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Decolorization and Degradation of Basic Blue 3 and Disperse Blue 56 Dyes Using Fenton Process

Elham Keshmirizadeh[*], **Mina Farajikhajehghiasi**
Department of Chemistry, Islamic Azad University, Karaj Branch, Iran
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Abstract

In this study, oxidative discoloration of Basic blue3 (B.B3) and Disperse blue56 (D.B56) dyes in synthetic textile wastewater has been studied using Fenton (Fe^{2+}/H_2O_2) process. The Fenton's technique showed satisfactory color removal efficiency. The operating parameters such as concentration of Fe^{2+}, dose of H_2O_2, initial concentration of dye, time contact, initial volume of wastewater that affected of discoloration in Fenton'sprocess were investigated. The optimized condition was determined and it was found that the obtained efficiency was about 99%for B.B3 and D.B56 dyes after 2 to 40 min ofcontact time based on initial concentration of dye for a given initial $pH_i=3$. Chemical oxygen demand (COD)removal indicates partial and significant mineralization and degradation of two dyes B.B3 (88%) and D.B56(72%).The results of experiments showed that degradation of B.B3 and D.B56 in Fenton oxidation can be described with a pseudo-first-order kinetic model.

Keywords: *Basic Blue3, Disperse Blue56, Operating parameters, Fenton, COD.*

Introduction

Wastewaters from textile and dye industries are highly colored. These wastewaters are a large problem for conventional treatment plants in the entire world[1]. The dischargeof dye wastewaters into aqueous bodies adversely affect aquatic environmental by reducing light penetration and photosynthesis [2]. According to chakrabarti et al.[3], nearly40,000 dyes and pigments are listed which consist of over 7000 different chemical structures[4]. For environmental protection, there are a number of methods (chemical, physical, and biological) for treating discolored dye effluents from various industries [5]. Several physico- chemical methods are being used like chemical precipitation [6], adsorption by active carbon[7], natural absorbents,

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[*] ***Corresponding author:*** *Dr. Elham Keshmirizadeh, Assistant Prof., Department of Applied Chemistry, Karaj Branch, Islamic Azad University, POBOX: 31485-313, Karaj–Iran. Email: ekeshmirizadeh@yahoo.com, Tel: 026-34182305, Fax: 026-34418156.*

polycatalytic oxidation[8], ozonation, and Advanced oxidation processes (AOPs such as Fenton'soxidation [9]).

AOPS has been reported successfully degrades organic pollutant into environmental friendly products [10]. The basic principle of AOPS is based on the generation of reactive radical species such as hydroxyl radicals,OH• that oxidize organic pollutant non- selectively and quickly.Finally, Fenton's reagent has been demonstrable effectively in decolorizing both soluble and insoluble dyes [11].

The Fenton reaction reacts ferrous salts with H_2O_2 to produceOH• as shown in:

Eqs.(1-3)[12]:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + OH\bullet + H_2O \quad (1)$$

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

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

The pH of the solution, amount of ferrous ions, concentration of H_2O_2 , initial concentration of the pollutant and presence of other ions considerably effects the Fenton process[13-14]. This effective technology of wastewater purification leading to complete mineralization of organic pollutants in water and wastewater by generating highly reactive Hydroxyl radical (OH•) inthe system, which is remarkably unstable but provided with very high oxidative potential of 2.8 E_0 (V) ascompare to any other oxidant except Fluorine.

The oxidation reaction of B.B3 by hydroxyl radicals can be written as follow (Eq.4), [15]:

$$C_{20}H_{22}N_3O + 91OH\bullet + 3H^+ \rightarrow 20CO_2 + 3NH_4^+ + 52\,H_2O \quad (4)$$

The main objective of this study is to analyze the feasibility of decolorization and mineralization (removal of COD) of B.B3 and D.B56 dyes by Fenton processes. The influences of different operational parameters (Fe^{2+} concentration, dose of H_2O_2, B.B3 and D.B56 initial concentration, Volume of wastewater, Time contact) which affect the efficiency of Fenton reaction have been investigated. The kinetic or thermodynamic parameter of the process was determined.

In the advanced oxidation process, Fenton's reagent wastried for oxidation of pollutants using jar test apparatus. Fenton's oxidation process was carried out at ambient temperature and pressure, as reveals that, thermodynamically this process is exothermic in nature hence, high temperaturehave negative impact on H_2O_2 stability, which favored the maximum removal of organics.

