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Comparative study of advanced oxidation for textile wastewater

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ABSTRACT

It was conducted to evaluate the efficiency for oxidations of a typical azo dye by advanced oxidation such as Fenton process and Fenton-like process. The ratio parameters affecting the decolorization efficiency of C.I. Basic Red 22 such as initial concentration of Fe^{2+}, Fe^{3+} and H_2O_2, initial pH of dye solution, and reaction temperature were investigated. The results showed that the decolorization efficiency of C.I. Basic Red 22 in Fenton oxidation was much higher than that of the Fenton-like oxidation in the initial stages and the decolorization efficiency was similar but trends to the similar level for both systems after 45 min. For the two oxidation systems, the decolorization efficiency of C.I. Basic Red 22 depended on $[Dye]_0$, $[Fe^{2+}]_0$ or $[Fe^{3+}]_0$, $[H_2O_2]_0$, pH, and temperature.

Keywords: Comparative; Textile; Advanced oxidation

1. Introduction

Today, increasing waste from industrial product and practices is threatening public health and the environment [1]. Among all industrial sectors, textile industries are rated as high polluters, taking into consideration the volume of discharge and effluent composition [2]. In general, several difficulties are encountered in removal of dyes from wastewaters. By design, dyes are highly stable molecules, made to resist degradation by light, chemical, biological, and other exposures. Commercial dyes are usually a mixture of large complex and have often been unreported molecular structure and properties. Dyes also vary widely in chemical composition. Furthermore, dyeing wastewater includes many other materials such as particulates, processing assistants, salts, surfactants, acids, and alkalis [3]. Basic dyes are considered as one of the most problematic classes of dye. Generally, basic dyes are cationic dyes with cationic properties originating from the positive charge that is generally delocalized throughout the chromophoric system, although it is probably more localized on the nitrogen atoms. Basic dyes are also called because of their affinity to basic textile materials with net negative charge. Basic dyes have been classified according to their chemical constitution as well as dyeing properties. In chemical classification, the term ‘‘cationic dyes’’ is usually preferred [4,5]. This class of dye can be applied to wool, silk, and leather and also to tanninmordanted cotton. According to Anliker et al. [6], basic dyes have been classified as toxic colorants. Therefore, improved or effective technologies are required to remove them from textile effluents.

In recent years, advanced oxidation processes using ozone, photocatalytic process UV/TiO_2, and Fenton’s reagent (H_2O_2 and ferrous ion) have received

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considerable attention as effective pretreatment processes of less biodegradable wastewater [7,8]. Among them, Fenton's has been widely used because it is cost effective, easy to treat, reacts well with organic compounds, and does not produce toxic compounds during oxidation [9]. The Fenton's reaction mainly includes the following reactions [10]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^+ \quad (2)$$

$$Fe^{3+} + {}^{\bullet}OOH \rightarrow Fe^{2+} + H^+ + O_2 \quad (3)$$

$$\cdot OH + H_2O_2 \rightarrow \cdot OOH + H_2O \quad (4)$$

$${}^{\bullet}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (5)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (6)$$

$${}^{\bullet}OH + {}^{\bullet}OOH \rightarrow O_2 + H_2O \quad (7)$$

In the process, hydroxyl radicals (${}^{\bullet}OH$), which is the second strongest oxidant ($E^0 = 2.87$ V, vs. normal hydrogen electrode) and only inferior to fluoride ($E^0 = 3.06$ V), was produced. Hydroxyl radicals can rapidly and nonselectively react with a wide range of organic pollutants through hydrogen abstraction, electrophilic addition, and/or electron transfer to mineralize them to CO_2, H_2O, and inorganic ions [11].

