

Original Research

Direct Blue 71 Degradation in the Presence of ZVI and H₂O₂ Advanced Fenton Process: Determination of Optimum Conditions and Kinetics

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Abstract

This study investigated color and COD removal of azo dye Direct Blue 71 (DB71) by a Fenton-like process in zero-valent iron (Fe⁰ = ZVI). The UV-vis spectra of DB71 exhibit three main absorption bands – two in the UV region and one in the visible region. UV-vis spectra showed that the azo linkages in the molecule structure of the dyes were destroyed during the decolorization. The influence of various operational parameters such as pH, ZVI dosages, hydrogen peroxide (H₂O₂) concentrations and temperature are studied to determine the optimum conditions for color and COD removal. pH is highly effective parameter of decolorization and COD destruction in this work. However, H₂O₂ concentration and ZVI dosages were not only effective in the removal of COD for 100 mgL⁻¹ initial DB71 concentration. Therefore, the optimum ZVI:H₂O₂ ratio is based on determining the value of COD removal. Optimum conditions were accepted to be pH of 2.5, ZVI:H₂O₂ ratio 4:1 and 20°C temperature. The result indicated that 100% of decolorization efficiency was achieved within 20 min in the range of 150-400 mg/L initial DB71 concentrations by using optimal conditions. Residual COD values were 15.38, 22.35, 22.58, 27.04, 31.86 mg/L for 150, 200, 250, 300, 400 mg/L initial DB71 concentrations at the end of reaction time, respectively. Additionally, increasing the reaction temperature from 20 to 40°C negatively affected the decolorization and degradation rate DB71. The experimental kinetic data are fitted very well the Behnajady-Modirshahla-Ghanbery model for color removal of DB71 dye.

Keywords: azo dye, Direct Blue 71, Fenton-like process, zero-valent iron

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Introduction

Environmental pollution and the resulting global warming are worrying global problems. In this context, wastewater pollution and wastewater treatment is a severe environmental problem among these problems [1]. Industrial activities are responsible for hazardous waste in the environment. Industrial wastewater containing dyes is one of the most critical hazards. Colored wastewater is a serious problem, especially in the aquatic environment [2]. These waters reduce the light transmittance and prevent the aquatic flora from performing photosynthesis. In addition, some dyes cause health problems such as dermatitis, allergies, skin irritation and cancer [3, 4]. There are many different classes of dyes and azo dyes are the most significant group of synthetic dyes. Yearly, produced half of the dyes are azo group dyes. These dyes are commonly used may industries such as textile, food, cosmetics, etc. [5]. Although there are many chemicals in textile wastes, azo dyes are a major environmental problem since they are discharged as wastewater to a large extent [6]. Biodegradation of azo dyes is very difficult because of their complex structure and synthetic nature [7]. The cleavage of an azo bond ($-N=N-$) in the azo dye's chromophore leads to the decolorization of the dye solution [8, 9]. Advanced Oxidation Technologies (AOPs) have recently received rising attention for the deterioration of various resistant organic pollutants [10]. Among these technologies, the Fenton process is one of the best methods since reagent components are easy to handle and environmentally benign [11]. In the Fenton process, the $\cdot OH$ radicals from the reaction between Fe^{2+} and H_2O_2 remove resistant pollutants, and past studies have shown a certain degree of successful applications [12]. Although Fenton processes look promising, the homogeneous catalyst usually added as an iron salt cannot be retained in the degradation process. The addition of more ferrous salts is necessary to achieve complete degradation. The production of large quantities of sludge and the formation of high

concentrations of anions in the treated wastewater are among the disadvantages of the Fenton process [13]. Therefore, in recent years, ZVI has been widely used as a heterogeneous supported catalyst for Fenton and Fenton-like processes. Heterogeneous iron catalysts show similar degradation properties to homogeneous iron catalysts [9]. The heterogeneous Fenton-like process effectively avoids the production of iron sludge. ZVI is a strong reducing agent as well as cheap and easy to produce. It has already been known as effective in removing organics as dye [14, 15]. In the study of Minella et al., ZVI-Fenton was a suitable technique for the efficient degradation of ibuprofen and phenol under various operating conditions. Efficient degradation of ibuprofen was achieved with ZVI-Fenton technique in the pH range of 3-6 under various conditions of H_2O_2 concentration and ZVI loading [16]. In another study conducted with Fenton and Fenton-like processes for azo dye removal, Fenton-like process shorter reaction time and less reagent consumption, which Superior cost effectiveness in removing DR343 [14].

This study developed a Fenton-like process using heterogeneous catalyst (ZVI) was developed the oxidation reaction, including azo dye aqueous solution. The objective of this study is to investigate the efficient method to maximize both color and COD removal of DB71 with ZVI. The effects of ZVI, H_2O_2 concentrations, initial dye and COD concentrations, initial pH solution and temperature were investigated in decolorization and COD removal of DB71.

Materials and Methods

Dye

In this study, DB71, was selected for removal of dye from an aqueous solution by a Fenton-like oxidation process. Molecular weight 1029.86, C.I number 34140 and the molecular structure of DB71 is shown in Fig. 1 [17]. DB71 was obtained by Aldrich.