The advantage of the Fenton reagent is that no energy input is necessary to activate hydrogen peroxide.Therefore, this method offers a cost-effective source of hydroxyl radicals, using easy- to- handle reagents [16].

The advantage of classic Fenton processes besides having a powerful oxidative capacity is that they neither transfer pollutants from one phase to the other nor produce massive amounts of hazardous sludge [17]. Although standalone coagulation process can remove the color content, however, it is not efficient enough to remove

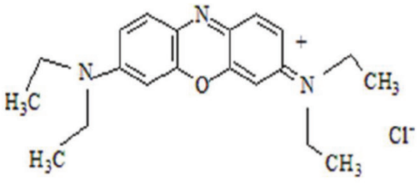
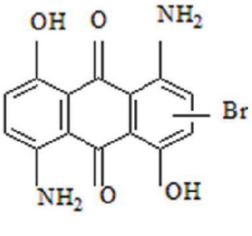
COD to meet the enviromentalregulation. On the othr side, standalone advanced oxidation process is very efficient in the removal of COD, but it has the limitation of the amount of oxidation reagent such ashydrogen peroxide. This is due to the enviromental and health constraints on the dosage of hydrogen peroxide, which represents a limitation towards a practical use of this approach[18].

Experimental

Materials

Ferrous sulfate ($FeSO_4.7H_2O$) and %30 hydrogen peroxide (H_2O_2) were purchased from Sigma Aldrich. Other chemicals used in the experimental were all of analytical grade.Basic Blue3 and Disperse Blue56were purchased from Alvan-sabet-rang Company (Iran). All dyes were used without further purification.A stock solution of each dye (500 mg/L) was prepared and suitably diluted in deionized water to the required initial concentration.The structures of two dyes used in the study are shown in Table1.

Table1. Structure and characterization of B.B3 and D.B56.

Name	Formula	Structure	M_W	λ_{max}(nm)
Basic Blue3 (B.B3)	$C_{20}H_{26}ClN_3O$		359.89	654
Disperse Blue56(D.B56)	$C_{15}H_{13}BrN_2O_4$		365.18	550

Fenton Experiment

The experiments were performed in the following manner: firstly, the appropriate $FeSO_4$ dosage (2-20 mg/ L as Fe^{2+}) was added to the model dye solution from10 to 500 mg/L, which was followed by pHadjustment to the desired value (3-9) and the addition of the required amount of H_2O_2 (30–100mM). Each experiment lasted 60 min.The experiments were carried out at $pH_{optimum}$ =3.0.

The mineralization and degradation were conducted at temperature of 20°C and atmospheric pressure in a 100 mL batch reactor. The synthetic wastewater's initial pH was adjusted using NaOH (0.2 M) or H_2SO_4 (0.2 M). A fixed concentration of Fe^{2+} was transferred to the reactor. To initiate the reaction, H_2O_2 was introduced underconstant stirring at 200 rpm (to homogenize the mixture). Then, 10 mL of the sample was periodically withdrawn at predetermined timeinterval to follow the extent of mineralization and degradation with time. Thereafter, the reaction was terminated by spiking the samplewith NaOH (1M), which adjusted the pH to 8.5 ± 0.3 in order to prevent further generation of hydroxyl radicals. This consequently resulted in precipitating iron as $Fe(OH)_3$ which would then befiltered using 0.45μm filter and subsequently analyzed for the COD (chemical oxygen demand) and UV-Vis spectra. The batch reactions were duplicated and the resultsobtained suggested reproducibility within an error range of 3%.

Analytical Methods

The chemical oxygen demand (COD) was determined in the liquid phase of the sampled aliquots bythe closed reflux method and oxidative combustion, respectively. For the COD, Hach method number 8000 was adopted where sampleswere added to Hach vials containing potassium dichromate solution in an acid medium and digested in a HACH DR/200 reactor for 120min. This action reduces the dichromate ions to chromic ions and subsequently the COD is read from absorbance measurements in aHACH DR/890 colorimeter accordingto the standard methods for examining water and wastewater [19]. The interferences of H_2O_2 with COD measurements were eliminated by destroying residual H_2O_2 in thetreated solution through catalyst addition after the pH adjustment.

This work attempts to treat wastewater of one synthetic dyes by using low concentration of iron ions (<10 mg/L) to decolorize the wastewater, the maximum limit total iron in effluent is 10 mg/L [20].