The main drawback of this technique is represented by the cost of the reactants, H_2O_2 and Fe^{2+}. For this reason, various methods have been introduced to use the lower cost Fe^{3+} salts rather than Fe^{2+} salts, which have resulted in photo-Fenton and electro-Fenton techniques [12]. While Fenton-like oxidation should also be effective, little work has been reported on the Fenton-like oxidation of dyes. Several studies have shown that the rate of decomposition of H_2O_2 and the rate of oxidation of organic solutes are much slower using Fe^{3+}/H_2O_2 than Fe^{2+}/H_2O_2 and are optimal at pH 3.0 [13]. However, as the solution pH in many cases is neutral or alkaline, the necessity to acidify the reaction medium limits the applicability of the Fenton process in environmental technology. Moreover, despite numerous studies of the Fe^{3+}/H_2O_2 system, the chemistry and kinetics of the oxidation of organic compounds by Fe^{3+}/H_2O_2 have not been well elucidated [14].

In this paper, we conducted a experiment to evaluate the relationship between Fenton and Fenton-like reactions by the Fenton and Fenton-like oxidations of a typical azo dye. The ratio parameters affecting the decolorization such as initial concentration of Fe^{2+}, Fe^{3+}, and H_2O_2, initial pH of dye solution, and reaction temperature were investigated.

2.1. Materials

The C.I. Basic Red 22 was chosen as the model dye. The C.I. Basic Red 22 was commercial samples and was used without further purification. Fig. 1 depicts the chemical structure. The pH of the solutions was adjusted using H_2SO_4 and NaOH solutions.

2.2. Experimental procedures

All tests were conducted in a 500 mL Erlenmeyer flask as a batch reactor. Each experiment was performed by the addition of ferrous ion or ferric ion and diluted with deionized water to 200 mL. Batch experiments of the C.I. Basic Red 22 decolorization were performed by adding H_2O_2 to the dye solution and then the pH was adjusted to the desired value by the addition of a few drops of either 0.1 mol/L H_2SO_4 or 0.1 mol/L NaOH. Following the pH adjustment, the Fe^{2+} ions or Fe^{3+} ions were quickly added to the dye solution. The flask was then placed in a thermostated water-bath shaker and agitation was provided at 150 rpm. Samples were taken at predetermined intervals into the tubes containing sodium hydroxide solution to quench the reaction by increasing pH around 8.0. Then, they were mixed for 10 min with magnetic stirred bar. After leaving alone for 20 min, the supernatant was centrifuged for 10 min at 15,000 rpm.

2.3. Analytical methods

The UV–Vis spectra of C.I. Basic Red 22 solution were recorded from 200 to 800 nm using a UV–Vis spectrophotometer with a spectrometric quartz cell (UV752, China). The maximum absorbance wavelength of C.I. Basic dye 22 was found at 553 nm. In the whole reaction process, it was found that the measure of concentration of C.I. Basic dye 22 is not inter-

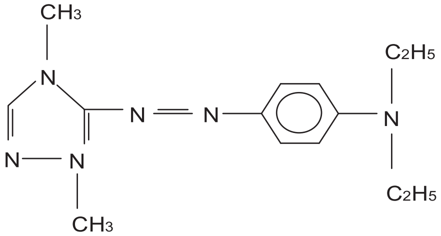

Fig. 1. Chemical structure of C.I. Basic Red 22.

fered by the decolorization products. Therefore, the concentration of C.I. Basic dye 22 in reaction mixture at different reaction times was determined by measuring the absorption intensity of solution at 553 nm and using a calibration curve [12].

The decolorization efficiency of C.I. Basic Red 22 was defined as follows:

$$\text{Decolorization efficiency} = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \qquad (8)$$

where C_0 is the initial concentration of C.I. Basic Red 22 and C_t is the concentration of C.I. Basic Red 22 at reaction time (min).

3. Results and discussion

3.1. Comparison of Fenton and Fenton-like oxidations

A comparison of the dye decolorization of C.I. Basic Red 22 with Fe^{2+}/H_2O_2 and Fe^{3+}/H_2O_2 was investigated at 40 mg/L [dye], 0.05 mmol/L [Fe^{2+}] or 0.05 mmol/L [Fe^{3+}], 2.0 mmol/L [H_2O_2], pH3.5, and 30℃.