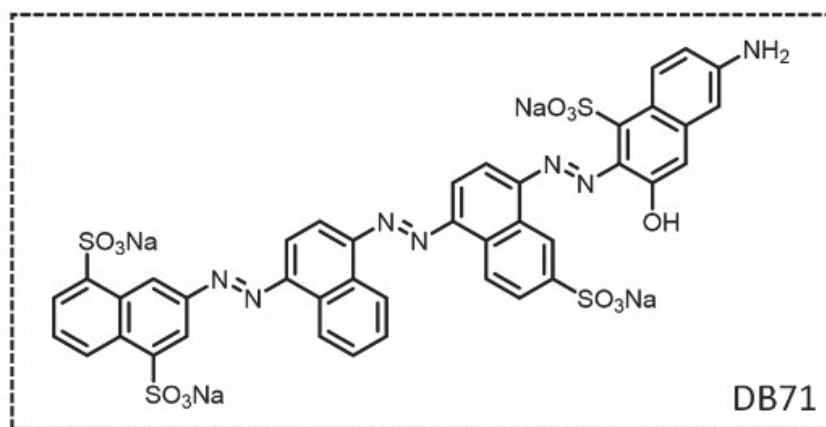


Fig. 1. Chemical structure of DB71.

The maximum absorbance wavelength (λ_{\max}) of DB71 was found to be 587 nm. The dye solutions were prepared by dissolving the desired quantity of the DB71 in deionized water.

Other Chemicals

ZVI (10 μm particle size) was obtained by Merck. H_2O_2 (30%) was supplied by Ridel-de Haen. The pH of the reaction solution was adjusted to the desired value by using H_2SO_4 and NaOH (Merck).

Analyses

After the samples were passed through a 0.45 mm membrane filter, they were analyzed spectrophotometrically. The color concentration of the solution was determined by using UV spectrophotometer (Shimadzu-160A). The chemical oxygen demand (COD) of the DB71 solution was carried out by Merck Spectroquant TR320 and was measured at 600 nm with spectrophotometer. In addition, in the COD analysis, the amount of H_2O_2 that causes the enterprise was determined by the I_3 method, and then the actual COD values were found by subtracting them from the amount of COD obtained. Finally, the color, COD and H_2O_2 of water samples were measured according to procedures described in Standart Methods.

Procedures

Fenton Like Oxidation Process in the presence of ZVI

The stock solution of DB71 was prepared in a 1000 ml flask, and a practical solution was designed from the stock solution at an appropriate concentration. Oxidation of DB71 dyestuff was achieved by Fenton-like oxidation obtained in the presence of H_2O_2 and ZVI. After obtaining the desired pH with ZVI and H_2O_2 added in order of experiments, studies were carried out in a 250 ml solution volume in a reactor whose mixing speed and temperature could be adjusted (Fig. 2).

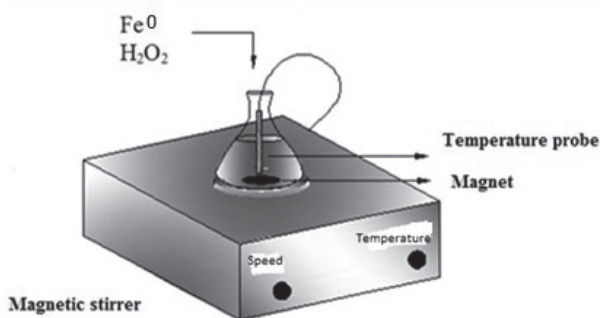
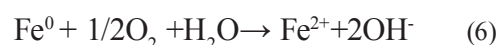
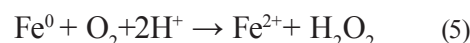
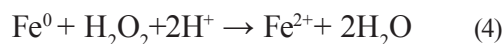
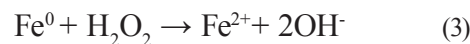
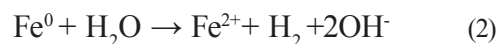
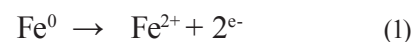


Fig. 2. Experimental setup.

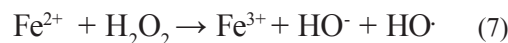
Theoretical

Mechanism

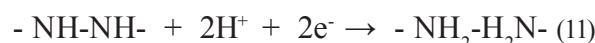
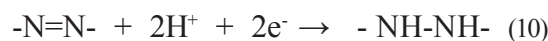
In aquatic solution metallic iron, ZVI with an $E_{\text{H}}^0 = 0.440 \text{ V}$, as a reducing agent, according to the following reaction converted to Fe^{2+} [18]:



In this reaction, as seen above, two free electrons are generated and work as reducing agents [19]. Classical homogeneous Fenton reactions continue after the first reaction [20].



The reduction of dye molecules usually accomplishes the removal of dyestuff with ZVI. The ZVI oxidation is accompanied by the decolorization of the dyestuff, which reduces and cleavages the azo bonds present in the dye [21, 22].



Kinetics

In the present study, Behnajady-Modirshahla-Ghanbery model kinetic models were used to study the decolorization kinetics of DB71 by ZVI Fenton-like oxidation process. Behnajady, Modirshahla and Ghanbary have derived a mathematical equation shown in Eq. (12):

$$\frac{C_t}{C_0} = 1 - \frac{t}{m + b} \quad (12)$$

Where C_t ; Dye concentration at time t , C_0 ; initial dye concentration, m and b are constants related to reaction kinetics and oxidation capacity, respectively. The physical meanings of m and b parameters were determined by examining the extreme cases in Eq. 12.

