

REDUCING DEGRADATION OF AZO DYE BY ZERO-VALENT IRON IN AQUEOUS SOLUTION

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Abstract

The reducing degradation kinetics of five azo dyes, Acid orange II, Acid orange IV, Acid orange GG, Acid red 3B and Orange I, by zero-valent iron powder in aqueous solution were studied. It showed that the degradation is a two-step reaction, with the first step being reversible. Solution acidity and iron surface area are the factors greatly influencing the degradation rates, and with increasing of acidity and iron surface area, the degradation rates increase. ©1998 Elsevier Science Ltd. All rights reserved

Introduction

Since organic dye, Marveine, was synthesized by W H. Perkin [1], in 1875, the dye industry has been developing rapidly. Today the annual world production amounts to nearly one million tons, more than half of them are azo dyes. Dye makes our world beautiful, but it brings us pollution. At present, the major techniques in treating dye waste water are biological treatment, activated carbon method and light-degradation. However, there are shortcomings in these techniques, for example, activated carbon method results in transferring the dyes to another place; light-degradation treatment is energy consuming and limited in treating amount; and the conditions of biological process in microorganism treatment are difficult to control to reach a satisfactory level [2].

Zero-valent iron, Fe^0 , in the form of powder, is a strong reducer, and it is cheap and easy to get. Studies on reducing degradation of organic compounds, especially that of halogenate organic compounds [3-9], have been developing rapidly. The practical application of zero-valent iron in treating ground water [10] has been made. Treated by Fe^0 , dye waste waters can be decoloured, and the products (aromatic amine) are easily degraded by microorganisms [10].

The azo dyes, Acid orange II, Acid orange IV, Acid orange GG, Acid red 3B and Orange I, studied in this paper are similar in molecular structure, and have a mono-azo group. The degradation kinetics and its influential factors are studied in this paper.

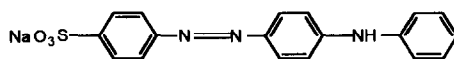
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Experiments

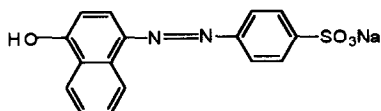
Instrument Shimadzu UV 2201 UV-VIS recording spectrophotometer with the functions of spectrum scanning and single wavelength photometric measurement was used through out the experiment.

Material Iron powder (purity >98%, single point surface area at p/p_0 of 0.2183 is $0.8955 \text{ cm}^2/\text{g}$).

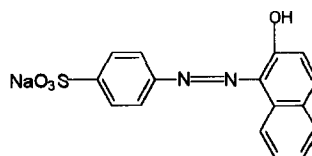
Acid orange II, Acid orange IV, Acid orange GG, Acid red 3B, Orange I are provided by Harteam-Leddon Co., USA. Their molecular structures are shown as follow.



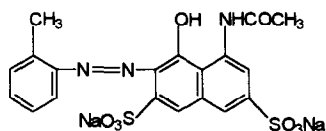
Acid orange IV



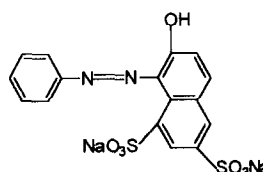
Orange I



Acid orange II



Acid red 3B



Acid orange GG

Experimental Procedures In N_2 atmosphere, 1.5 g iron powder is pretreated by 10 mL 1M HCl for 10 minutes, then washing with distilled water for more than three times to remove the residual HCl and Fe^{2+} . Stock solution of each dye is prepared in distilled water, and their characteristic absorption wavelengths are recorded.

In the degradation procedure, 60 mL stock solution and 1.5 g pretreated iron powder were added in a 100 mL bottle, blowing N_2 and shaking it on a temperature-controlled (20°C) platform. At intervals, 3 mL aliquot was removed with syringe and transferred into a 5 mL centrifuging tube and centrifuged for 2 minutes at 1500 r/min. The supernatant was pipetted out and subjected to UV-VIS spectrum scanning. The changes of the spectrums during the degradation process were recorded and shown in Figure 1 and Figure 2 from which the degradation mechanism was advanced.

