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The use of ultrasound to enhance the decolorization of the C.I. Acid Orange 7 by zero-valent iron

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Abstract

The effect of pH, iron loading and initial dye concentration on the decolorization of C.I. Acid Orange 7 by zero-valent iron combined with ultrasound radiation was investigated. It was shown that the reduction of C.I. Acid Orange 7 was enhanced by ultrasound and the decolorization appeared to be a first order reaction. With the pH range of 3–7, iron loading range of 0.5–2.0 g L^{-1} and initial dye concentration of 50–250 mg L^{-1}, the decolorization efficiency decreased with the increasing pH or initial dye concentration, but increased with the increase of iron loading. Accordingly, the first order rate constant k_1 decreased by 0.026 min^{-1} when pH dropped by one unit. It increased linearly with the increasing iron loading, but decreased nonlinearly with the increase of the initial dye concentration.

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Keywords: Ultrasound; Zero-valent iron; C.I. Acid Orange 7; Decolorization; Kinetics; Enhancement

1. Introduction

Azo dyes are widely used in the textile and dyestuff industries. Nearly half a million tones of azo dyes are produced each year all over the world, which account for almost half of all dye productions [1]. Due to their biological recalcitrance, conventional biological treatment processes such as activated sludge process are ineffective to remove these dyes from wastewater [2].

Zero-valent iron (Fe^0) is a mild reducing agent with an ${E_H}^0 = -0.440$ V. The elemental iron metal powder is inexpensive and is easy to obtain. Studies on reductive degradation of organic compounds, such as chlorinated solvents [3], nitro aromatic compounds [4], nitrates [5], and pesticides [6], have attracted more and more interest during the last decade. The use of zero-valent iron powder has also been shown to decolorize the solution containing azo dyes and enhance its biodegradability [1,7–9].

The rates of chemical reactions of elemental iron metal power are dependent on the surface concentrations of the segments such as surface sites. The surface is found to be deactivated over time due to the precipitation of iron oxides/hydroxides on the iron surface and the decrease of porosity of the surface accordingly [3,4]. As acoustic cavitation is known to increase the surface area of the reactive solids by causing particles to rupture, sonication in the presence of zero-valent iron has been explored for the reduction of carbon tetrachloride as well as nitrobenzene [10,11]. In this study, the combination of ultrasound and elemental iron metal powder (US/Fe^0) for the decolorization of azo dye using C.I. Acid Orange 7 as a model compound was investigated.

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2. Materials and methods

2.1. Materials

C.I. Acid Orange 7 was purchased from Wenzhou Rosi Dyesituff Co. Ltd. (China) and used without further purification. Iron metal power (analytical grade) was obtained from Shanghai No.2 Metallurgical Plant (China).

2.2. Methods

In nitrogen atmosphere, a given amount of iron powder was pretreated for 3 min by rinsing with 1 M HCl, and then washed with distilled water for 1 min. Stock solution of C.I. Acid Orange 7 was prepared in distilled water. HCl or NaOH was used to adjust the pH of the dye solution. The stock solution was fed into a glass reactor, and nitrogen gas was bubbled into the solution to keep the anaerobic circumstance. Then the pretreated iron powder was added into the reactor. Sonication was performed with a KS-250 ultrasonic generator (250 W, 20 kHz, Ninbo Kesheng Instrument Co., China) equipped with a titanium probe transducer. The tip of the probe was 1 cm in diameter and was placed 2 cm into the liquid layer. The sonication was administered in pulses with a 50% duty cycle. The reactor was immersed into a water bath to keep the temperature around 20 °C (see Fig. 1). A predetermined amount of aliquot was removed with syringe at different intervals and transferred into a centrifuging tube, then centrifuged for 2 min at 4000 r/min. The absorbency of the supernatant was measured using a Shimadzu UV-1600 spectrophotometer at maximum absorption wavelength of 485 nm. The morphology of the iron surface before and after the experiment was examined using a Field Emission Gun Scanning Electron Microscope (FEG-SEM, EEI, Sirion).