Accordingly, m and b terms determined by taking the derivative of the equation are given in Eq. (13).

$$\frac{dC_t/C_0}{dt} = \frac{-m}{(m+b)^2} \quad (13)$$

When t is very short or approaching zero, Eq. (14) can be written as follows:

$$\frac{dC_t/C_0}{dt} = \frac{-1}{m} \quad (14)$$

The equation expressed shows the rate of color removal of the dye during the reaction time. The $1/m$ value is directly proportional to the initial color removal rate of the dye. $1/b$ value; It expresses the maximum oxidation capacity at the end of the reaction (15):

$$\frac{1}{b} = I - \frac{C_{t \rightarrow \infty}}{C_0} \quad (15)$$

The linear forms of Behnajady–Modirshahla–Ghanbery models are given in Eq. (16) [23, 24]:

$$\frac{t}{1 - (C_t - C_0)} = m + bt \quad (16)$$

Results and Discussion

UV-vis Spectra

The absorption spectra of DB71 were scanned in the range 200–800 nm. Fig. 3 shows the UV-vis spectrum obtained for the DB71 solution at different times during the Fenton-like decolorization process in the presence of

ZVI, at pH 3.5 and 20°C. Regarding the dye spectrum, it is characterized by two bands in the ultraviolet region located at 210 nm and 290 nm and by one band in the visible region, with a maximum located at 587 nm. The absorbance peaks in the ultraviolet region are due to the benzene and naphthalene rings of DB71. The peak at 210 and 290 nm are attributed to the π - π^* transition of benzene and naphthalene ring in the DB71 molecule. The band in the visible region is due to the chromophore containing azo linkage in azo dye. In the visible band, the peak at 587 nm was attributed to the absorption of the n - π^* transition related to the $-N=N-$ group for the DB71 molecule [8]. As shown in Fig. 3, in the visible region, the characteristic absorption band at 587 nm decreased rapidly following the Fenton-like process and disappeared after 20 min.

This can be explained by the opening of $-N=N-$ bonds as a result of the attack of $\cdot OH$ radicals are produced by heterogeneous Fenton reactions on azo groups in the presence of ZVI. As seen in Fig. 3, the near-perfect disappearance of the band at 587 nm reveals that the DB71 dyestuff was eliminated by the Fenton reactions obtained in the presence of ZVI at the end of the reaction time. However, there is strong absorbance in the range of 200–400 nm, which means that some intermediates exist after the degradation of DB71 by the heterogeneous Fenton process. In the ultraviolet region, the peaks of the DB71 molecule exhibit a moderate decrease in 20 min. These results indicate that the $\cdot OH$ radical firstly attacks the azo groups on the dye molecules since the absorption energy values of the n - π^* transitions are much lower than those of the π - π^* transitions and opens the $-N=N-$ bonds. This means that the azo linkage in the DB71 molecule is more destroyed than the benzene and naphthalene rings. Similar results have been reported for absorbance reduction in ultraviolet and visible bands of DB71 by Fenton process [25], UV/TiO₂ advanced

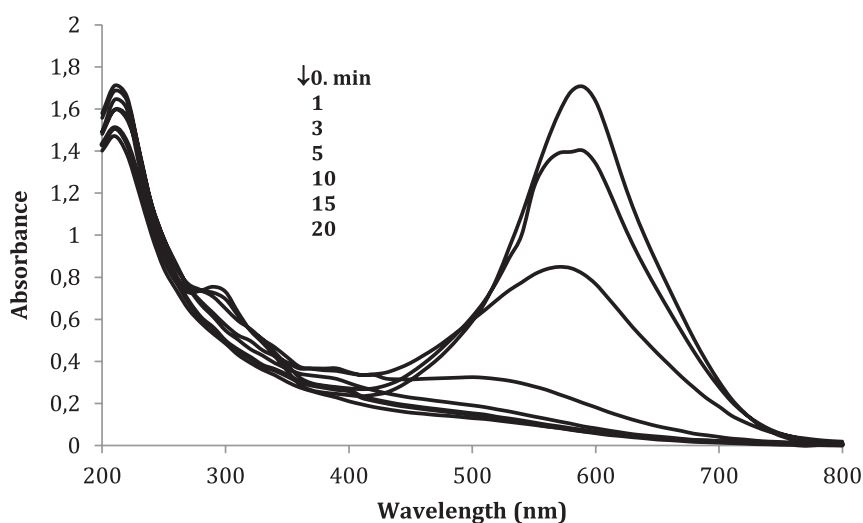


Fig. 3. UV-vis spectra changes of DB71 in the aqueous suspension at different times ($C_0 = 30 \text{ mgL}^{-1}$, $ZVI = 0.1 \text{ g L}^{-1}$, $H_2O_2 = 50 \text{ mg L}^{-1}$, $pH = 3.5$ and $T = 20^\circ\text{C}$).

oxidation process [26] and Orange II (azo dye) by Fenton oxidation using nanoscale ZVI [9].

In addition, the calculated rate constants k (min^{-1}) between 0-5 minutes and 5-20 minutes for UV and visible regions. As shown in Fig. 4a), within the first 5 minutes, the color removal rate in the visible region is much higher than the removal aromaticity rate in the UV region. The rate constants are 0.0125 min^{-1} and 0.0234 min^{-1} at 210 and 290 nm wavelengths. The constant rate value is also 0.2999 min^{-1} at 587 nm in the visible region. These results indicated that decolorization was very fast in the first minutes. Between 5-and 20 minutes, rate constants in both visible and UV regions are lower than the first 5 minutes of each period.

The results of absorbance reduction efficiency for 0-5 min and 0-20 min at different periods are presented in Fig. 4b). Absorbance reduction efficiencies were 2.919%, 16.556%, and 88.159% at 210 nm, 290 nm, and 587 nm at first 5 minutes. At the end of the 20 min, absorbance reduction efficiencies slightly increased in both UV and visible regions. These efficiency values were 10.523%, 29.536% at 210 and 290 nm wavelengths in UV region, respectively. In the visible region, reduction was 96.014% at 587 nm. According to this study, the ZVI-Fenton-like process effectively decolorizes DB71 azo dye in experimental conditions.