1M HCl or 1M NaOH was used to adjust the pH values of the degradation solution to observe the effect of pH on the degradation rate. Different amount of iron powder is used to study the effect of relative iron surface area on the degradation rate. Absorbance at the maximum visible wavelength of the tested dye was measured and dye concentration was calculated according to Beer Law. Consequently, the degradation rate was calculated by the disappearing rate of the dye. The results were shown in Figure 4, Table 1 and Table 2.

Results and Discussion

Reducing Degradation Mechanism of Acid Orange II in Fe⁰-H₂O System

It is well known that the azo group (—N=N—) of the dye is the basic reason for its visible color. The maximum visible absorption wavelengths of the tested dyes, namely, Acid orange II, Acid orange IV, Acid orange GG, Acid red 3B and Orange I, are 483, 460, 475, 538 and 478 nm respectively. Each dye has its characteristic absorption wavelengths in UV area, too. For Acid orange II, they are 191 and 228 nm.

Degradation of each dye in Fe-H₂O-dye system, we observed that the visible absorbance of each degradation solution becomes lower, and that the characteristic UV absorption wavelengths shift to the longer wavelength. Take Acid orange II for example, the absorbance at 483 nm decreased from 0.402 to near zero, and the characteristic wavelengths at 191 nm and 228 nm shift to 199 nm and 247 nm respectively (Figure 1) with the continuing of the reaction.

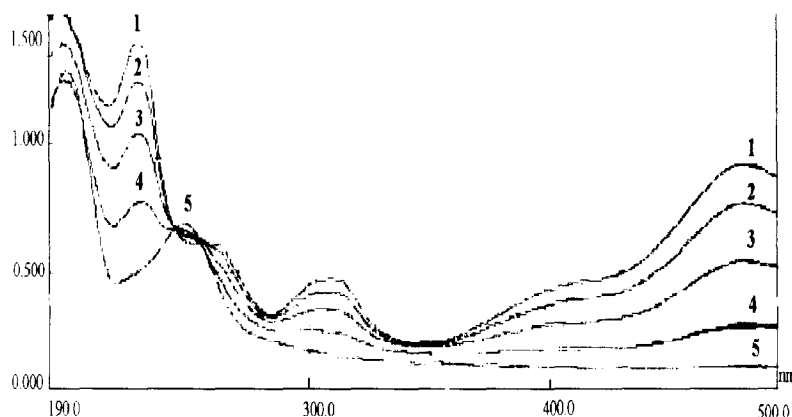


Figure 1. UV-visible Absorption Spectrum of the Degradation Solution of Acid orange II at Different Reaction Time (curve 1: 0 min., curve 2: 3 min., curve 3: 6 min., curve 4: 9 min., curve 5: 12 min.)

These are explained by considering the breaking down of the azo bond and the formation of the products of the aromatic amine. When the azo dye is reduced, the azo double bond is destroyed, and the absorbance caused by the azo group (483 nm) becomes lower, so do the absorbance caused by the aromatic parts of the molecule (191 and 228nm). As the reaction continues, products (substituted aromatic amine) form and increase in quantity, consequently, the characteristic absorption of the products appear and become significant (as shown in curve 5 of Figure 1). Since the amino-group is an auxochrome, it causes the wavelength shift to the longer area.

In our experiment, we found that the visible color of the dye solution deepened during scanning and rescanning after several minutes' delay. So, we recorded the absorption curve scanned immediately after taken from the reaction bottle and the rescanned curve after several minutes, and the curves were shown in Figure 2.

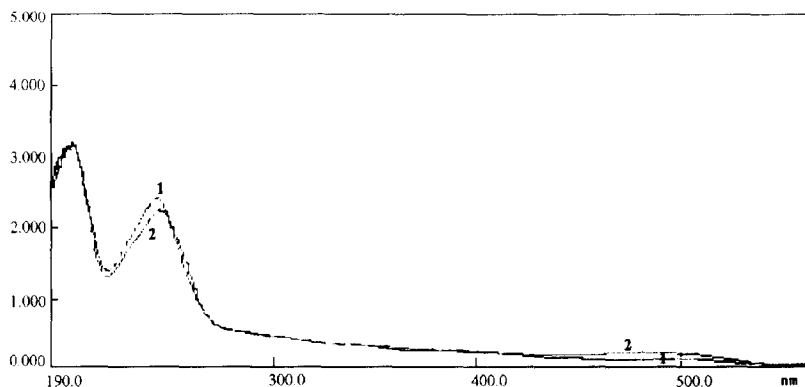


Figure 2. UV-visible Absorption Spectrum of the Degradation Solution of Acid orange II (curve 1 is the spectrum scanned immediately after the solution was taken out of the reaction bottle; curve 2 is the rescanned spectrum of the same solution after several minutes' delay)