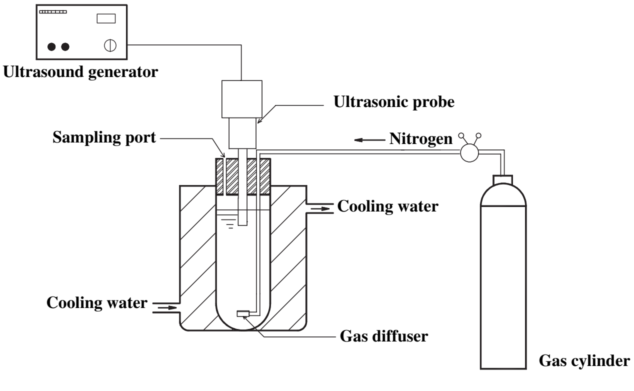


Fig. 1. The experimental set up.

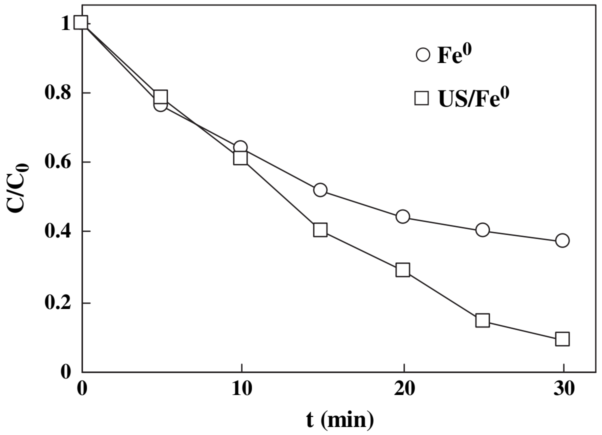


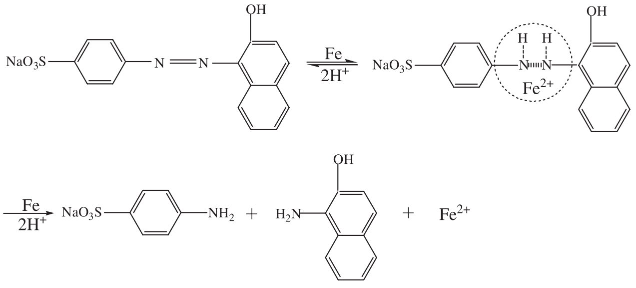
Fig. 2. Decolorization of C.I. Acid Orange 7 by Fe^0 with/without sonolysis. $C_0 = 50$ mg L^{-1}, pH = 5, [Fe^0] = 1 g L^{-1}.

3. Results and discussion

3.1. Decolorization of C.I. Acid Orange 7 in different systems

Experiments were performed with Fe^0 alone, ultrasound alone and the combined US/Fe^0 system, respectively, to investigate the enhancement of sonication on the decolorization by Fe^0. As shown in Fig. 2, the decolorization efficiency reached 91% in the coupled US/Fe^0 system after 30 min of treatment, while only 63% of decolorization efficiency was achieved with Fe^0 alone, where ultrasound had no effect on the decolorization (data not shown).

It is well known that the reduction of azo dyes using Fe^0 occurs on the surface of metal iron [1,12]:



The heterogeneous reaction involves five steps: (i) mass transfer of the reactant to the Fe^0 surface from the bulk solution; (ii) adsorption of the reactant on the Fe^0 surface; (iii) chemical reaction at the Fe^0 surface; (iv) desorption of the products from Fe^0 surface; and (v) mass transfer of the products into the bulk solution [13]. It has been observed that the decolorization kinetics of azo dyes by Fe^0 is limited by mass transfer of the substrates to the Fe^0 surface [7,8]. In the presence of ultrasound irradiation, transient cavitation results in turbulent flow conditions within the reactor that