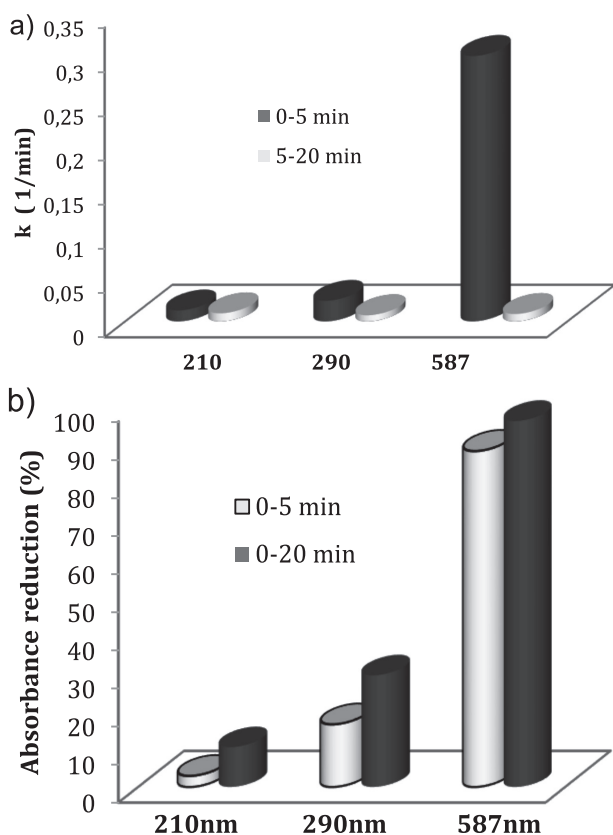


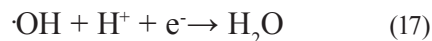
Fig. 4. a) Absorbance reduction rate constant values (k , min^{-1}) at different peaks (210, 290, 587 nm) and time (0-5 min and 5-20 min in the range), b) Reduction of absorbance (%) 0-5 min and 0-20 min in the range.

Effect of Initial pH Solution on Color and COD Removal

The fact that Fenton processes take place in a narrow pH range is considered a disadvantage, so in recent years, different catalyst development studies have been focused on overcoming this [27, 28]. In addition, since the pH value affects the properties of the catalyst, the formation of different iron derivatives in the aqueous solution at different pH values is an important parameter for the OH radicals that are expected to be formed by Fenton and Fenton-like reactions. Also, the color removal rate is faster in acidic environments [29, 30].

With more H^+ in the solution, the reaction occurred more quickly and the reaction constant was high [30].

On the other hand, the scavenging effect of the $\cdot\text{OH}$ radical by H^+ is limited.



For this reason, the Fenton oxidation efficiency declines at higher pH. Since the oxidation product Fe^{3+} easily precipitates in $\text{Fe}(\text{OH})_3$, which will decompose the H_2O_2 to oxygen, Fenton reactions are always conducted at pH 3.0 or even lower [30, 31]. In this study, Fenton-like experiments performed pH values between 2.0-6.0 (2.0, 2.5, 3.0, 4.0, 5.0 and 6.0), H_2O_2 (100 mgL^{-1}) and ZVI (0.2 gL^{-1}) dosages within 20 min. Fig. 5 shows the pH effect on efficiency color and COD removal by Fenton-like system at different pH. The results given indicated that pH has been effective in the Fenton-like process. ZVI process was more effective in decolorizing and COD removal of DB71 under acidic conditions. The results indicate that the decolorization efficiency of DB71 dye at the same dose of H_2O_2 and ZVI dosage under both acidic and weak acidic conditions were very similar and appear to be independent of the initial pH.

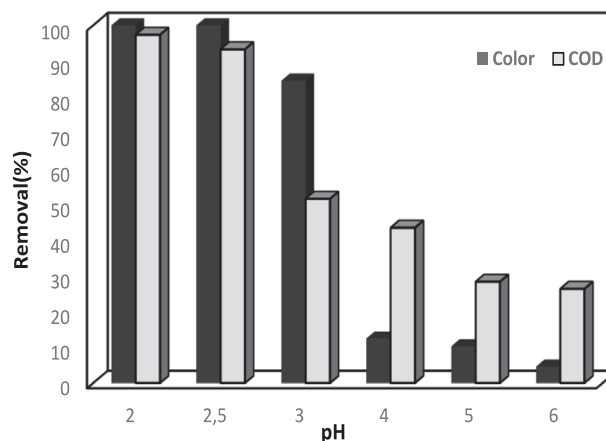


Fig. 5. Effect of pH on color and COD removal by Fenton-like process ($C_0 = 100 \text{ mgL}^{-1}$, $\text{COD}_0 = 139.9 \text{ mgL}^{-1}$, $\text{Fe}^0 = 0.2 \text{ gL}^{-1}$, $\text{H}_2\text{O}_2 = 100 \text{ mgL}^{-1}$, temperature = 20°C , contact time = 20 min).

When the initial pH values were 2.0, 2.5, 3.0, 4.0, 5.0 and 6.0, the decolorization efficiencies of DB71 were approximately 100, 100, 85, 13, 10 and 5% respectively, after a reaction of 20 min in the Fenton like process. Similarly, when the initial pH increased, the removal of COD decreased. For example, when initial pH were 2.0, 2.5, 3.0, 4.0, 5.0 and 6.0, the COD removal efficiencies were approximately 97, 93, 52, 44, 29 and 26 %, respectively, at the same time. The results of this study indicate that the efficiency of decolorization of the DB71 azo dye and COD removal by ZVI Fenton-like oxidation increased with a decrease in the system pH. Since hydroxyl radicals are generated efficiently under acidic conditions. Surface of ZVI at low pH is prone to higher degree of oxidation than at higher pH [32]. Elmorsi et. al. 2010 and Moon et. al. 2011 have observed similar results for the decolorization of Mordant Red 73 and Orange II azo dyes from aqueous solution using ZVI Fenton processes and photo-Fenton process, respectively [9, 31]. In this study, COD and color removal results obtained show that the optimum pH 2.5 for DB71 azo dye with Fenton-like process. Therefore, pH 2.5 was chosen as the initial solution pH for further experiments.