We can see from Figure 2 that, the characteristic absorption wavelength of the Acid orange II has shifted from 242.9 nm to 246.2 nm and the corresponding absorbance decreased from 2.341 to 2.214; the absorbance decrease at 198 nm is not clear, but it does exist; while the absorbance at 483nm (visible color of Acid orange II) increased from 0.12 to 0.18. The wavelength shift and absorbance decrease at 198 and 242.9 nm shows the formation of the products, while it seems inconsistent with the absorbance increase at 483 nm which reflects the increasing in amount of the Acid orange II during the several minutes' delay. This seeming inconsistency can be explained by following reaction mechanism, that is, the degradation is a two-step reaction with the first step reversible. In detail, Degradation solution taken out of the reaction bottle is composed of four components, namely, Acid orange II, two degradation products and the transitional compound, in certain proportion (reflected in spectrum as curve 1 in Figure 2). During the several minutes delay, some of the unstable transitional compound decomposes into (the second step in the degradation) the products resulting in the wavelength shifting of 242.9 nm and the absorbance decreasing at 198 and 242.9 nm; and meanwhile, some of the transitional compound returned into Acid orange II (the reversed reaction of the first step) which results in the absorbance increasing at 483 nm (curve 2 in Figure 2).

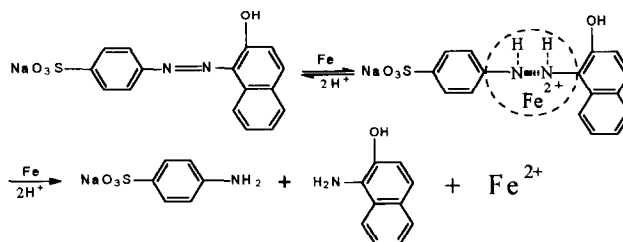


Figure 3. Degradation Mechanism of Acid Orange II in $\text{Fe}^0\text{-H}_2\text{O}$ System

Effects of pH and Iron Surface Area

It is well known that the degradation reaction of organic compounds using Fe^0 occurs on the surface of metal iron [11], and it is the same to azo dyes [12]. Take Acid orange II for an example, when effective collision between dye molecular and iron happens, iron, as an electron donor, loses electrons, the dye molecule, as an electron acceptor, accepts electrons and combines with H^+ and turns into the a transitional product. This product gets electrons from iron and combines with H^+ again, then it turns into terminal products. So, pH and iron surface area would affect the degradation reaction. Degradation with different amount of iron: 0.0083g/mL, 0.017g/mL, 0.025g/mL, 0.034g/mL at pH 7, 5 or 9 were studied.

The results show that the disappearing of the dye fit well with the Langmuir model as follows.

$$^1L = -dC/dt = kC/(1+kC) \quad (1)$$

where 1L is the degradation rate, C is the concentration of the degraded dye, t is the reaction time, k is the observed rate constant. Degradation rate constant was calculated by computer fitting (by Statgraphics Software Inc., 1988) of reaction time, t, and the dye concentration, C, to Equation 2 which is the integrated form of Equation 1, where C_0 is the initial concentration of the dye; then, the degradation half-life, $t_{1/2}$ was calculated.

$$t = (\ln C_0 + kC_0) - (\ln C + kC) \quad (2)$$

Table 2 showed the reaction constants and half-lives of Acid orange II at different pH and iron surface area when the initial dye concentration was 0.75 mmol/L.

