Removal of COD and color from Direct Blue 71 azo dye wastewater by Fenton’s oxidation: Kinetic study

Nese Ertugay *, Filiz Nuran Acar

Department of Environmental Engineering, Faculty of Engineering, Ataturk University, 25240 Erzurum, Turkey

Received 8 August 2012; accepted 13 February 2013
Available online 27 February 2013

Abstract In this paper, degradation of Direct Blue 71 (DB71) by Fenton’s oxidation process was investigated. The effect of initial pH, dosages of Fe$^{2+}$ and H$_2$O$_2$, dye concentration and temperature on the color and Chemical Oxygen Demand (COD) removal was studied in a batch reactor. The optimal conditions for the decolorization and COD removal of DB71 were determined as pH = 3.0, Fe$^{2+}$ = 3 mg L$^{-1}$ and H$_2$O$_2$ = 125 mg L$^{-1}$. Under the optimal conditions 94% color and 50.7% COD removal efficiency of the dye in 100 mg L$^{-1}$ aqueous solution were achieved after 20 min of reaction. Results indicated that the removal efficiency was strongly dependent on initial pH, initial concentration of Fenton’s reagents, initial DB71 concentration and reaction temperature. Additionally increasing the reaction temperature from 20 to 60 °C showed a positive effect on the decolorization efficiency of DB71. The experimental data were analyzed using the first and second-order and Behnajady–Modirshahla–Ghanbery (BMG) kinetic models. BMG model provides the best correlation of the data. The present study can provide guidance to relational industry operators and planners to effectively treat the DB71 contaminated wastewater by Fenton’s oxidation process.

1. Introduction

Approximately 80% of all reactive dyes are based on azo chromogen (Su et al., 2011). Azo dyes are characterized by the nitrogen double bond (–N═N–) which together with other chromophores is responsible for the color (Idel-aouada et al., 2011; Ameta et al., 2012). Azo dyes are typically used in textile processing and paper manufacturing industries. A massive amount of azo dyes from these sources is discharged into natural waterways (Su et al., 2011). All these different sources of water pollution contain hazardous mixtures which come from organic and inorganic pollutants in addition to heavy metals which have adverse effects on the environment, aquatic life and human health. Earlier investigations revealed that more than 25% of the total world population suffers from health and hygienic problems related to water pollution (Soon and Hameed, 2011). Removal of dyes from industrial effluent is environment-
Dyes have obtained notoriety as hazardous substances, because most of them are toxic and considered to be resistant to biological degradation. Traditionally, the treatment of solutions containing soluble dyes is performed by biochemical and coagulation processes. All these methods are either costly, inefficient or result in the production of secondary toxic waste products. Recently, advanced oxidation processes (AOP) have received considerable attention because it is possible to degrade organic compounds and color from wastewaters (Schrank et al., 2007; Chanderia et al., 2017). Fenton process as an important AOP technology has been attracting growing interest. It is well known that \( \text{Fe}^{2+} \) ions can be produced by Fenton's reaction of \( \text{H}_2\text{O}_2 \) with \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) salts as presented in the following equations.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{H}_2\text{O} \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HO}_2 + \text{H}^+ \\
\text{Fe}^{3+} + \text{HO}_2 & \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+
\end{align*}
\]

The generated \( \cdot\text{OH} \) radical is a powerful oxidant and starts a cascade of oxidation reactions that can convert the organic matter in solution completely into water, carbon dioxide, and inorganic compounds (Han et al., 2011). By tailoring the conditions of the reaction, \( \cdot\text{OH} \) radicals which possess powerful oxidizing potential up to +2.8 V can attack a wide variety of toxic contaminants (Soon and Hamed, 2011).

The main objective of this work is to determine the influences of various parameters on the degradation of DB71 dye by the Fenton process in aqueous solution. The effect of pH, the concentration of \( \text{H}_2\text{O}_2 \), \( \text{Fe}^{2+} \) and dye and the temperature were investigated to determine the optimal operating conditions for a better performance of the degradation. COD of the mixture was determined.

### 2. Materials and methods

Solutions of DB71 dye (C\(_{40}\)H\(_{23}\)N\(_7\)Na\(_4\)O\(_{13}\)S\(_4\), Aldrich) of different concentrations were prepared in distilled water.

Then, they were homogenized by stirring until completely dissolving the dye. The pH of the reaction mixture was adjusted by adding sulfuric acid and was measured by a pH-meter (330i WTW 82362, Weilheim). The dye oxidation was achieved by Fenton’s reagent which was composed of a mixture of FeSO\(_4\).7H\(_2\)O and H\(_2\)O\(_2\) 30% (products Riedel-de Haën). The necessary quantities of Fe\(^{2+}\) and H\(_2\)O\(_2\) were added simultaneously in the dye solution. The experimental device was constituted of a perfectly agitated reactor in which a volume (500 ml) of solution was studied. The maximum absorbance wavelength (\( \lambda_{\text{max}} \)) of DB71 was found to be 587 nm. The kinetics of the oxidation was followed by taking samples at regular time intervals. The residual concentration of the dye in the solution at different times of sampling was determined by UV Visible spectroscopy. COD was determined (Merck Spectroquant TR320) by a closed reflux colorimetric method according to Standard Methods for the Examination of Water and Wastewater (APHA, 1985). The amount of H\(_2\)O\(_2\) causing enterprise in COD analysis was subtracted from the amount of COD determined by using the I\(_3^-\) method (Kang et al., 1999). The chemical structure of DB71 is shown in Fig 1 (Saien and Soleymani, 2007).