Effect of ZVI Dosage for Color and COD Removal

Besides having an excellent catalytic effect in the oxidation steps of AOP, ZVI is also used as a reducing agent in groundwater remediation studies [33-35]. Iron powder can be used as a catalyst instead of iron salt in the Fenton oxidation process. To explain the effect of Fe⁰ dosage on the decolorization and COD removal of DB71 by heterogeneous Fenton like oxidation, experiments were run with different ZVI dosages in Fig 6. The effect of ZVI dosage was investigated by adding different weights of iron powder (0.1, 0.2, 0.3 and 0.4 g/L) into 250 ml dye solution for color and COD removal, respectively. ZVI in acidic media results in an increase of Fe (II) concentration that accelerates

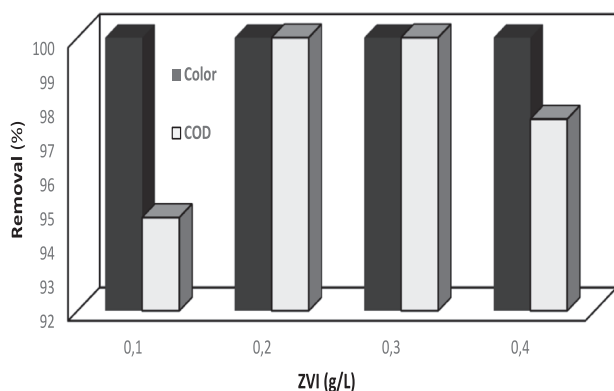


Fig. 6. Effect of ZVI mass on color and COD removal ($C_0 = 100 \text{ mgL}^{-1}$, $\text{COD}_0 = 139.9 \text{ mgL}^{-1}$, $\text{pH} = 2.5$, Contact time = 20 min., temperature = 20°C, $\text{H}_2\text{O}_2 = 50 \text{ mgL}^{-1}$).

the production of $\cdot\text{OH}$ through Eq. (1-6) and ZVI is dissolved and releases ferrous iron from the surface of ZVI powder under acidic conditions [36]. According to this study, ZVI is very effective material in the removal of DB71 dye [37]. After 20 min, all iron dosage of 100 % of color removal efficiency was obtained. The situation is similar to the removal of COD. The highest COD removal was 100% at 0.2 and 0.3 g/L ZVI dosages. However, the COD removal efficiency decreased slightly at 0.4 g/L iron dosage and this efficiency value is 97.62% and was also 94.74% at 0.1 g/L iron dosage. As a result of this study, 0.2 g/L of the appropriate dosage is determined by color and COD removal of DB71 azo dye.

Effect of H_2O_2 Concentration for Color and COD Removal

Initial H_2O_2 dosage is very important for Fenton and Fenton, like the oxidation process. In this experiment, initial H_2O_2 concentrations were selected from 15 to 150 mg/L concentration. In studies of removal of DB71 dyestuff with Fenton-like oxidation, it is important to use H_2O_2 in an appropriate amount in terms of both cost and harmful effects. According to the experimental results, the optimal dosage of H_2O_2 was 50 mgL^{-1} , in which 100% dye could be removed in 20 min. With the further increase of H_2O_2 concentration, COD removal efficiency was decreased. Fig. 7. shows the effect of initial H_2O_2 concentration on decolorization and COD removal efficiencies during Fenton-like system. According to Fig.7., decolorization efficiencies for all H_2O_2 concentrations are 100%. The effect of increasing H_2O_2 concentration from 15 to 50 mg/L was positive for COD removal of DB71. The reason for this is due to the increase in oxidation power thanks to the $\cdot\text{OH}$ radicals increase with the increase of H_2O_2 concentration. In other words, the increase in degradation efficiency depends on an increase in the production $\text{OH}\cdot$ radical [38].

However, it should be pointed out that when the concentration of H_2O_2 was over 50 mg/L, the COD removal of DB71 decreased. For example, COD removal efficiencies were 89.01 and 87.88% at 75 and 150 mg/L H_2O_2 concentrations, respectively. This can be explained by the reduction in the number of $\text{OH}\cdot$ radicals, which means that at higher H_2O_2 concentrations $\cdot\text{OH}$ radicals are scavenged. (Eq.18-20) [39-42].



The very reactive $\cdot\text{OH}$ radical could be consumed by H_2O_2 and results in the generation of less reactive $\text{HO}_2\cdot$ radical. Hydroperoxyl radicals ($\text{HO}_2\cdot$) are generated

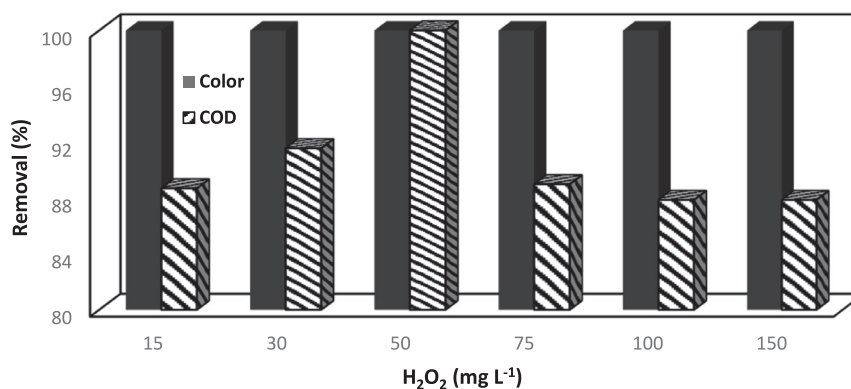


Fig. 7. Effect of H₂O₂ concentration on color and COD removal ($C_0 = 100 \text{ mgL}^{-1}$, $COD_0 = 139.9 \text{ mgL}^{-1}$, $\text{pH} = 2.5$, contact time = 20 min, temperature = 20°C, $ZVI = 0.2 \text{ gL}^{-1}$).

in the presence of excess H₂O₂. HO₂ radical promotes the radical chain reactions, but its oxidation potential is much lower than that of OH⁻ [13]. Hence, the optimum dosage 50 mg/L was adopted for this study.