The % removal of dye was used in the study, which is defined as follows:

$$\% \text{ Removal of dye} = ((C_{dye,0} - C_{dye,t})/C_{dye,0}) \times 100 \quad (5)$$

Where $C_{dye,t}$ and $C_{dye,0}$ are the concentration of dye at λ_{max} at reaction time tand 0, respectively.

The UV- VIS spectra of the dyes were recorded from 200 to 800 nm using a UV- VIS spectrophotometer (Model:UV- IKON922). The maximum absorbance wavelength (λ_{max}) of B.B3 is 654 nm and D.B56 is 550 nm from the spectra. Therefore, the concentration of dyes in water was determined by the absorption intensity at λ_{max}. All measurements are based on standard method [19].

Results and discussion

Effect of important operating parameters:

Effect of pHi

The initial pH has a major effect on the efficiency of Fenton's treatment. Figure 1 illustrates the % removal of B.B3 dye at which solution pH is systematically varied. Concentration of 50mg/L of dye was used because it corresponded to the level of pollution found in strongly colored polluted waters located close to textile manufacturing sites. When dye is treated withFenton's reagent, it may be that the reactant H_2O_2 added might not be sufficiently utilized. At alkaline pH, H_2O_2 is unstable and loses its oxidizing potential [21]. The reaction was done and equilibrated for 2min under controlled pH condition with concentration of Fe^{2+} (8mg/L), dose of H_2O_2 (1.5g/L). The pH of this study focuses on the range 3-5. The optimum pHi was observed at a pHi about 3 for both synthetic dye solutions. The results were closely agreed with the literatures [10, 15].

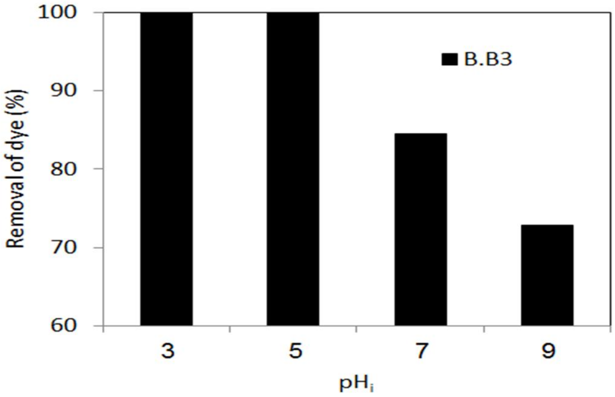


Figure 1. Effect of pH_i versus % removal of dye. Conditions: C_0:50mg/L, Initial volume of wastewater:50mL, Concentration of Fe^{2+}:8mg/L, Dose of H_2O_2:1.5g/L,Contact time: 2min, Mixing rate:200rpm.

Effect of Fe^{2+} concentration as a catalyst

Dye degradation efficiency by Fenton process is influenced by the concentration of Fe^{2+} ions which catalyze hydrogen peroxide decomposition resulting in OH •radical production and consequently the degradation of organic molecule. According to the literature[22],in the absence of Fe^{2+} no radical or other active intermediate species are formed when hydrogen peroxide is added to a wastewater, by increasing ferrous salt concentration degradation rate of organic compound also increases to certain level where further addition of iron becomes in efficient. The feature of an optimal dose range for the iron catalyst is characterized by Fenton's reagent, although the definition of the range varies for different contaminated wastes. Typical ranges are $[Fe^{2+}]:[H_2O_2]=$ 1:100 (reported by Hsuehet al., 2005 for azo red dye). This is due to the fact that Fe^{2+} plays a very important role in initiating the decompositions of H_2O_2 to generate the OH• in the Fenton process.

On the other hand, the iron concentrations left in solution with time can be reasonably monitored for (2-20) mg/L of iron with 50 mg/L of initial dye concentration shown in Fig.2.It can be clearly seen that increased concentration of Fe^{2+} was resulted with the decrease in time contact.Samples were withdrawn at 1,1.5, 2, 8 min and immediately analyzed.However the maximum allowable limit of total iron in effluent is 10 mg/L. In detail,the best results of color removalfor all two dyes 99% were achieved at Fe^{2+} dosages about 8mg/L in this point total visual discoloration was achieved, whereas the COD removal for B.B3 and D.B56 were 88%, 72% respectively. Hsuehreported Fe^{2+} concentration:5.6mg/L for azo red dye removal [15], but no results are found in previous literature for removal of B.B3 and D.B.56 by Fenton oxidation.

