Chemical Engineering Journal 155 (2009) 680–683

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Fenton oxidative decolorization of the azo dye Direct Blue 15 in aqueous solution

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ARTICLE INFO

Article history:
Received 21 January 2009
Received in revised form 14 August 2009
Accepted 28 August 2009

Keywords:
Azo dye
Direct Blue 15
Decolorization
Fenton process
AOPs

ABSTRACT

In this paper, the application of Fenton oxidation process for the decolorization of an azo dye Direct Blue 15 (DB15) in aqueous solution was investigated. The effect of initial pH, dosage of H_2O_2, H_2O_2/Fe^{2+} and H_2O_2/dye ratios and the reaction temperature on the decolorization efficiency and kinetic of the DB15 were studied, the operating parameters were preferred by changing one factor at one time while the other parameters were kept constant. The optimal conditions for the decolorization of DB15 were determined as pH = 4.0, $[H_2O_2] = 2.8 \times 10^{-3}$ mol/L, H_2O_2/Fe^{2+} ratio = 100:1, H_2O_2/dye ratio = 60:1 and temperature = 30 °C. Under the optimal conditions, 4.7×10^{-5} mol/L of the DB15 aqueous solution can be completely decolorized by Fenton oxidation within 50-min reaction time and the decolorization kinetic rate constant k was determined as 0.1694 min^{-1}. Additionally increasing the reaction temperature from 20 to 40 °C showed a positive effect on the decolorization efficiency of DB15. The present study can provide guidance to relational industry operators and planners to effectively treat the DB15 contaminated wastewater by Fenton oxidation process.

1. Introduction

Dyes widely used in textile dyeing, leather tanning, paper production and printing industries are important sources of environmental contamination, especially for water pollution. About half a million tonnes of azo dyes are manufactured each year all over the world and account for nearly 50% of all dyes produced, it is assumed that 1–2% dye loss in production and 1–10% loss during use are a fair estimate [1,2]. The effluent streams from textile plants are highly colored in most cases. The decolorization of this kind of wastewater becomes very important in the public water treatment plants (WWTP), not only for aesthetic reasons, but also because many dyes and their breakdown products are toxic to aquatic life and mutagenic to humans [3,4].

Azo dyes are characterized by containing one or more azo group (–N=N–) bound to an aromatic ring. It has to be emphasized that due to their complicated and steady molecular structure, they are usually difficult to remove or inefficiency to remove from water by using conventional physical, chemical and biological treatment methods [6,7]. Therefore, it is desired to look for alternative methods or techniques for the treatment of this kind of wastewater to reduce their environmental impact.

Advanced oxidation processes (AOPs), based on the generation of hydroxyl radicals ($^{\cdot}OH$) with great oxidizing potential ($E^o = 2.8$ V), can be a good option to treat this type of wastewater because of their powerful oxidizing capability to oxidize numerous organic compounds to CO_2 and H_2O. Among the various AOPs, application of Fenton's reagent is more attractive for several reasons, Fe is widely available, H_2O_2 is easy to handle and excess decomposes to environmentally safe products, additionally the simplicity of equipment and the mild operation conditions and rapid kinetics are another competitive advantages of Fenton oxidation process [8].

Basically, Fenton oxidation process is performed by reacting Fe^{2+} with H_2O_2 to generate $^{\cdot}OH$ which then degrades the organic pollutants (Org.). The oxidation mechanisms of Fenton oxidation process are shown in the following stages [9–11]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH, \quad k_1 = 76\,M^{-1}\,s^{-1} \tag{1}$$

$$\text{Org.} + {}^{\cdot}OH \rightarrow {}^{\cdot}\text{Org.} \rightarrow \ldots \rightarrow CO_2 + H_2O, \quad k_2 \approx 10^7\text{–}10^{10}\,M^{-1}\,s^{-1} \tag{2}$$

$$H_2O_2 + {}^{\cdot}OH \rightarrow H_2O + {}^{\cdot}O_2H, \quad k_3 = (1.2\text{–}4.5) \times 10^7\,M^{-1}\,s^{-1} \tag{3}$$

