect of H_2O_2 Dosage

At the beginning, the effect of H_2O_2 only (without Fe) dosage (from 50 to 500 mg/dm^3 at 3.5 pH) on color removal from simulated wastewater was investigated. There was no case in which the visual discoloration was achieved and the efficiency of absorbance changed from 10% to 23% for minimum and maximum dose, respectively. Therefore, further experiments were carried out with iron ($\text{H}_2\text{O}_2/\text{Fe}^0$ process).

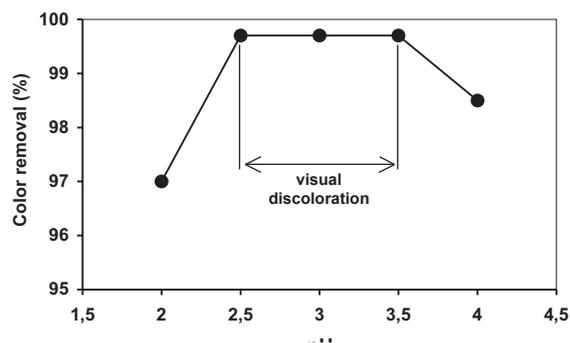


Fig. 3. Effect of pH on color removal by $\text{H}_2\text{O}_2/\text{Fe}^0$ process ($\text{Fe}^0 = 1 \text{ g/dm}^3$; $\text{H}_2\text{O}_2 = 60 \text{ mg/dm}^3$).

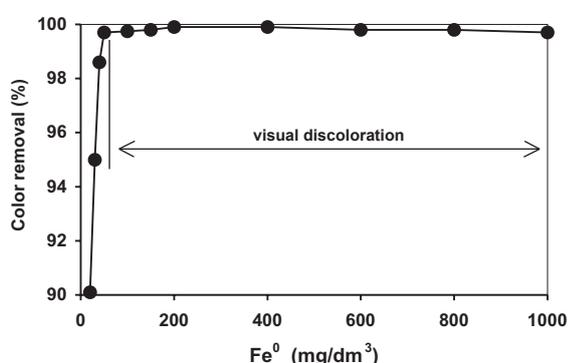


Fig. 4. Effect of Fe^0 amount on color removal by $\text{H}_2\text{O}_2/\text{Fe}^0$ process ($\text{H}_2\text{O}_2 = 60 \text{ mg/dm}^3$; 3.0 pH).

The effect of the H_2O_2 dosage (from 30 to 150 mg/dm^3) at $\text{Fe}^0 = 1 \text{ g/dm}^3$ on color removal from simulated wastewater is shown in Figure 2. The color removal efficiency (decrease in absorbance at 510 nm) was increased with increasing the dosage of H_2O_2 . As the dosage of H_2O_2 increased from 30 to 60 mg/dm^3 color removal reached 99.1–99.7%. When increasing the H_2O_2 dosage from 60 to 150 mg/dm^3 , color removal increased slightly from 99.7 to 99.8%. In this range, total visual discoloration was achieved. At 50 mg/dm^3 H_2O_2 a pale yellow color was still observed. Therefore, further experiments concerning the optimization of pH and iron dosage were continued at H_2O_2 dose of 60 mg/dm^3 .

Effect of pH

In aqueous solutions, under acidic conditions, iron powder release Fe^{2+} to the solution. It has been shown that the iron powder dissolves faster at lower pH than at high pH [19]. This remains in agreement with the fact, that the Fenton reaction is effective in acidic conditions. Then, Fe^{2+} will decompose H_2O_2 to generate hydroxyl radicals according to the Fenton reaction. The optimal pH in the range of 2.5–4.0 was reported to be a highly important factor for effective Fenton oxidation [20–22].

In order to estimate the pH effect on color removal, the experiments were conducted at pH values varying between 2 and 4. As presented in Figure 3, the best results and visual discoloration were achieved in the pH range 2.5–3.5. However, if the pH value dropped to 2.0, a substantial decrease in efficiency of color was observed. These phenomena could be explained by the high excess of hydrogen ions, behaving as an OH^\cdot radical scavenger according to reaction [23]:

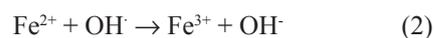


As the pH changed from 3.5 to 4.0, rapid decrease in discoloration efficiency was also achieved. A diminishing efficiency of $\text{H}_2\text{O}_2/\text{Fe}^0$ process at pH 4 was in accordance with another report that near and above pH 4 rapid hydrogen peroxide decomposition, probably on the surface of the ferric hydroxide floc, would not produce appreciable amounts of available hydroxyl radicals in the solution [24].