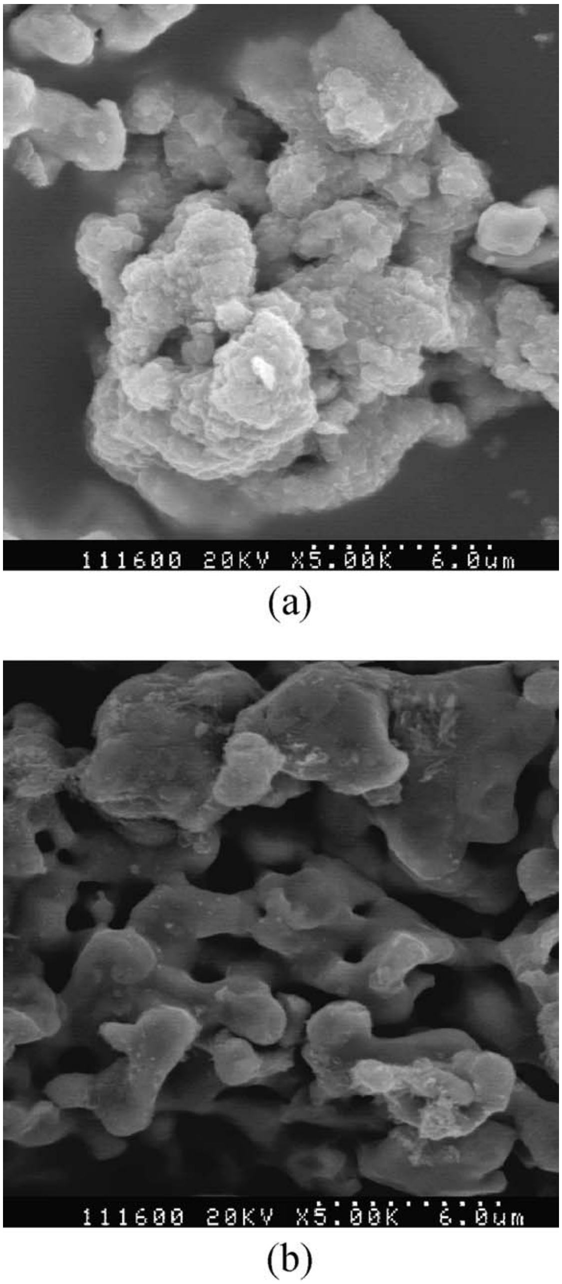


Fig. 3. SEM photographs of the iron surface after 30 min of reaction (a) in the Fe^0 system; (b) in the combined US/Fe^0 system.

enhance overall mass transport [10,11]. On the other hand, acoustic cavitation leads to the rupture of particles. Research has shown that surface defects increase the percentage of active sites on the iron surface [14]. Ultrasound causes pitting and cracking of the metal surface thus increasing the degradation reaction rates. Moreover, cavitational bubble collapse directly on the Fe^0 surface may cause direct damage by shock waves produced upon implosion, while cavitational collapse near the Fe^0 surface in the aqueous phase will cause microjets to hit the surface and produce a nonsymmetrical shock wave. The latter leads to the cleaning action of ultrasound. As a result of these events, more reactant surface area is readily formed for further surface reactions [10,11]. Therefore, compared to Fe^0 alone, higher decolorization efficiency in the coupled US/Fe^0 system was achieved which can be attributed to the indirect chemical effects associated with the continuous ultrasonic cleaning and activation of the Fe^0 surface, the enhancement of mass transfer resulting from the turbulent effects of cavitation [10,11].

The morphology of the iron surface after 30 min treatment with/without sonication was examined via Scanning Electron Microscope (Fig. 3). It can be seen that the sonicated samples were visibly cleaned due to the continuous ultrasonic cleaning. In addition, the pitting on the surface caused by shock waves produced upon implosion was apparent.

3.2. The effect of pH on the decolorization of C.I. Acid Orange 7

Fig. 4 illustrates the decolorization of C.I. Acid Orange 7 in the combined US/Fe^0 system at different pH. It shows that the decolorization efficiency increased with the decrease of pH. When pH was 3, the decolorization efficiency reached 91% after 20 min treatment. However, when pH rose to 7, the decolorization efficiency dropped to only 15%. When effective collision between dye molecule and elemental iron happens, elemental iron, as an electron donor, loses electrons, the dye molecule, as an electron acceptor, accepts electrons, combines with H^+ and turns into the transitional product. This product gets electrons from elemental iron and combines with H^+ again, and then it turns into terminal products [1]. As a consequence, pH would

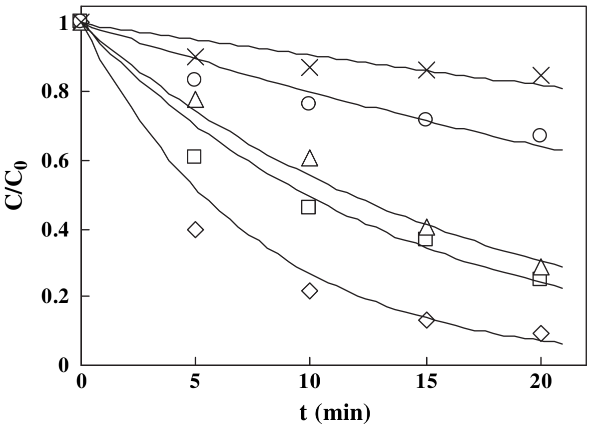


Fig. 4. The effect of pH on the decolorization. $C_0 = 50\ mg\ L^{-1}$, $[Fe^0] = 1\ g\ L^{-1}$. ◇, pH = 3; □, pH = 4; △, pH = 5; ○, pH = 6; ×, pH = 7; the solid lines are the fitting results.