$$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^-, \quad k_4 = 4.3 \times 10^8\,M^{-1}\,s^{-1} \tag{4}$$

$${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2, \quad k_5 = 5.3 \times 10^9\,M^{-1}\,s^{-1} \tag{5}$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + {}^{\cdot}O_2H, \quad k_6 = 0.01\text{–}0.02\,M^{-1}\,s^{-1} \tag{6}$$

$$Fe^{3+} + {}^{\cdot}O_2H \rightarrow Fe^{2+} + H^+ + O_2, \quad k_7 = 3.1 \times 10^5\,M^{-1}\,s^{-1} \tag{7}$$

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doi:10.1016/j.cej.2009.08.027

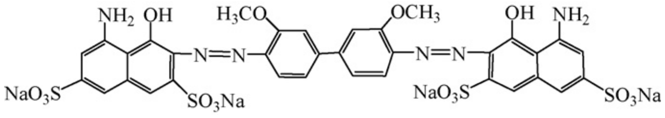

Fig. 1. Chemical structure of DB15.

Eq. (1) shows the generation of ·OH, which reacts with organic compounds (Eq. (2)). Eqs. (3)–(5) show the scavenging effect of ·OH by H_2O_2, Fe^{2+} and itself. Eqs. (6) and (7) indicate a new generation of Fe^{2+} by the reaction between H_2O_2 and Fe^{3+}, i.e. Fenton-like process [11]. During the past 20 years, the Fenton oxidative process has shown a promising applied perspective in the treatment of several kinds of azo dyes contaminated wastewaters such as Acid Orange 7, Acid Yellow 23, Orange G and Orange II [6,12–15].

In the present study, the application of Fenton oxidative process for the decolorization of an azo dye Direct Blue 15 (DB15, the molecular structure is shown in Fig. 1) in aqueous solution was investigated. Although Dong et al. [16] recently reported that DB15 could be photocatalyticly decolorized by using Fe (III)–oxalate complexes/H_2O_2 system, the decolorization of DB15 wastewater by Fenton oxidation has not been reported. Therefore, the aim of the present study is to investigate the feasibility of the decolorization of DB15 in aqueous solution by using the Fenton oxidation process. The effect of various operating parameters, including initial pH, dosage of H_2O_2, H_2O_2/Fe^{2+} and H_2O_2/dye ratios, as well as reaction temperature on the decolorization efficiency and kinetic of DB15 were systematically studied, they are performed by changing one factor at a time while the other parameters were kept constant. Hopefully, the present study can provide guidance to relational industry operators and planners for the effective treatment of DB15 contaminated wastewater.

2. Materials and methods

2.1. Reagents

Azo dye Direct Blue 15, H_2O_2 (30%, w/w), $FeSO_4·7H_2O$, H_2SO_4 and NaOH were all obtained from Shanghai Chemical Reagents Co. (Shanghai, China). All the chemicals were analytical grade and used directly without further purification. Deionized water was used throughout this study.

2.2. Experimental procedures

All experiments were carried out in a 200 mL double glass cylindrical jacket reactor (experimental set-up was the same as in the previous studies) [17]. The reactor allows cycle water to maintain the temperature of the reaction mixture constant at 30 ± 1 °C by using a thermostat. The mixing of the reaction solutions was provided by using a magnetic stirrer at a 200 rpm rotating rate. To start each test, appropriate volumes of the stock DB15 solution and ferrous sulfate solution were placed into the reactor and diluted with deionized water to 100 mL. The concentration of DB15 in the prepared aqueous solution was 4.7×10^{-5} mol/L. The initial pH of solutions was adjusted by using 1.0 mol/L sulfuric acid or 1.0 mol/L sodium hydroxide solution. During the experiment, no adverse effects for the reactions between Fenton's reagent and the DB15 by the addition of sulfuric acid or sodium hydroxide were observed. The pH value was measured by using a PHS-3C model pH meter (Dongxing Instrument Factory, Hangzhou, China). Before the experiments, the pH meter was calibrated by using standard buffers (pH 4.0, 6.86 and 9.18). Finally, the required amounts of H_2O_2 were added to the reactor and the time was recorded.