Effect of Iron Powder Dosage on Discoloration Efficiency

As previous papers had reported [3, 8, 20], increasing the $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ ratio has a great effect on the efficiency of the classical Fenton reaction. Therefore, further experiments concern the effect of Fe^0 amount on discoloration efficiency of the modified Fenton process ($\text{H}_2\text{O}_2/\text{Fe}^0$). Figure 4 presents the removal of color at different Fe^0 dosages using a constant H_2O_2 concentration of 60 mg/dm^3 .

Experiments concerning the optimization of Fe^0 dosages show that in the range of 20–50 mg/dm^3 Fe^0 , color removal significantly increases with an increase in Fe^0 amounts. The visual color completely disappeared at 50 mg/dm^3 Fe^0 and more. The best results of color removal (99.7–99.9%) were achieved at Fe^0 dosages in the range of 50–400 mg/dm^3 , but visual discoloration was also observed at the higher Fe^0 dosages. However, above Fe^0 dosage of 400 mg/dm^3 , a slight decrease in color removal from 99.9% to 99.7% was observed. This inhibitory effect at the higher Fe^0 dosages could be explained by an observation (referring to the classical Fenton reaction) that in the absence of organic substrates, excessive ferrous ions (formed from Fe^0 in the $\text{H}_2\text{O}_2/\text{Fe}^0$ process) are the dominant hydroxyl radical's scavenger through the following reaction [23]:



A very important factor was also the reaction time. As shown in Figure 5, absorbance was found to decrease (i.e. color removal increase) with the reaction time increase. When the reaction time was extended above 15 minutes, the visual discoloration was also achieved at the iron powder dosages in the range of 10–40 mg/dm^3 . These amounts of iron powder were not sufficient for total discoloration at reaction time of 15 minutes. The visual color complete-

ly disappeared even at 10 mg/dm³ Fe⁰ after 90 minutes of reaction time. Generally, the smaller dose of iron powder, the greater reaction time needed for visual discoloration.

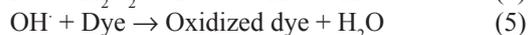
Effect of Iron Powder Dosage on Final pH

Figure 6 shows the final pH (after H₂O₂/Fe⁰ process) at different Fe⁰ dosages and a constant H₂O₂ concentration of 60 mg/dm³. The results show that at Fe⁰ amount in the range of 10–600 mg/dm³, final pH increases linearly with an increase in Fe⁰ dosage. A strict linear correlation ($R^2 = 0.9935$) was found between these parameters. This phenomenon can be explained by the removal of hydrogen ions from the solution as a result of reaction between the hydrogen ions and zero-valent iron (Fe⁰). However, further increase in Fe⁰ dosage (up to 1000 mg/dm³) did not cause the final pH increase, which remained between 5.4–5.6.

This implies that using excessive amounts of iron powder could reach a higher final pH in the H₂O₂/Fe⁰ process. Thus, smaller doses of base will be required for final neutralization of wastewater. Moreover, the same iron powder can be used repeatedly in the process. The above considerations suggest that the H₂O₂/Fe⁰ process has undoubted advantages in comparison with the classical Fenton reaction.

Effect of Time between Fe⁰ and H₂O₂ Addition on Discoloration Time

Because of the iron powder release Fe²⁺ to the solution under acidic conditions, iron dissolution is an initial step for the oxidation of contaminants (e.g. dyes) by the H₂O₂/Fe⁰ process. When dye oxidation occurs, the initial Fe²⁺ ions are consumed, and then the oxidation rate will depend on the dissolution rate of Fe⁰. The following chemical reactions can be used to describe the mechanism of dye oxidation in the H₂O₂/Fe⁰ system:



Therefore, further experiments were performed at different times between Fe⁰ and H₂O₂ dosage. After initial acidification of wastewater containing Acid Red 18 to pH 3, 200 mg/dm³ of iron powder was added from 0 to 10 minutes before the optimal dose of H₂O₂ (60 mg H₂O₂/dm³) was added. The results are shown in Figure 7. As the time between Fe⁰ and H₂O₂ introduction increased from 0 to 10 minutes, discoloration time decreased from 11 to 5 minutes. An exactly linear correlation ($R^2 = 0.9868$) was observed.

Longer reaction time caused a higher amount of Fe²⁺ ions in solution due to the iron powder dissolution in acidic conditions. Thus, a larger amount of hydroxyl radicals is generated in the system and the oxidation rate of Acid Red 18 in the Fenton reaction is higher.

