The Modified Fenton Process for Decolorization of Dye Wastewater

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Abstract

A novel modified Fenton process using heterogeneous catalyst (swarf) was developed to catalyze the oxidation reaction of azo dye Acid Red 18. It was found that swarf could be used to replace iron salts as a catalyst for the Fenton reaction. The examined continuous Fenton process proved to be very efficient for decolorization of simulated wastewater containing 100 mg/dm^3 Acid Red 18. Performance of the Fenton reactor and regeneration method of the catalyst was discussed. The simplified mechanism of hydroxyl radical production in the presence of swarf as a catalyst also was proposed.

Keywords: Fenton reagent, swarf, azo dye, Acid Red 18

Introduction

The development of novel treatment methods encompasses investigations of advanced oxidation processes (AOPs), which are characterized by production of the hydroxyl radical (OH·) as a primary oxidant [1]. Among various AOPs, the Fenton reagent (H_2O_2/Fe^{2+}) is one of the most effective methods of organic pollutant oxidation. The Fenton reagent has been found to be effective in treating various industrial wastewater components including aromatic amines [2] and a wide variety of dyes [3, 4] as well as many other substances, e.g. pesticides [5, 6] and surfactants [7, 8]. Therefore, the Fenton reagent has been applied to treat a variety of wastes such as those associated with the textile and chemical industries.

The advantage of the Fenton reagent is that no energy input is necessary to activate hydrogen peroxide [9]. Therefore, this method offers a cost-effective source of hydroxyl radicals, using easy-to-handle reagents. However, disadvantages in using the Fenton reagent include the production of a substantial amount of $Fe(OH)_3$ pre-

cipitate [10] and additional water pollution caused by the homogeneous catalyst that added as an iron salt, cannot be retained in the process [9]. To solve these problems, the application of alternative iron sources as catalysts in oxidizing organic contaminants has been studied extensively. A number of researchers have investigated the application of iron oxides such as hematite, ferrihydrite, semicrystalline iron oxide and crystalline goethite [11−15]. They generally have observed a greatly accelerated decomposition of hydrogen peroxide but variable amounts of contaminant were lost. The Fenton reactions also were observed with an iron-containing zeolite [16]. Chou and Huang [10] developed a novel supported iron oxyhydroxide (γ-FeOOH) granular catalyst and proved that it can be effective catalyst of H_2O_2 in oxidizing benzoic acid.

Another group of investigations consisted in the application of iron powder in the H_2O_2/Fe^0 system. Zero-valent iron metal (Fe^0) is a very promising reactive medium due to its low-cost, effectiveness, ability to degrade contaminants and its accessibility [17, 18]. It was found that iron powder could be used to replace iron salts as a catalyst for the Fenton reaction [9, 19, 20].

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In this study a novel modified Fenton process using heterogeneous catalyst (swarf) was developed to catalyze the oxidation reaction of azo dye wastewater [21]. A continuous process was conducted to demonstrate the feasibility of color removal from dye wastewater by the novel oxidation technology. The performance of the Fenton reactor and regeneration method of the catalyst was discussed. The simplified mechanism of hydroxyl radical production in the presence of swarf as a catalyst also was proposed.

Materials and Methods
Dye Wastewater

The simulated dye wastewater was prepared by diluting commercial azo dye Acid Red 18 (Boruta S.A., Poland) in water. The dye was in high purity and used without further purification. The concentration of dye was 100 mg/dm³. The wastewater was characterized by an intensive red-ponceau colour, high clarity and COD = 94 mg/dm³. The structure of Acid Red 18 is shown in Fig. 1.