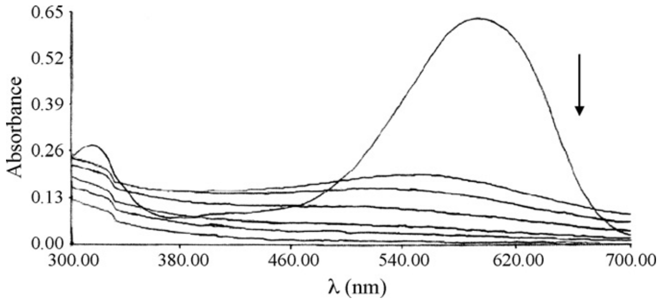

Fig. 2. UV/Vis absorbance spectra of DB15 during the decolorization process by Fenton oxidation. Experimental conditions: [DB15] = 4.7×10^{-5} mol/L; $H_2O_2 = 2.8 \times 10^{-3}$ mol/L; $Fe^{2+} = 2.8 \times 10^{-5}$ mol/L; temperature = 30 °C. Reaction time 0, 1, 2, 5, 10, 20 and 30 min.

2.3. Analytical methods

Samples were taken out from the reactor periodically using a pipette for UV/Vis spectrophotometric analysis (Lambda 17, Perkin-Elmer). The absorption spectrum of DB15 in aqueous solution was recorded and it was found that the maximum wavelength was at 597 nm and no other absorption peaks occurred nearby (Fig. 2). Therefore, the decolorization of DB15 at different reaction times was determined by measuring the absorption intensity of the solution at 597 nm. The decolorization efficiency of DB15 was defined as follows:

$$\text{Decolorization efficiency}\,(\%) = \frac{A_0 - A_t}{A_0} \times 100 \qquad (8)$$

where A_0 and A_t are the absorbency of DB15 in aqueous solution at reaction time 0 and t min, respectively.

3. Results and discussion

3.1. Effect of initial pH

The effect of initial pH on the decolorization of DB15 by Fenton process is shown in Fig. 3. The optimum pH was observed in the range of 3.0–4.0, either increasing or decreasing the pH value will cause adverse effects on the decolorization of DB15. This is because the concentrations of Fe^{2+} and H_2O_2 are affected by the solution pH conditions, correspondingly affect the yield of the active ·OH. The

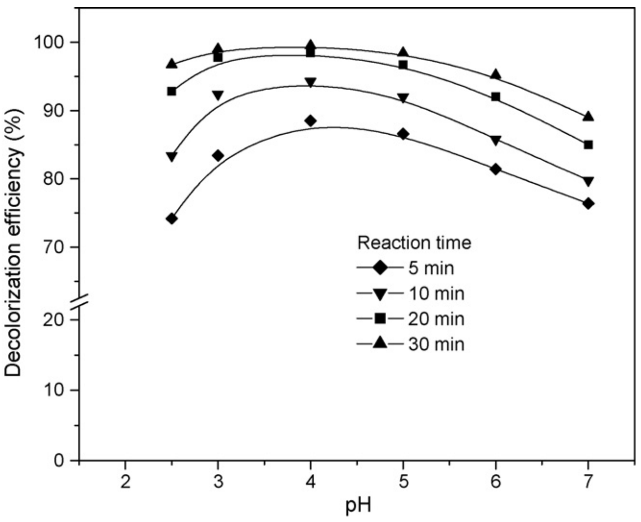

Fig. 3. Effect of initial pH on the decolorization of DB15 by Fenton oxidation. Experimental conditions: [DB15] = 4.7×10^{-5} mol/L; $H_2O_2 = 2.8 \times 10^{-3}$ mol/L; $Fe^{2+} = 2.8 \times 10^{-5}$ mol/L; temperature = 30 °C.