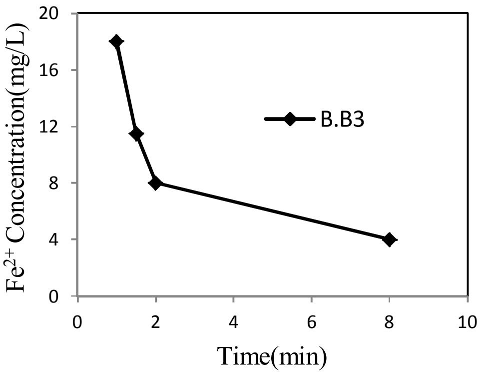


Figure 2. Effect of Fe^{2+} concentration. Conditions: pH_i:3, C_0=50mg/L, Initial volume of wastewater:50mL,Dose of H_2O_2:1.5g/L, Mixing rate:200rpm, %Removal of dye:99%.

Effect of the H_2O_2 *concentration*

Addition of H_2O_2 is known to influence the decomposition of organic compound through Fenton reaction. Experiments were carried out for duration of 2 min with initial dye concentration of 50 mg/L. The reaction was done at pH 3 with the constant concentration of Fe^{2+} (8mg/L). The dose of H_2O_2 was varied from 1.0 to 3.5g/L (30-100 mM). It is obvious that the removal of dye increases at lower H_2O_2, These phenomena could be explained by the high excess of hydrogen ions, behaving as an OH radical scavenger according to the following reaction [6-9]:

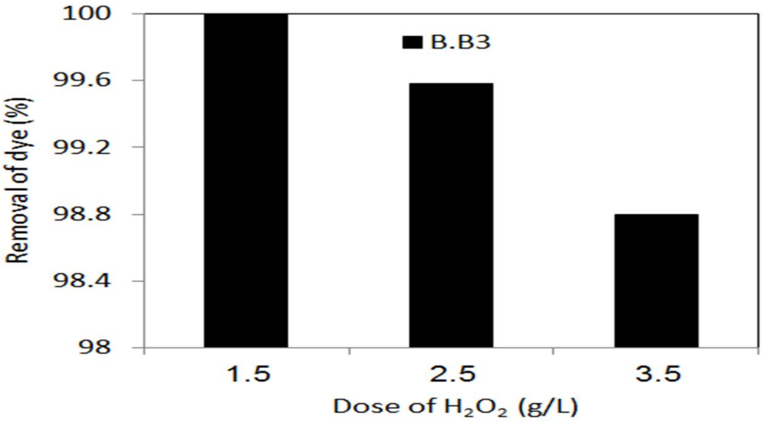


Figure 3. Effect of dose of H_2O_2. Conditions:pH_i:3, C_0=50mg/L,Initial volume of wastewater:50mL,Concentration Fe^{2+} :8g/L, Time contact:2min, Mixing rate:200rpm.

$H_2O_2 + \bullet OH \rightarrow H_2O + HO_2\bullet$ (6)

$HO_2\bullet + \bullet OH \rightarrow H_2O + O_2$ (7)

$\bullet OH + \bullet OH \rightarrow H_2O$ (8)

$\bullet OH + H + + e\text{-} \rightarrow H_2O$ (9)

The better removal efficiency for B.B3 was in the optimum dose of H_2O_2: 1.5 g/L (45mM) (Figure 3).Hashemian et.al reported H_2O_2:1.7 g/L for removal of methyl violet dye [1].

Effect of contact time and initial dye concentration

The effect of initial concentration was investigatedfor B.B3 and D.B56 dyes using the same amount of Fenton's reagents, since pollutant concentration is an important parameter in wastewater treatment.This phenomenon can be explained by the fact that an increase in the initial dye concentration leads to increasing the number of dye molecules. The number of hydroxyl radicals remains the same. Concentrations of H_2O_2 and Fe^{2+} were kept constant, which causes a decrease in efficiency of discoloration. When the dye concentration is low, the concentration of H_2O_2 is in excess compared to the latter and traps the OH• radicals [1].Also the effect of contact time was investigated in this step (Figure.4), however contact time was about 2-50 min based on initial dye concentration of 50 – 500 mg/L, for two types of dyes, the dose of H_2O_2: 1.5g/L, concentration of Fe^{2+}: 8mg/L were achieved. In Fig.5 the percent removal of two dyes was compared with each other obviously, other experimental conditions were mentioned. Itcan be noted that when the initial dye concentration increases, the reaction time increases correspondingly. At low concentration of dye, the percentage conversion is higher compared to that at higher concentration [23].A quick oxidation during the first 2 min for B.B3 was followed(based on decreasing in COD to 88% and %removal of dye to 99%) however by a much slower reaction for D.B56.The color removal for B.B3 and D.B56 are 32% and 22% at 40 to 48 min for initial dye concentration of 500mg/L respectively. Further decrease in the dye decolorization in high concentrations of dye was probably due to the formation of dimmer molecules [25] through a sequence of reactions from single dye molecules. Decolorization of the dimmer molecule is more difficult, leading to the leveling off color removal.