### 3. Results and discussion

#### 3.1. Effect of Fe\(^{2+}\) dosage

The \( \cdot\text{OH} \) radicals are trapped by Fe\(^{2+}\) ions in excess as shown in the reaction (4) (Bouasla et al., 2010). To see the effect of Fe\(^{2+}\) dosage in the Fenton process and to determine the most appropriate concentration of Fe\(^{2+}\), a series of experiments were conducted at different concentrations of Fe\(^{2+}\) from 0 to 5 mg L\(^{-1}\). H\(_2\)O\(_2\) concentration was 50 mg L\(^{-1}\) at an initial pH of 3.0. As shown in Fig. 2, Fe\(^{2+}\) concentration was...
Since the high level of decolorization is much easier to achieve than the high level of mineralization, the effect of process parameters on mineralization aiming to find optimal conditions was investigated (Papic et al., 2009). However, removal efficiency would decrease when H$_2$O$_2$ addition was higher than 125 mg L$^{-1}$. According to the reaction (1), the concentration of ‘OH is expected to increase with increasing H$_2$O$_2$ dosage, leading to increased oxidation rates of organic compounds. However, as mentioned above, excess H$_2$O$_2$ interferes with the measurement of COD. The residual H$_2$O$_2$ in the Fenton process can consume K$_2$Cr$_2$O$_7$, leading to the increase of inorganic COD (Kang et al., 2002). Additionally above the limiting point, ‘OH efficiently reacts with H$_2$O$_2$ and produces HO$_2$-.

$$\text{HO}_2^- \text{radicals are less reactive than ‘OH, increasing HO}_2^-\text{results in negligible contribution (Schrank et al., 2007).}$$

$$\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{HO}_2^- + \text{H}_2\text{O}$$

### 3.3. Effect of pH

The actual dye wastewater has a wide range of initial pH values, and the solution pH is an important operating parameter affecting DB71 removal efficiency in AOP. It affects directly the mechanism of oxidation dye, because a change in pH of the solution, involves a variation of the concentration of Fe$^{2+}$, and therefore the rate of production of ‘OH radicals responsible for oxidation dyes, will be restricted (Bouasla et al., 2010). The effect of pH value on the DB71 color and COD removal was assessed at five initial pH values, 2.0, 3.0, 4.0, 5.0 and 6.0. From Fig. 4, initial pH value of the solution was remarkably influenced the color and COD removal. When pH was 3.0, the color removal was 94% and the COD removal was 50.7%. The reaction rates of Fenton oxidation of the dyes are rather slow in alkaline medium while they are fast in acidic medium (Gul and Ozcan-Yildirim, 2009). In a study, the highest yield was obtained at pH 3.0 by the Fenton’s oxidation process (Kavitha and Palanivelu, 2005).

### 3.4. Effect of initial concentration of dye

Initial concentration of dyes is an important parameter in practical application. The effects of initial dye concentrations 25, 50, 75, 100, 125 and 150 mg L$^{-1}$ on color and COD re-
moval efficiencies of DB71 were evaluated at 125 mg L$^{-1}$ H$_2$O$_2$ and 3 mg L$^{-1}$ Fe$^{2+}$ at pH 3.0. As shown in Fig. 5, the color and COD removal efficiency gradually decreased with an increase in the initial concentration. This is due to non-availability of sufficient number of hydroxyl radicals. The presumed reason is that when the initial concentration of DB71 is increased, the OH concentration is not increased correspondingly. However, the higher the concentration, the more the dye decolorized in 20 min. This happens because the increase in concentration enhances the interaction between the dye and OH (Wu et al., 2010).

### 3.5. Effect of temperature

The effect of temperature at 20, 30, 40, 50 and 60 °C on DB71 degradation was investigated. It can be seen from Fig. 6 that increasing temperature had a positive effect on the DB71 degradation. The efficiency of color and COD removal of DB71 were increased from 94% to 99.0% and from 50.7% to 65.0% when the temperature increased from 20 to 60 °C, respectively. Temperature affects the reaction between H$_2$O$_2$ and Fe$^{2+}$. This can be explained by the fact that Fenton’s reaction could be accelerated by raising the temperature which improved the generation rate of OH and therefore enhancing the decolorization of DB71 (Emami et al., 2010; Sun et al., 2009).