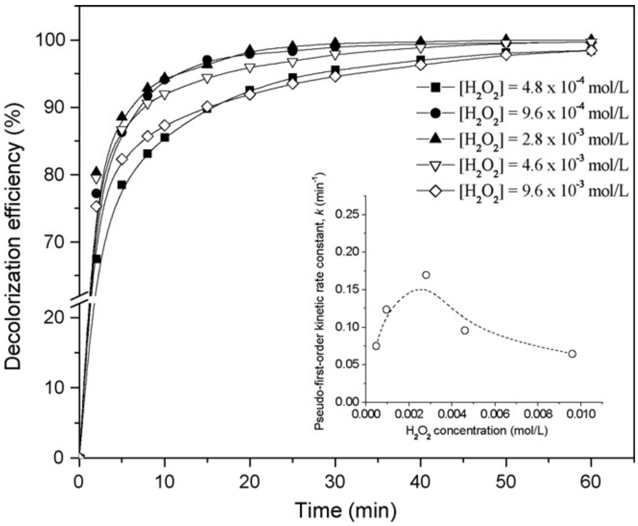

Fig. 4. Effect of initial H_2O_2 dosage on the decolorization of DB15 by Fenton oxidation. Experimental conditions: [DB15] = 4.7×10^{-5} mol/L; [Fe^{2+}] = 2.8×10^{-5} mol/L; pH = 4.0; temperature = 30 °C.

decolorization efficiency of DB15 was decreasing with the increase of pH from 4.0 to 7.0. This is mainly caused by the fact that ferrous and ferric oxyhydroxides are formed when pH is higher than 4.0, which inhibit the reaction between Fe^{2+} and H_2O_2 and only a small amount of the $^{\cdot}OH$ is generated. In addition, when the pH was lower than 3.0, the decolorization efficiency of DB15 was also decreased. This is because H_2O_2 reacts with excessive H^+ to form oxonium ion ($H_3O_2^+$), which is stable and cannot react with Fe^{2+} to form the $^{\cdot}OH$. At the same time, the $^{\cdot}OH$ can also be scavenged by excessive H^+ [18].

3.2. Effect of initial H_2O_2 dosage

Fig. 4 shows the relationship between the decolorization efficiency and kinetic rate constant *k* of DB15 and initial H_2O_2 concentrations. The results indicate that increasing initial H_2O_2 concentration from 4.8×10^{-4} and 2.8×10^{-3} mol/L had a positive effect on the decolorization of DB15, the *k* value accordingly increased from 0.0748 to 0.1694 min^{-1}. This is because of the increase of initial H_2O_2 concentration allowing an enhancement in the quantum yield of active $^{\cdot}OH$. While H_2O_2 concentration was higher than 2.8×10^{-3} mol/L, the *k* value decreased with further increasing initial dosage of H_2O_2. Theoretically H_2O_2 is the source of active $^{\cdot}OH$ generation and more $^{\cdot}OH$ should be formed at high concentration of H_2O_2, however, this does not seem likely. Indeed, this phenomenon has been widely reported by many researchers [5,10,11,15]. An explanation is that there is a critical concentration of H_2O_2 in the Fenton oxidation process, and when the concentration of H_2O_2 is beyond the critical value, the scavenging of $^{\cdot}OH$ by excessive H_2O_2 (Eq. (3)) will became more significant and cause the degradation efficiency and rate of pollutants to decrease [10,15].

3.3. Effect of different H_2O_2/Fe^{2+} ratios

The H_2O_2/Fe^{2+} ratio is an important parameter in Fenton's reactions because it directly influences the quantum yield of $^{\cdot}OH$ generation. The decolorization of DB15 under different H_2O_2/Fe^{2+} ratio conditions were studied with a constant H_2O_2 dosage of 2.8×10^{-3} mol/L, and results are shown in Fig. 5. It was observed that the suitable H_2O_2/Fe^{2+} ratio for the decolorization of DB15 was about 100:1. Increasing the H_2O_2/Fe^{2+} ratio from 29:1 to 100:1 had a positive effect on the decolorization of DB15, the *k* value correspondingly increased from 0.0303 to 0.1694 min^{-1}. At fixed H_2O_2 dosage, small H_2O_2/Fe^{2+} ratio leads to small *k* value, because although more $^{\cdot}OH$ could be generated according to Eq. (1) at relative higher concentration of Fe^{2+}, the $^{\cdot}OH$ can be scavenged by Fe^{2+} or self-scavenging reaction as Eqs. (4) and (5) [15,18]. It also can be seen that when H_2O_2/Fe^{2+} ratio is higher than 100:1, the *k* value decreases with further increasing H_2O_2/Fe^{2+} ratio, the decolorization efficiency of DB15 at 30-min reaction time decreased from 99.5% to 86.8% when the H_2O_2/Fe^{2+} ratio increased from 100:1 to 600:1. The fact that a high H_2O_2/Fe^{2+} ratio can also lead to a small *k* value and poor decolorization efficiency of DB15 is due to the relatively less Fe^{2+} reacts with H_2O_2, which result in the yield of the $^{\cdot}OH$ decreasing. At the same time, part of the $^{\cdot}OH$ is scavenged by a relative excess of H_2O_2 (Eq. (3)).