Experimental Procedure

The experimental reactor was designed as illustrated schematically in Fig. 2. The simulated dye wastewater was adjusted with H_2SO_4 to pH 2.5 and then H_2O_2 (30 wt%) dose of 150 mg/dm³ was added. The obtained solution was pumped (with a flow rate of 0.67 m/h) with the help of a peristaltic pump to the Fenton reactor consisting of a glass column (diameter of 2.5 cm, bed height 7 cm) filled with a swarf as a catalyst. The swarf was created during metal sawing and the particle size of swarf was in the range of 0.5-2.5 mm. Chemical constitution of the general-purpose steel used as a catalyst (swarf) is shown in Table 1. After selected times, samples of an effluent from the Fenton reactor were withdrawn and neutralized with 0.1 N NaOH up to pH 9 in order to prevent further generation of hydroxyl radicals through the Fenton reaction. Next, the samples were centrifuged at 3000 rpm (2.5 min) and were analyzed at the maximum adsorption wavelengths of 510 nm, using a Carl Zeiss Technology UV-VIS Spectrophoto-meter.
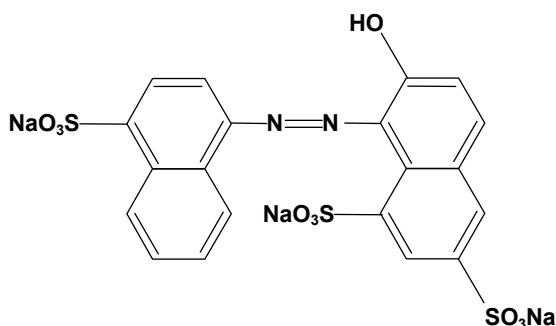
Iron ions released during the experiment were analyzed with atom absorption spectroscopy (AAS 3, Carl Zeiss Jena).

In the second part of the investigations, the experimental reactor also was operated in the same manner as described above but this time H_2O_2 was not added to simulated dye wastewater. This experiment was carried out in order to investigate the efficiency of wastewater decolorization due to chemisorption of the dye on the swarf surface. For example, Tang and Chen [19] concluded that chemisorption of the dye on the iron powder surface was considered a possible mechanism of decolorization because oxygen and nitrogen atoms in the dye molecule can serve as ligands in complexing with Fe^{2+} and Fe^{3+} sites on the iron powder surface.

Results and Discussion
Decolorization of Dye Wastewater with H_2O_2

The experiment was carried out to find out if the swarf can be used as a catalyst in the continuous modified Fenton process. Simulated dye wastewater was decolorized through catalytic oxidation in the Fenton reactor for 120 hours. The changes of color removal efficiency in the course of 24-hour Fenton oxidation are shown in Fig. 3. Color removal efficiency was rapidly increased to 95.4% within the first 60 minutes, and then a slight increase in color removal was observed within up to 240 minutes. After that, color removal efficiency rapidly decreased from 96.6 to 91.6% and then slowly diminished to 89.8% within up to 10 hours. Color removal efficiency in the range of 89.8%−89.1% was maintained up to 24 hours and then its slight decrease to 88.7% at 120 hours was observed. The presence of iron cause the effluent from the Fenton reactor to be slightly yellowish, but after being neutralization with NaOH, total visual decolorization was achieved (Fig. 3). The absorbance of effluent after being neutralizing with NaOH was maintained at lower than 0.022 nm. After 120 hours of operation (nearly 39 dm³ of wastewater was decolorized), the effluent became increasingly pink and then a specific red-ponceau colour was observed. The catalyst (swarf) seemed to be no longer active, which may have been caused by iron oxides forming on the surface of the swarf.
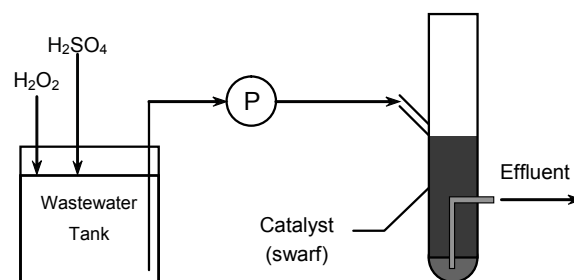

Fig. 1. Structure of the azo dye Acid Red 18.

Fig. 2. Schematic diagram of lab-scale Fenton reactor.

Table 1. Chemical constitution of the general-purpose steel used as a catalyst.

Symbol of steel	Chemical constitution (%)								
	C	Mn	Si	P	S	Cr	Ni	Cu	Mo
45	0.42-0.50	0.50-0.80	0.10-0.40	0.040	0.040	0.30	0.30	0.30	max 0.10

In order to regenerate the catalyst, the Fenton reactor was flushed with distilled water and filled with H_2SO_4 (1+9). After 1 hour, the Fenton reactor was once more flushed with distilled water and within the next 30 hours simulated dye wastewater was decolorized through catalytic oxidation. This phenomenon could be explained by the dissolution of iron oxides formed on the surface of the swarf, reactivating the catalyst.

The effect of catalyst regeneration time on time in which dye wastewater was effectively decolorized by the Fenton reactor was not investigated in this study. However, it may be assumed that longer regeneration time of catalyst will be causing more effective decolorization of dye wastewater.