As seen from Fig. 2, it shows that both Fenton and Fenton-like oxidations are effective in dye decolorization. The decolorization efficiency was 97% after 45 min. However, the decolorization efficiency changed at different rates for the Fenton and Fenton-like oxidations. The decolorization efficiency in Fenton oxidation was much faster than that of the Fenton-like oxidation in the initial stages and the decolorization efficiency was similar for both systems after 45 min. It is known that the hydroperoxyl radical has lower oxidation capability than $^{\bullet}OH$ [15]. Several investigations into the Fenton oxidation of organic compounds have shown that the initial rate of mineralization is faster with Fenton than with Fenton-like reagents, due to the immediate formation of hydroxyl radicals in the case of Fenton reagent [16].

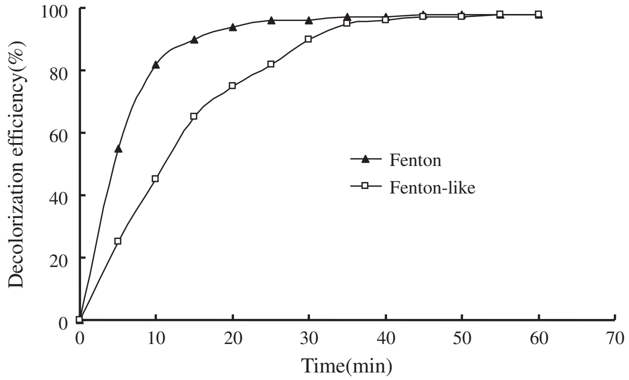

Fig. 2. A comparison of the decolorization efficiency of C.I. Basic Red 22 by Fenton and Fenton-like reaction.

3.2. Effect of H_2O_2 concentration

The effect of H_2O_2 was studied by varying the amount of H_2O_2 used for the experiment from 1.0 to 4.0 mmol/L with 0.05 mmol/L of [Fe^{2+}] or 0.05 mmol/L of [Fe^{3+}], 40 mg/L of dye solution, $pH_0 = 3.5$, reaction time of 20 min, and 30℃. Fig. 3 shows the relationship between decolorization of the dye at different initial concentrations.

As seen from Fig. 3, it shows that the decolorization of the dye increases with increasing H_2O_2 concentration. When the H_2O_2 concentration increased to 2 mmol/L in the Fenton reaction the decolorization efficiency could reach to 94% after 20 min. H_2O_2 concentration above 2 mmol/L would not induce significant change in decolorization efficiency. In Fenton-like reaction, 75% of decolorization efficiency could be achieved after 20 min when the H_2O_2 concentration was 2 mmol/L. The unreacted H_2O_2 will act as a scavenger of $^{\bullet}OH$ and produces a less potent perhydroxyl radical, resulting in less dye decolorization.

3.3. Effect of initial pH

The effect of initial pH was studied by varying pH in the solution from 2.5 to 6.0 with 0.05 mmol/L of [Fe^{2+}] or 0.05 mmol/L of [Fe^{3+}], 40 mg/L of dye solution, 2.0 mmol/L [H_2O_2], $pH_0 = 3.5$, reaction time of 20 min, and 30℃. Fig. 4 shows the relationship between decolorization of the dye at different initial concentrations.

It shows that lower pH resulted in higher efficiency of dye decolorization. For the Fenton reaction, 94% of decolorization was achieved in 20 min at a pH < 3.5 and when the pH was further decreased, the

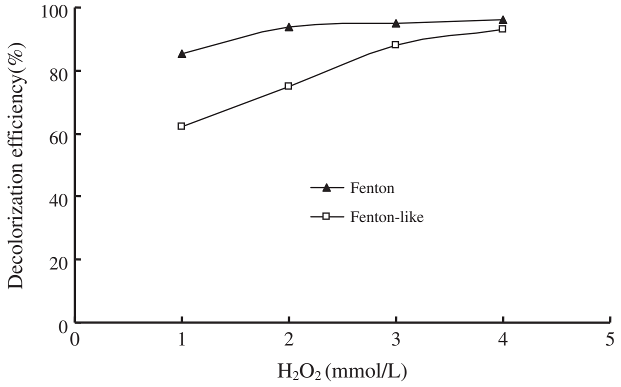

Fig. 3. Effect of initial H_2O_2 concentration on decolorization of C.I. Basic Red 22 by Fenton and Fenton-like reaction.