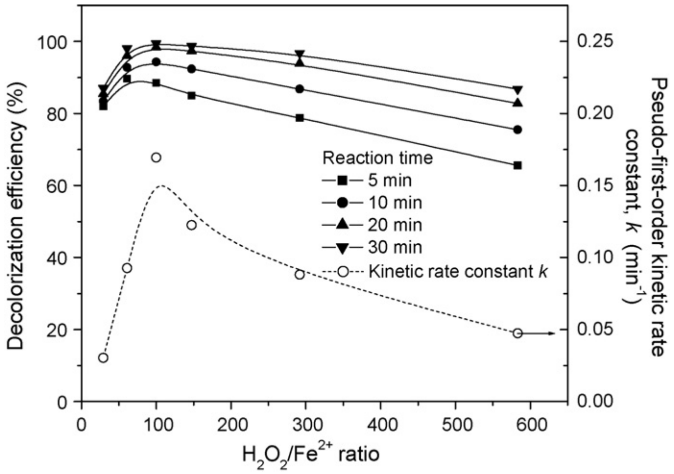

Fig. 5. Effect of H_2O_2/Fe^{2+} ratios on the decolorization of DB15 by Fenton oxidation. Experimental conditions: [DB15] = 4.7×10^{-5} mol/L; [H_2O_2] = 2.8×10^{-3} mol/L; pH = 4.0; temperature = 30 °C.

3.4. Effect of different H_2O_2/dye ratios

The effect of different H_2O_2/dye ratios on the decolorization of DB15 was also studied and results are shown in Fig. 6. It can be seen that there is an optimum H_2O_2/dye ratio for the decolorization of DB15. When H_2O_2/dye ratio is smaller than 60:1, the *k* value increases with the increase of H_2O_2/dye ratio. However, the *k* value decreases when H_2O_2/dye ratio is beyond 60:1. For instance the *k*

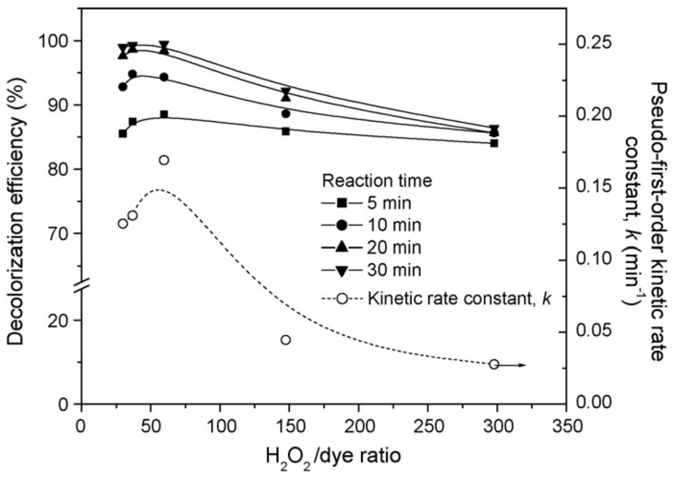

Fig. 6. Effect of H_2O_2/dye ratios on the decolorization of DB15 by Fenton oxidation. Experimental conditions: [H_2O_2] = 2.8×10^{-3} mol/L; [Fe^{2+}] = 2.8×10^{-5} mol/L; pH = 4.0; temperature = 30 °C.