Decolorization of Dye Wastewater without H_2O_2

In the second part of investigations, simulated dye wastewater was treated in the experimental reactor without adding H_2O_2 to the wastewater tank. Fig. 4 shows the changes of color removal efficiency in the effluent during the first 7 hours of decolorization of dye wastewater. The effectiveness of color removal was increased only to 26.4% within the first 60 minutes. After that, color removal efficiency rapidly decreased to 12.1% (120 minute) and then slowly diminished to 10.2% within up to 180 minutes. The color removal efficiency in the range of 9.8%−10.5% was maintained up to the 7th hour, when the experiment was finished. In no case was visual decolorization achieved, even after being neutralizing with NaOH.
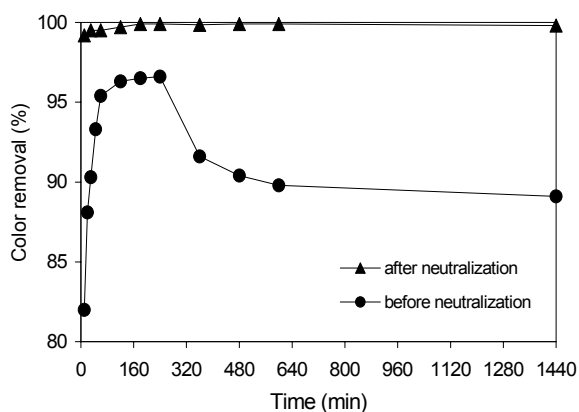
At the same time, the pH was rapidly increased from 2.5 to 5.0 within the first 10 minutes. After that, a clear decrease in pH to the range of 4.0−4.2 was observed up to the 7th hour when the experiment was finished.

The above results clearly showed that chemisorption of the dye on the swarf surface has occurred only in a small degree. This process does not have significant influence on decolorization efficiency of investigated dye wastewater.

Mechanism of the Modified Fenton Process

Decolorization of the dye wastewater by catalytic oxidation using swarf as a catalyst can be explained by the fact that in an aqueous solution, under acidic conditions, Fe^{2+} ions are released to the solution by the swarf. This phenomenon was observed previously by Tang and Chen [19] in relation to iron powder. This acknowledges the fact that the Fenton reaction is effective at acidic conditions.

The changes of Fe concentration in the course of 24 hours of Fenton oxidation are shown in Fig. 5. Iron ion concentration rapidly increased to 92.6 mg/dm^3 within the first 240 minutes. After that, Fe concentration rapidly dropped from 92.6 to 67.1 mg/dm^3 and then slowly diminished to 61.6 mg/dm^3 within up to 10 hours. Then, a small decrease in Fe concentration to 59.3 mg/dm^3 was observed within up to 24 hours.

Analysis of Figs. 3 and 5 clearly shows a potential relationship between Fe concentration in the solution and color removal efficiency. Fig. 6 presents the effect of Fe

Fig. 3. Changes of color removal in the effluent vs. reaction time.
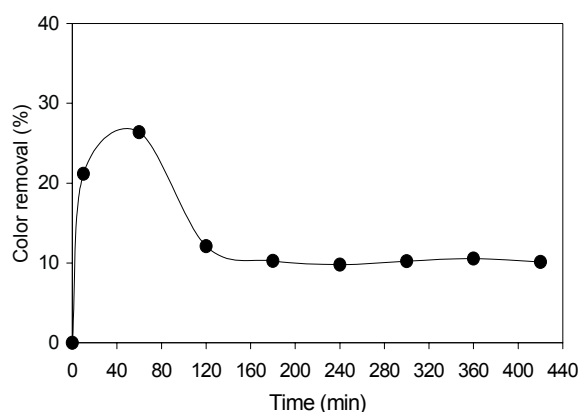
Fig. 4. Changes of color removal in the effluent vs. reaction time (process without of H_2O_2).

concentration released from the swarf on color removal efficiency in the modified Fenton process. The color removal efficiency enhanced while the concentration of Fe ions was increased. As the Fe concentration increased from 3.2 to 37.5 mg/dm^3, color removal efficiency rapidly increased from 82.0 to 95.4%. However, when the concentration of Fe ions exceeded 37.5 mg/dm^3, only a slight increase from 95.4 to 96.6% was observed. On the contrary, the decrease of Fe concentration in the solution caused a significant, nearly linear decrease in color removal.