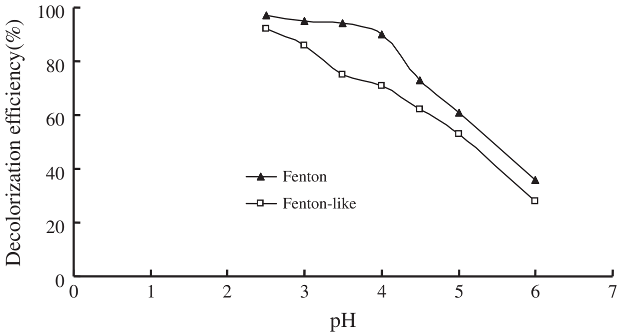

Fig. 4. Effect of initial pH on decolorization of C.I. Basic Red 22 by Fenton and Fenton-like reaction.

decolorization efficiency was similar. However, in the Fenton-like reaction, 75% of decolorization efficiency was obtained after 20 min at pH <3.5.

It is considered that more $Fe(OH)^+$ is formed at low pH and the activity of $Fe(OH)^+$ is higher than Fe^{2+} in Fenton oxidation. In contrast, ferrous ions are unstable at a pH above 4.0 and they easily form ferric ions, which have a tendency to produce ferric hydrogen complexes. Hydrogen peroxide is also unstable in basic solution and may decompose to give oxygen and water, and lose its oxidation ability. Thus, hydrogen peroxide and ferrous ions have difficulty in establishing an effective redox system and their decolorization is also less effective [17].

3.4. Effect of temperature

Temperature is critical to the reaction rate, the product yield and distribution. In order to determine the effect of reaction temperature on the decolorization of C.I. Basic Red 22, a series of tests were conducted at 10, 20, 30, and 40℃, respectively. The reaction condition is $pH_0 = 3.5$, 40 mg/L of dye solution, 2.0 mmol/L of $[H_2O_2]$, 0.5 mmol/L of $[Fe^{2+}]$ or 0.5 mmol/L of $[Fe^{3+}]$, and reaction time of 20 min. The reaction results are illustrated in Fig. 5.

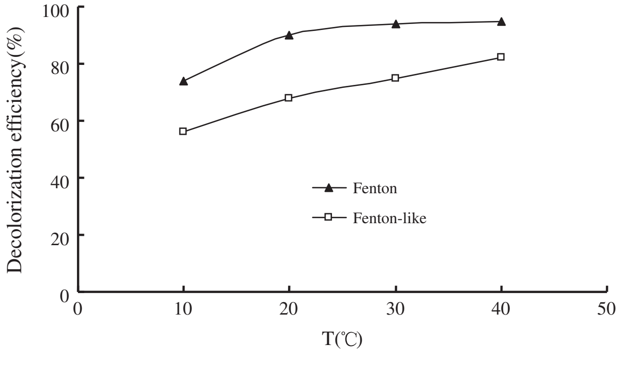

Fig. 5. Effect of temperature on decolorization of C.I. Basic Red 22 by Fenton and Fenton-like reaction.

It can be seen that the temperature exerted a strong effect on the decolorization efficiency of C.I. Basic Red 22 and the decolorization efficiency was accelerated by a rise in temperature. This is because higher temperature increases the reaction rate between hydrogen peroxide and any form of ferrous/ferric ion, thus increasing the rate of generation of oxidizing species such as •OH radical.

3.5. Effect of the initial dye concentration

The effect of the initial dye concentration on Fenton processes and Fenton-like processes was investigated with $pH_0 = 3.5$, 0.05 mmol/L of $[Fe^{2+}]$ or 0.05 mmol/L of $[Fe^{3+}]$, 2.0 mmol/L of $[H_2O_2]$, reaction time of 20 min, and 30℃. The influence of the dye concentration is shown in Fig. 6.