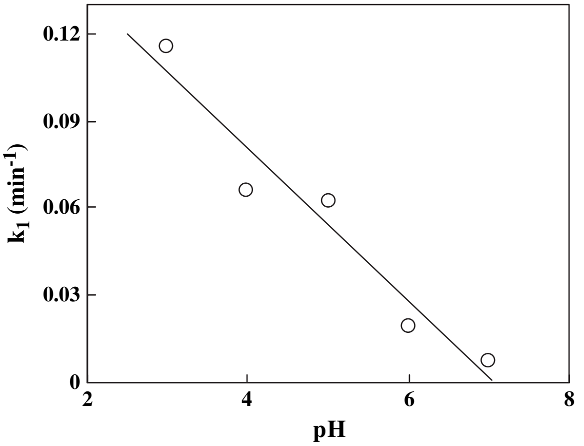


Fig. 5. The effect of pH on the observed first order rate constant.

strongly affect the reduction of C.I. Acid Orange 7, i.e., the reaction rate increases with the increasing acidity.

Fig. 4 also illustrates the kinetics of C.I. Acid Orange 7 reduction in the coupled US/Fe^0 system. The decolorization of C.I. Acid Orange 7 fits the first order kinetic model:

$$C = C_0 \exp(-k_1 t)$$

where C is the dye concentration at time t, C_0 is the initial dye concentration, and k_1 is the pseudo first order decolorization rate constant. The relationship between the first order rate constant and pH is shown in Fig. 5, which indicates that the first order rate constant is a linear function of pH. In other words, the rate constant would increase by $0.026\ \mathrm{min}^{-1}$ when pH decreases by one unit.

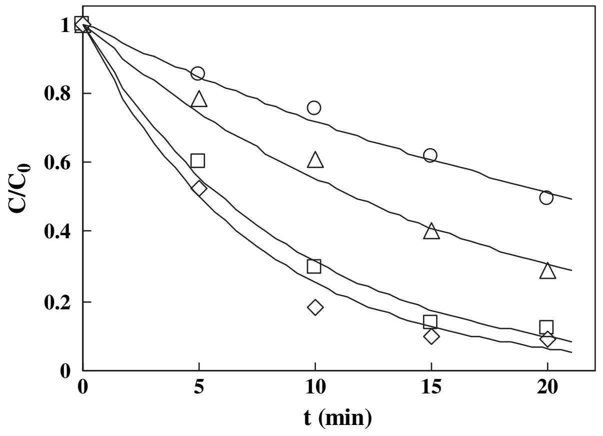


Fig. 6. The effect of iron loading on the decolorization. $C_0 = 50\ \mathrm{mg\ L}^{-1}$, pH = 5. $[Fe^0]$ (g L^{-1}): ○, 0.5; △, 1.0; □, 1.5; ◇, 2.0; the solid lines are the fitting results.

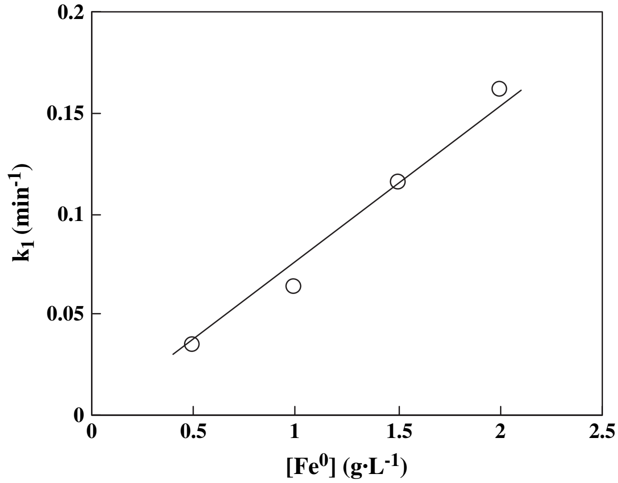


Fig. 7. The effect of iron loading on the observed first order rate constant.