The swarf acts as a heterogeneous catalyst for the activation of hydrogen peroxide. When swarf is used as a solid catalyst, Fe ions are leached from the solid material. Then, the iron ions act as homogeneous catalyst for the activation of H_2O_2 to generate hydroxyl radicals according to the Fenton reaction.

Because the swarf release Fe^{2+} ions to the solution under acidic conditions, iron dissolution is an initial step for the oxidation of contaminants (e.g. dyes) by the H_2O_2/swarf process. When dye oxidation occurs, the initial Fe^{2+} ions are consumed, and then the oxidation rate will depend on the dissolution rate of Fe^{2+}. The proposed mechanism of hydroxyl radical production in the presence of the swarf catalyst is presented in Fig. 7. This mechanism has three stages: 1st - dissolution of swarf and release of
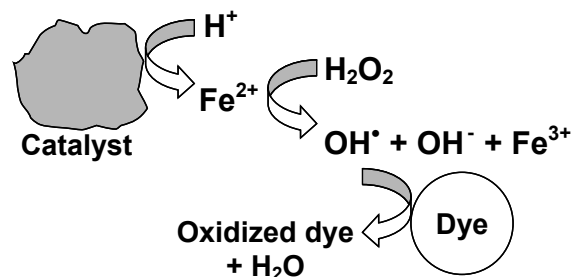

Fig. 7. The proposed mechanism of hydroxyl radical production in the presence of swarf as a catalyst.

Fe^{2+} ions, 2nd - the Fenton reaction including formation of hydroxyl radicals OH$^\bullet$, and 3rd - oxidation of dye.

Conclusions

The results confirm the thesis that swarf can be used as a source of Fe ions (catalyst) in the continuous Fenton process. It was observed that swarf acted as a heterogeneous catalyst for the activation of hydrogen peroxide. The modified continuous Fenton process was found to be very efficient for decolorization of simulated wastewater containing 100 mg dm^{-3} of the commercial azo dye Acid Red 18. A simplified mechanism of hydroxyl radical production in the presence of swarf as a catalyst was proposed.

These results suggest that, compared with both the classical Fenton reaction and Fenton reaction with alternative iron sources, the novel Fenton process (H_2O_2/swarf) has clear advantages. This process is relatively economical because the swarf can be used as a discard material, e.g. from machining. The continuous Fenton process is easy to operate, allowing it to retain the catalyst in the process and thus the catalyst (swarf) can be used repeatedly. The modified Fenton reaction with the use of steel swarf in continuous-flow systems offers greater possibilities for practical application of Fenton reagent. Further experiments concerning the optimization of the novel Fenton process are in progress.

Fig. 5. Changes of Fe concentration vs. reaction time.

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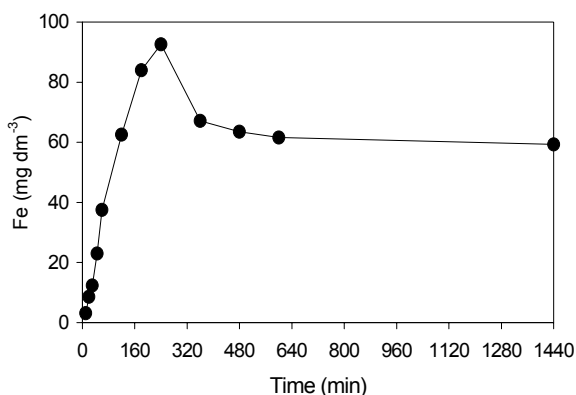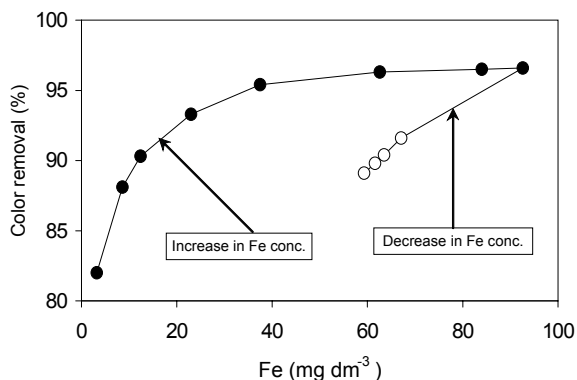
Fig. 6. Effect of Fe concentration on color removal.

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