Table 2. Reaction Constants and Half-lives of Acid orange II at Different pH and Iron Surface Area

pH of the Dye Solution	Amount of Iron Used (g iron/mL dye solution)	Surface Area of Iron ($\text{cm}^2/\text{mmol dye}$)	Rate Constant, k (mmol/L.min)	Half-life, $t_{1/2}$ (sec.)
7	0.008	9.87	0.056	300
7	0.017	19.7	0.127	260
7	0.025	29.7	0.153	140
7	0.034	40.5	0.195	120
5	0.025	29.7	0.178	130
9	0.025	29.7	0.058	290

We can see from Table 2 that pH strongly affects the degradation rate, and with acidity increasing, the degradation rate increases. For example, when the iron amount is constant at 0.025 g per mL dye solution the rate constants of Acid orange II at pH 5, 7 and 9 are 0.178, 0.153 and 0.058 mmol/L.min respectively, that is, the more acid the solution is, the more rapidly the degradation rate. With more H^+ in acid solution than that in alkaline solution, the reaction in acid solution is easier and the reaction constant is higher.

Table 2 also shows that iron amount affect the degradation rate. The iron amount used is expressed in iron surface area in cm^2 per mmol dye. Figure 4 shows four curves where concentration of Acid orange II is plotted against reaction time, and each curve represents the reaction under different iron surface area. It is clear from Figure 4 and Table 2 that, with the increasing of iron surface area, the degradation rate of Acid orange II is fastened. The reaction constant is linearly correlated with relative iron surface area.

$$k=0.0052A \quad r=0.994, n=4, SE=0.017$$

where A is the relative iron surface area of the reaction solution.

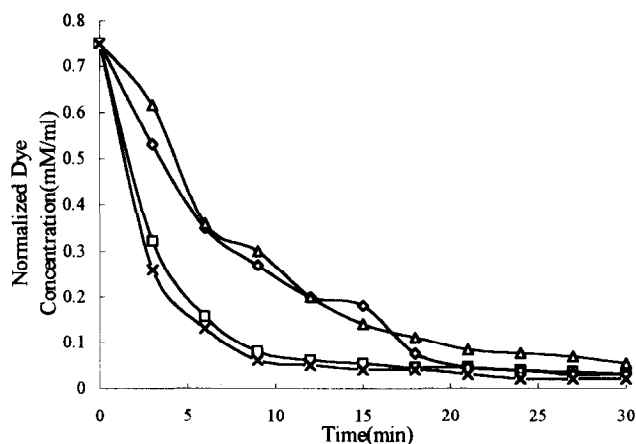


Figure 4 Degradation of Acid orange II at Different Iron Surface Area

× 40.5 cm²/mmol dye □ 29.7 cm²/mmol dye
 ◇ 19.7 cm²/mmol dye △ 9.87 cm²/mmol dye

We also investigated the degradation of other four azo dyes, namely, Acid orange IV, Acid orange GG, Acid red 3B and Orange I, with the initial dye concentration of 0.5 mmol/L and iron powder used of 0.025 g per mL solution. The degradation rate constants and half-lives were listed in Table 3. Clearly, the half-lives of the dyes in the conditions mentioned above is very short (several minutes).

Table 3 Reaction Constants and Half-lives of Four Azo Dyes

Dye	Rate Constant, k (mmol/L.min)	Half-lives, t _{1/2} (sec.)
Acid orange IV	0.135	160
Acid orange GG	0.159	110
Acid red 3B	0.167	105
Orange I	0.138	150

It is found in our experiments that: the degradation with pretreated iron powder occurs much easier than with unpretreated iron. For the pretreatment using HCl can break down the oxide layer of iron, clean the surface and enlarge the effective surface area.

Summary

The reducing degradation kinetics of five azo dyes, Acid orange II, Acid orange IV, Acid orange GG, Acid red 3B and Orange I, by zero-valent iron powder in aqueous solution were studied. The results showed that the degradation is a two-step reaction, with the first step reversible; solution acidity and iron surface area are the factors greatly influencing the degradation rates, and with the increasing of acidity and iron surface area, the degradation rates increase. Any measurement, such as acidifying the degradation solution and pretreating iron powder with HCl, to increase the acidity and iron surface area would lead to the increasing in degradation rates. The reducing degradation of the azo dyes with zero-valent iron powder is effective with half-lives of several minutes.

Acknowledgment

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