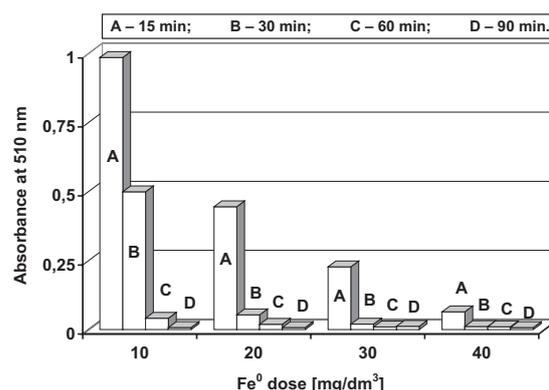


Fig. 5. Effect of reaction time on color removal by H₂O₂/Fe⁰ process (H₂O₂ = 60 mg/dm³; 3.0 pH).

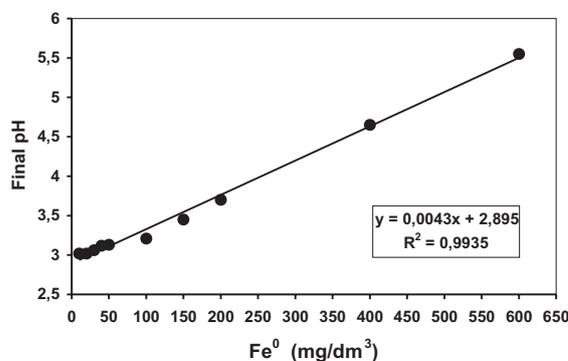


Fig. 6. Effect of iron powder dosage on final pH (60 mg H₂O₂/dm³; pH = 3,0).

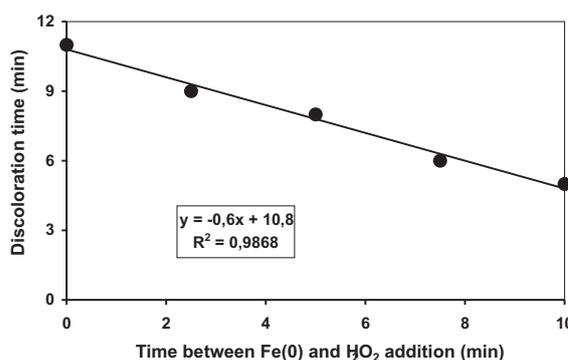


Fig. 7. Effect of time between Fe⁰ and H₂O₂ addition on discoloration time (pH = 3,0; 60 mg H₂O₂/dm³; Fe⁰ = 200 mg/dm³).

Conclusions

The examined H₂O₂/Fe⁰ process was found to be very efficient for discoloration of simulated wastewater containing 100 mg/dm³ commercial azo dye Acid Red 18. The optimal doses of H₂O₂ and Fe⁰ were 60 mg/dm³ and 50 mg/dm³, respectively, at pH 3. At described conditions, total visual discoloration was achieved. Generally,

the smaller dose of iron powder, the longer reaction time is needed for visual discoloration. Visual discoloration was achieved in the range 2.5–3.5 pH. If the pH value dropped to 2.0 or changed from 3.5 to 4.0, a rapid decrease in discoloration efficiency was achieved. It can be stated that pH is a highly important factor for effective Fenton oxidation.

An exactly linear correlation was observed between Fe^0 amount in the range of 10–600 mg/dm³ and final pH. As the iron powder dose increased, the final pH increased. This suggests that the $\text{H}_2\text{O}_2/\text{Fe}^0$ process has undoubted advantages in comparison with the classical Fenton reaction, because using excessive amounts of iron powder could reach higher final pH in the $\text{H}_2\text{O}_2/\text{Fe}^0$ process. Thus, smaller doses of base will be required for final neutralization of wastewater. Moreover, the same iron powder can be used repeatedly in the process.

It was also found that the time of dissolution of iron powder at acidic conditions (before H_2O_2 was added) is an important parameter that influences the rate of discoloration time. A longer time of iron powder dissolution caused a higher amount of Fe^{2+} ions in solution and in consequence, a larger amount of hydroxyl radicals is generated in the system. Thus, the oxidation kinetic of Acid Red 18 in the $\text{H}_2\text{O}_2/\text{Fe}^0$ process is more effective.

Acknowledgements

The authors wish to thank Ms. J. Grocholl for her technical and analytical assistance.

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