In fact, the ZVI:H₂O₂ ratio is also important to determine for Fenton-like oxidation process, since this ratio can affect the production of ·OH radical in this system. The dosage of ZVI and H₂O₂ concentration studies indicated that, the decolorization and degradation of DB71 dye, in particular for the removal of COD, can be effectively achieved at a ZVI:H₂O₂ ratio 4:1 in optimum conditions. By obtaining the optimum concentration, the Fenton process is improved. In this way, the balance between the process and the consumed OH radicals is also ensured [16].

Effect of Temperature for Color and COD Removal

The Fenton-like DB71 aqueous solution in the presence of ZVI- H₂O₂ was carried out under different temperatures for $C_0 = 500 \text{ mgL}^{-1}$ ($COD = 593.2 \text{ mgL}^{-1}$) in Fig. 8. and Fig. 9. It was that DB71 decolorization and COD removal efficiency increased with increasing contact time. But, at the final contact time, color and

COD removal decreased at 20°C compared with that at 30°C and 40°C. The decolorization and COD removal efficiencies decrease by about 40.88 and 71.46% respectively, when the temperature rises from 20°C to 40°C at 20 min. As seen from Fig. 7 and 8, optimum temperature is 20 °C at which 98.04% color and 88.19% COD removal were obtained for 500 mgL⁻¹ ($COD = 593.2 \text{ mgL}^{-1}$) of DB71 concentration. The minimum color (57.16%) and COD removal (16.73%) for 500 mgL⁻¹ ($COD = 593.2 \text{ mgL}^{-1}$) of DB71 were also obtained at 40°C. The increase of iron ions, which scavenge OH radicals during Fenton reactions, negatively affected color and COD removal [43-45].

Effect of Initial Dye Concentration for Color and COD Removal

The effect of initial dye concentration on Fenton-like the process was observed since pollutant concentration is an important parameter in decolorization. The influence of the initial DB71 concentration is shown in Fig. 10. Decolorization efficiency of all concentrations is 100% at the end of 20 min. However, as the dye concentration increased, the color removal speed decreased. For example, the increase of DB71 concentration from 250

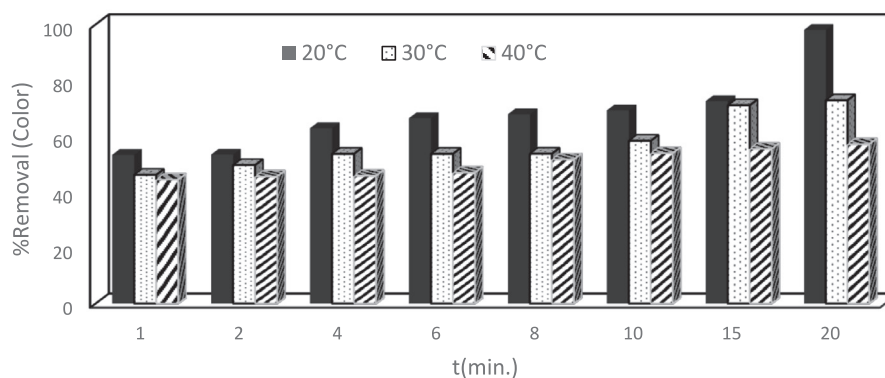


Fig. 8. Effect of the temperature on color removal by Fenton-like process (Dye solution = 500 mgL⁻¹ ZVI = 0.2 gL⁻¹, H₂O₂ = 50 mgL⁻¹, $\text{pH} = 2.5$, $COD_0 = 593.2 \text{ mgL}^{-1}$).

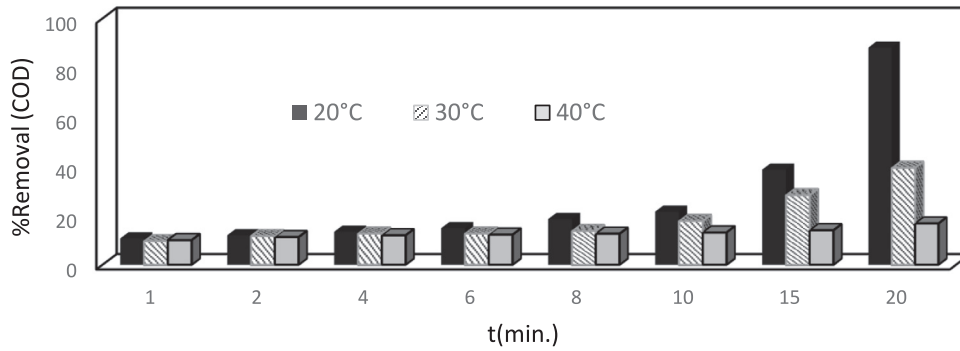


Fig. 9. Effect of temperature on COD removal by Fenton-like process ($C_0 = 500 \text{ mgL}^{-1}$, $ZVI = 0.2 \text{ gL}^{-1}$, $H_2O_2 = 50 \text{ mgL}^{-1}$, $pH = 2.5$, $COD_0 = 593.2 \text{ mgL}^{-1}$).

to 400 mg/L decreased the decolorization from 100 to 69% at 10 min. A higher concentration increases the number of dye molecules, reducing the removal efficiency [28].