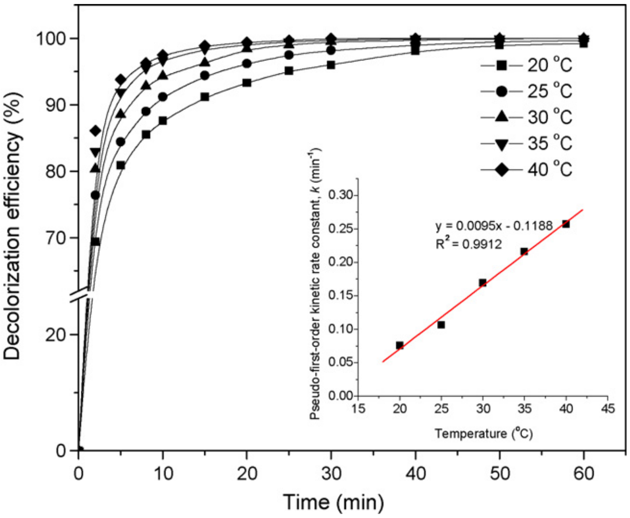

Fig. 7. Effect of temperature on the decolorization of DB15 by Fenton oxidation. Experimental conditions: [DB15] = 4.7×10^{-5} mol/L; [H_2O_2] = 2.8×10^{-3} mol/L; [Fe^{2+}] = 2.8×10^{-5} mol/L; pH = 4.0.

value was 0.0446 and 0.0276 min^{-1} with H_2O_2/dye ratio of 147:1 and 298:1, respectively. This can be explained by the competition between H_2O_2 and dyes for the $\cdot$OH, which means that there is an optimum H_2O_2/dye ratio. A smaller H_2O_2/dye ratio will result in relatively less H_2O_2 for Fenton's reactions to generate enough $\cdot$OH, but a bigger ratio can also cause the scavenging of the $\cdot$OH.

3.5. *Effect of temperature*

Several tests were performed to determine the effect of temperature on the decolorization of DB15 and the results are shown in Fig. 7. The results indicated that raising the temperature from 20 to 40 °C has a positive effect on the decolorization of DB15, the relationship between the *k* value and the temperature was observed to be linear ($R^2 > 0.99$). The decolorization efficiency and rate of DB15 increased with the raising of temperature, this is because Fenton's reactions can be accelerated at high temperature and more $\cdot$OH is formed [6]. Indeed, it is convenient for the application of Fenton oxidation process to treat DB15 contaminated wastewater since the discharged dye wastewater is normal with a high temperature.

4. Conclusion

The decolorization of DB15 in aqueous solution by Fenton oxidation process was effectively achieved. The results showed that the decolorization efficiency and rate of DB15 were significantly affected by initial pH of the solution, dosage of H_2O_2, H_2O_2/Fe^{2+} and H_2O_2/dye ratios and the reaction temperature. The optimum conditions were observed as: pH = 4.0, [H_2O_2] = 2.8×10^{-3} mol/L, H_2O_2/Fe^{2+} ratio = 100:1, H_2O_2/dye ratio = 60:1 and 30 °C reaction temperature. For the treatment of 4.7×10^{-5} mol/L of DB15 aqueous solution, 100% decolorization efficiency of DB15 was achieved within 50-min reaction time under the optimum conditions, the decolorization kinetic rate constant *k* was determined at 0.1694 min^{-1}. In addition, it was also found that increasing the temperature from 20 to 40 °C can enhance the decolorization of DB15. Overall, it can be concluded that it is feasible to treat DB15 contaminated wastewater by using Fenton oxidation process.

Acknowledgements

This work was supported by the Natural Science Research Foundation of Henan province (Grant No. 0611020900), PR China; Shanghai Tongji Gao Tingyao Environmental Science & Technology Development Foundation (STGEF); and the China Scholarship Council (CSC). The authors would like to thank Brian Merkey and Paul W. D'Alvise (Technical University of Denmark) for their helpful suggestions and comments.

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