3.3. The effect of iron loading on the decolorization of C.I. Acid Orange 7

As the decolorization of C.I. Acid Orange 7 by US/Fe^0 occurs at the Fe^0/H_2O interface, iron surface area would affect the decolorization rate. The more iron loading, more is the iron surface area. Therefore, as shown in Fig. 6, the decolorization efficiency increases with the increasing iron loading. Accordingly, the first order rate constant increases linearly with the increase of iron loading, as shown in Fig. 7.

3.4. The effect of initial dye concentration on the decolorization of C.I. Acid Orange 7

Fig. 8 indicates that the decolorization efficiency decreases with the increase of the initial dye concentration. When the initial dye concentration C_0 is $50\ \mathrm{mg\ L}^{-1}$, the decolorization efficiency reaches 71% in 20 min. When

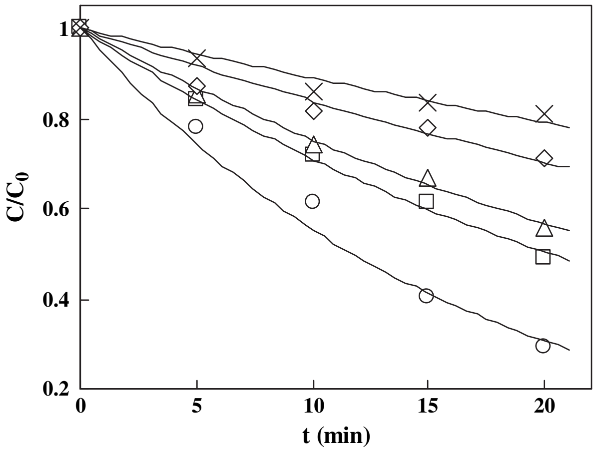


Fig. 8. The effect of initial dye concentration on the decolorization. $[Fe^0] = 1\ \mathrm{g\ L}^{-1}$, pH = 5. $[C_0]$ (mg L^{-1}): ○, 50; □, 100; △, 150; ◇, 200; ×, 250.

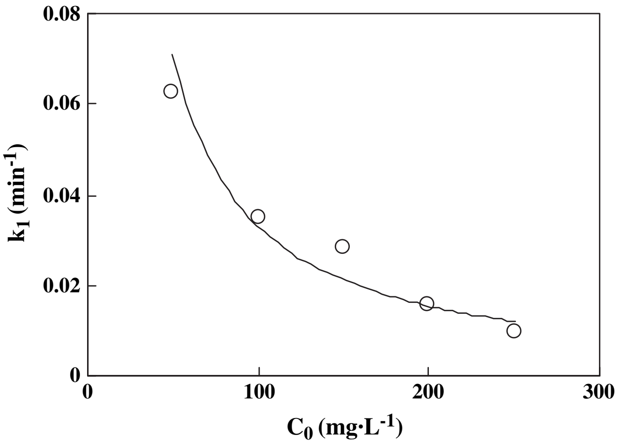


Fig. 9. The effect of initial dye concentration loading on the observed first order rate constant.

C_0 rises to $250\,\mathrm{mg\,L^{-1}}$, the decolorization efficiency drops to only 19%. The reduction of C.I. Acid Orange 7 in the coupled US/Fe^0 system is a kind of heterogeneous reaction, which involves mainly the adsorption of dye onto the iron surface and the sequent surface reaction. The adsorption capacity of iron is limited when the iron loading is fixed. The adsorption of dye molecules onto the iron surface would hinder other dye molecules in the bulk solution to be adsorbed and reduced on the iron surface. Fig. 9 shows that the first order rate constant decreases monotonically but nonlinearly with the initial dye concentration.

4. Conclusions

This study shows the synergistic effect achieved by combining zero-valent iron with ultrasound radiation for the decolorization of C.I. Acid Orange 7. The decolorization of C.I. Acid Orange 7 fits the first order kinetic model. The decolorization efficiency decreased with the increasing pH or initial dye concentration, but increased with the increase of iron loading. Accordingly, the first order rate constant k_1 decreased by $0.026\ \mathrm{min^{-1}}$ when pH dropped by one unit. The decolorization efficiency increased linearly with the increasing iron loading, but decreased nonlinearly with the increase of the initial dye concentration.

Acknowledgments

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