Fig. 11 shows the residual COD concentration of DB71 with process. Initial dye concentration of DB71 increased from 100 to 400 mg/L, while residual COD concentration increased. The value of COD declined

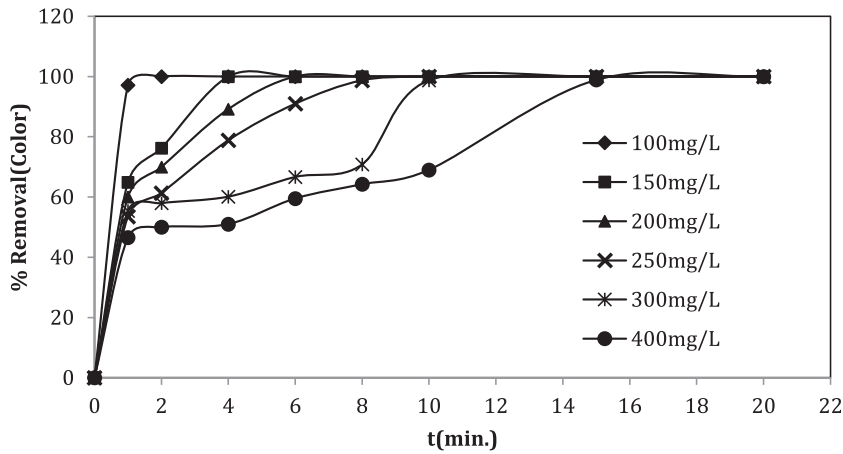


Fig. 10. Effect of the initial concentration of dye on color removal by Fenton-like process ($ZVI = 0.2 \text{ gL}^{-1}$, $H_2O_2 = 50 \text{ mgL}^{-1}$, $pH = 2.5$, $T = 20^\circ\text{C}$).

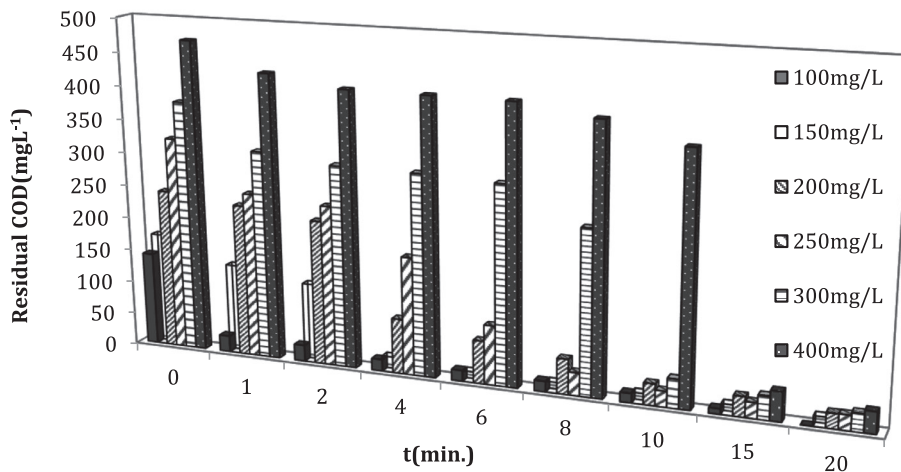


Fig. 11. Effect of the initial concentration of dye on COD removal by Fenton-like process ($ZVI = 0.2 \text{ gL}^{-1}$, $H_2O_2 = 50 \text{ mgL}^{-1}$, $pH = 2.5$, $T = 20^\circ\text{C}$). ($COD_{100} = 139.95$; $COD_{150} = 175.69$; $COD_{200} = 240.01$; $COD_{250} = 321.17$; $COD_{300} = 377.43 \text{ mgL}^{-1}$; $COD_{400} = 469.4 \text{ mgL}^{-1}$).

Table 1. The parameters of Behnajady–Modirshahla–Ghanbery kinetic models and correlation coefficients (R^2) for the decolorization of DB71 at different initial dye concentrations ($Fe^0 = 0.2 \text{ gL}^{-1}$, $H_2O_2 = 50 \text{ mgL}^{-1}$, $pH = 2.5$, $T = 20^\circ\text{C}$).

$C_0(\text{mg/L})$	$m \text{ (min)}$	$1/m \text{ (min}^{-1}\text{)}$	b	R^2
100	0.0096	104.1666	0,9930	1
150	0.3599	2.7785	0,9740	0,9989
200	0.5880	1.7007	0,9593	0,9985
250	1.0396	0.9619	0,9332	0,9976
300	2.4997	0.4000	0,8821	0,9477
400	3.5764	0.2796	0,8724	0,9164

from 139.95 to 0 mg/L (100% efficiency) for 100 mg/L initial dye concentration at the contact time. Residual COD values were 15.38, 22.35, 22.58, 27.04, 31.86 mg/L for 150, 200, 250, 300, 400 mg/L initial DB71 concentrations, respectively.

Decolorization Kinetics

Behnajady–Modirshahla–Ghanbery kinetic model has been used to test the fitting of experimental data points obtained from the decolorization processes [46, 47]. The obtained parameters for DB71 are given in Table 1. The correlation coefficient results with very high R^2 ranging from 0,9164 to 1.00 were observed, indicating that the DB71 decay kinetics was well described by the suggested model in Eq. (12). According to Eq. (12), by plotting $t/(1-C/C_0)$ versus t , a straight line with an intercept of m and a slope of b was obtained and the results are listed in Tables 1. A higher value of $1/m$ indicates faster degradation of the dyestuff. Behnajady–Modirshahla–Ghanbery kinetic model has been applied successfully to describe the decolorization kinetics DB71 azo dye.