### 3.6. Kinetic experiments

In the present study, first-order, second-order and BMG reaction kinetics were used to study the decolorization kinetics of DB71 by the Fenton oxidation process. The individual expression was presented as equations given below:
where \( C_t \) is the concentration of DB71 at any time, \( k_1 \) and \( k_2 \) represent the apparent kinetic rate constants of first-order and second-order reaction kinetics, respectively; \( t \) is the reaction time. By integrating the Eqs. (6) and (7), the following equations could be obtained Eqs. (8) and (9):

\[
\frac{dC_t}{dt} = -k_1 C_t
\]

(6)

\[
\frac{1}{C_t} = \frac{1}{C_0} + k_2 t
\]

(7)

The regression analysis based on the first and second-order reaction kinetics for the color of dye was conducted and the results are shown in Fig 7 and Table 1. As seen in Table 1, as dye concentration increases from 50 to 150 mg L\(^{-1}\), the second order model rate constants increase from 0.7904 to 0.9201 min\(^{-1}\). However, the first order model rate constants decrease from 0.1733 to 0.0757 min\(^{-1}\). The second order kinetics shows higher correlation than the first-order kinetics in the case of the Fenton reaction.

(BMG) kinetic model could be expressed as follows (Behnajady et al., 2007):

\[
C_t = \frac{C_0}{m + b}
\]

(10)

\[
\frac{t}{1 - \frac{C_t}{C_0}} = m + bt
\]

(11)

\( b \) and \( m \) are two characteristic constants relating to the reaction kinetics and oxidation capacities. By plotting \( t/(1 - C_t/C_0) \) versus \( t \), a straight line with an intercept of \( m \) and a slope of \( b \) was obtained.

The obtained parameters for DB71 are given in Table 1 and Fig 8. As it can be seen from Table 2, the values of correlation coefficient values for BMG model are mostly higher than those of the first-order and the second-order models. Generally, calculated regression coefficients (\( R^2 \)) of the BMG kinetic model were higher than 0.99. Therefore, BMG kinetic model is the best model to describe the decolorization of DB71 by the Fenton’s process (Tunc et al., 2012).

3.7. Spectral changes in the UV–vis absorption spectra of dyes during Fenton process

Typical scanning-kinetic outputs obtained during the decolorization process of 60 mg L\(^{-1}\) DB71, 1.5 mg L\(^{-1}\) Fe\(^{2+}\), 50 mg L\(^{-1}\) H\(_2\)O\(_2\), pH = 3.0 at 20 °C for 20 min are shown in Fig. 9. As seen from Fig. 9, prior to the initiation of decolorization reactions in the solution, the maximum absorption wavelengths of DB71 are at 587 nm, in the visible region. This absorption band observed due to the n→\( \pi^* \) transition corresponds to the chromophore containing azo linkage (N=N–) in the azo dyes. Benzene and naphthalene rings in the DB71 lead to the two absorption bands in the ultraviolet region located at 210 and 290 nm owing to the \( \pi^* \to \pi^* \) transition. The amount of diminution in the absorption peak located at 587 nm is much higher than those at 210 and 290 nm. These results indicate that the \( \cdot \)OH radical, produced from Fenton reagent, first attacks the azo groups of the dye molecules since the absorption energy values of the \( \pi^* \to \pi^* \) transitions are much lower than those of the \( \pi^* \to \pi^* \) transitions and opens the –N=N– bonds. In the case of DB71 decolorization process (Fig. 9), the intensity of the absorption peak in the visible
region observed at 587 nm displays a sharp decrease with increasing time, especially in the first 5 min, unlike the other peaks of DB71 in the ultraviolet region. This means that the \(-N=\text{N}\)– bonds in the DB71 molecule are destroyed more than the benzene and naphthalene rings (Tunc et al., 2012).

4. Conclusion

The treatment of a solution containing DB71 by the Fenton oxidation process has been taken into consideration in this study. The experimental results show that the initial concentration of H\(_2\)O\(_2\), Fe\(^{2+}\), DB71, the initial pH, and the temperature had great influence on the degradation of DB71 dye by the Fenton’s process. The optimal values of operating parameters during the oxidation of the DB71 dye by the Fenton’s process are Fe\(^{2+}\) = 3 mg L\(^{-1}\), H\(_2\)O\(_2\) = 125 mg L\(^{-1}\), pH = 3.0 and increasing temperature had a positive effect on the DB71 degradation. As is known, complete decolorization of the dye does not mean that the dye is completely degraded, so the degradation of DB71 in terms of COD removal was also investigated. As can be seen from the Figs, COD values decreased with optimum parameters. The initial COD of 139.9 mg L\(^{-1}\) DB71 was 68.9 mg L\(^{-1}\), after treatment by AOP. This is because the intermediate products of DB71 by AOP are difficult to oxidize, and complete oxidation may proceed in a longer time. The BMG kinetic model provided the best correlation of the used experimental data compared to the pseudo-first and second-order kinetic models. Spectral analyses have indicated that the destruction rate of the azo linkage in the azo dyes during the Fenton process is higher than that of benzene and naphthalene rings.

This process can be used to treat water discharge containing dyes such as DB71. The Fenton process is very suitable for the treatment of colored waters, very effective and less expensive than conventional processes.

References