It was observed that higher the initial dye concentration, lower the decolorization efficiency of C.I. Basic Red 22 by Fenton oxidation and Fenton-like reaction. This means that with constant $[H_2O_2]_0$ and $[Fe^{2+}]_0/[Fe^{3+}]_0$, more hydrogen peroxide was consumed because of a higher dye concentration.

3.6. Effect of Fe^{2+} and Fe^{3+} concentrations

A series of experiments were conducted with different $[Fe^{2+}]$ or $[Fe^{3+}]$ from 0.01 to 0.1 mmol/L, $pH_0 = 3.5$, 40 mg/L of dye solution, 2.0 mmol/L of $[H_2O_2]$, reaction time of 20 min, and 30℃. The results obtained are presented in Fig. 7.

It was observed that the decolorization efficiency of the C.I. Basic Red 22 by Fenton oxidation and Fenton-like reaction increased with increasing Fe^{2+} or

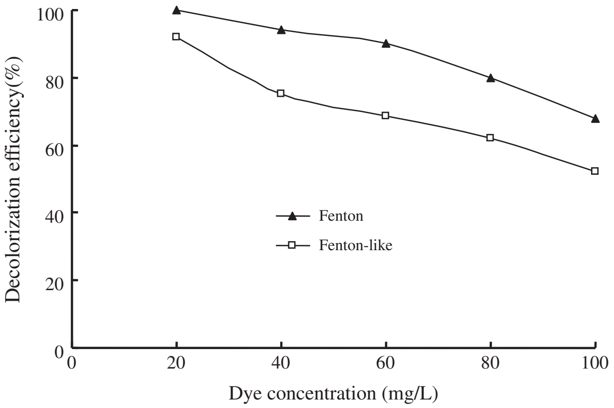

Fig. 6. Effect of the initial dye concentration on the decolorization of C.I. Basic Red 22 by Fenton oxidation and Fenton-like reaction.

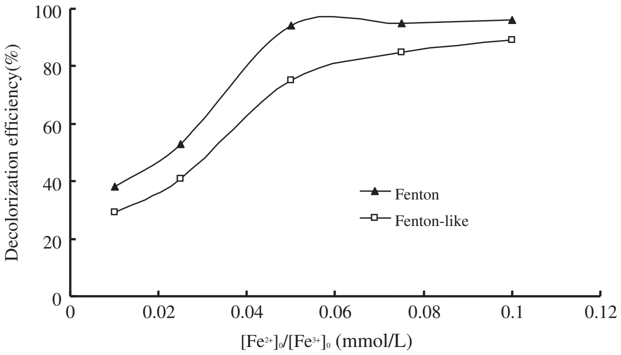

Fig. 7. Effect of Fe^{2+} and Fe^{3+} concentrations on the decolorization of C.I. Basic Red 22 by Fenton oxidation and Fenton-like reaction.

Fe^{3+} concentrations. In the case of Fenton oxidation, the decolorization efficiency of the C.I. Basic Red 22 was very small when the Fe^{2+} concentration was <0.025 mmol/L. When the Fe^{2+} concentration was 0.05 mmol/L, the decolorization efficiency of the C.I. Basic Red 22 was 94%. For Fenton-like oxidation, when the Fe^{3+} concentration was 0.025 mmol/L, the decolorization efficiency of the C.I. Basic Red 22 was 41%. By contrast, when the Fe^{3+} concentration was 0.05 mmol/L, the decolorization efficiency of the C.I. Basic Red 22 was 75%.

4. Conclusions

Fenton and Fenton-like oxidation can effectively decolorize C.I. Basic Red 22 in aqueous solution under neutral conditions. The decolorization efficiency in Fenton oxidation was much faster than that of the Fenton-like oxidation in the initial stages and the decolorization efficiency was similar for both systems after 45 min. For the two oxidation systems, the decolorization efficiency of C.I. Basic Red 22 depends on $[Dye]_0$, $[Fe^{2+}]_0$ or $[Fe^{3+}]_0$, $[H_2O_2]_0$, pH, and temperature.

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