To quantify these two constants, it was found that m and b can be correlated to the DB71 initial concentration, and the results are shown in Figs 12 and 13, where the correlations can be formulated in the following equations:

$$\log(1/b) = A \log(1/b) \log(C_0) + B \log(1/b) \quad (17)$$

$$\log(1/m) = A \log(1/m) \log(C_0) + B \log(1/m) \quad (18)$$

where A is slope and B is the intercept of each equation.

From these plots, it can be seen that the results obtained from the model were in agreement with experimental data because the correlation coefficients were 0.8962 and 0.8669 for maximum oxidation capacity ($1/b$) and initial decay ($1/m$), respectively. As seen from Fig. 12, as the concentration of DB71 was increased, the $1/b$ value increased logarithmically. In Fig. 13, when the concentration of DB71 was increased, initial decay values decreased in this study. According to the results obtained from plots, the equations can be written as:

$$\log(1/b) = 0.1016 \log(1/b) \log(C_0) - 0.2070 \log(1/b) \quad (19)$$

$$\log(1/m) = -4.0191 \log(1/m) \log(C_0) + 9.5995 \log(1/m) \quad (20)$$

Similar results are also available in previous studies [25, 46].

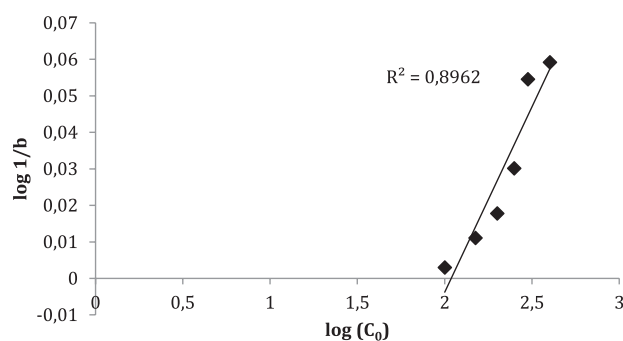


Fig. 12. Correlations of DB71 concentrations with maximum oxidation capacity ($1/b$) ($Fe^0 = 0.2 \text{ gL}^{-1}$, $H_2O_2 = 50 \text{ mgL}^{-1}$, $pH = 2.5$, $T = 20^\circ\text{C}$, $C_0 = 100, 150, 200, 250, 300, 400 \text{ mgL}^{-1}$).

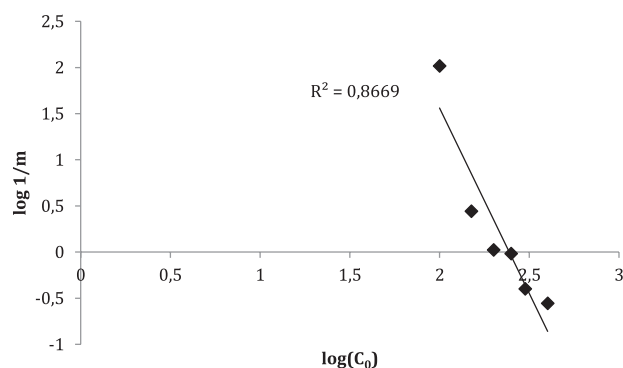


Fig. 13. Correlations of DB71 concentrations with initial decay ($1/m$) ($Fe^0 = 0.2 \text{ gL}^{-1}$, $H_2O_2 = 50 \text{ mgL}^{-1}$, $pH = 2.5$, $T = 20^\circ\text{C}$, $C_0 = 100, 150, 200, 250, 300, 400 \text{ mgL}^{-1}$).

Conclusion

Increasing environmental pollution, especially due to the decrease in water resources and deterioration of water quality, is one of the issues that should be emphasized. For this, the waste must be removed entirely. Therefore, all organizations responsible for textile industry wastewater must have sufficient awareness and are supervised by the management. Thanks to its various advantages in the treatment of this type of wastewater, AOP is one of the technologies that has been widely used recently. The Fenton-like process is among these technologies. As a result of the evaluation of the results obtained from this study, Fenton-like oxidation in the presence of ZVI was found to be a suitable method for color and COD removal of DB71 dyestuffs. The characteristic absorption band at 587 nm decreased rapidly after Fenton-like treatment and disappeared after 20 min in the visible region. As a result of these results, it was understood that the color and COD could be removed with the ZVI Fenton-like process.

The pH value, which has proven to be very effective in Fenton reactions, was also very related to our study in terms of both color and COD removal. A sharp decrease in removal efficiencies was observed at pH>3.0 in pH trials performed between 2.0-6.0. At pH 2.0, 2.5 and 3.0, the removal efficiency increased, and the highest efficiency in both color and COD removal was obtained at pH 2.5. The optimum pH value was accepted to be 2.5 for the degradation of DB71 in the examined pH values. While 100% efficiency was obtained in color removal in all trials in which the effect of ZVI and H₂O₂ were examined, the increase in ZVI and H₂O₂ decreased the COD removal after a certain value. In all the trials where the effect of ZVI and H₂O₂ were examined, 100% efficiency was obtained in color removal, while the increase in ZVI and H₂O₂ decreased the COD removal after a certain value. Accordingly, the optimum ZVI and H₂O₂ values were preferred as 0.2 mg/L and 50 mg/L, respectively.

DB71 decolorization and COD removal efficiency increased with increasing contact time. But, at the final contact time, color and COD removal decreased at 20 °C compared with that at 30°C and 40°C. While examining the effect of dye concentration, the color removal efficiency is 100% at the end of the 20th minute at all selected concentrations. However, as the dye concentration increased, the color removal rate decreased. For example, while the dye concentration was 100% at 250 mg/L at 10 minutes, it decreased to 69% at 400 mg/L due to the number of dye molecules. The experimental kinetic data in the different reaction conditions are represented well by Behnjady-Modirshahla-Ghanbery model.

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Conflict of Interest

The authors declare no conflict of interest.

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