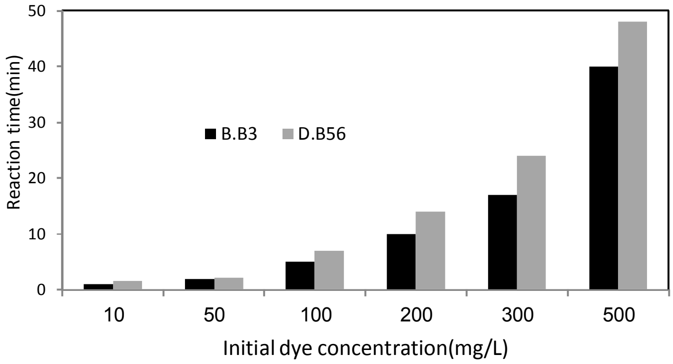


Figure 4. Effect of initial dye concentration. Conditions: pH_i:3,Initial volume of wastewater:50mL, Concentration of Fe^{2+} :8g/L,Dose of H_2O_2: 1.5g/L, Removal of dye (%):99%, Mixing rate:200rpm.

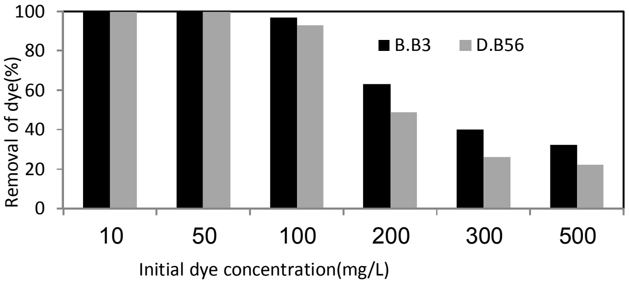


Figure 5. Effect of initial dye concentration. Conditions: pH_i:3,Initial volume of wastewater:50mL, Concentration of Fe^{2+}:8g/L ,Dose of H_2O_2: 1.5g/L,Reaction time:2min, Mixing rate:200rpm.

Effect of initial volume of wastewater

The changes in color removal efficiency influenced by variations in the initial volume of wastewater for B.B3 and D.B56 were studied. Four experiments with 50, 100, 300 and 500 mL of dye solutions were carried out at constant initial dye concentration (Fig.5). Therefore, under the present experimental conditions, the lower initialvolume of wastewater yields a better color removal efficiency for B.B3 dye from 94% to 99%. No results were found in the literature for the effect of initial volume of wastewater on %removal of dye.

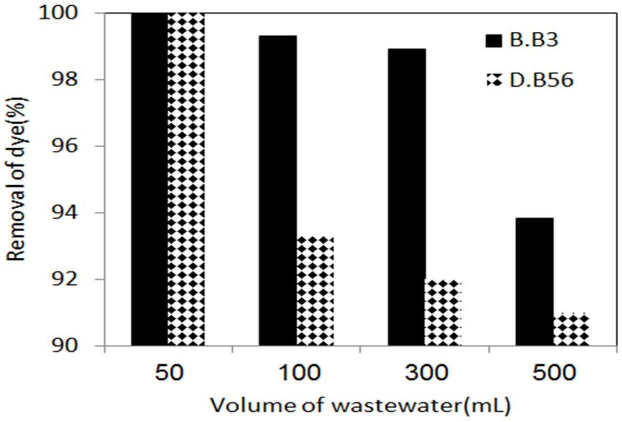


Figure 6. Effect of initial volume of wastewater. Conditions:pH_i:3,C_0=50mg/L, Concentration Fe^{2+}:8g/L, Reaction time: 2 min, Dose H_2O_2: 1.5g/L, Mixing rate:200rpm.

Kinetics

Kinetic studies for decolorization of dyes were done under the following experimental conditions: initial dye concentration 50 mg/L, Fenton's reagent (Fe^{2+}:8mg/L+H_2O_2 dose of 45 mM) with the pH:3. The decolorization of dyes by Fenton's reaction was observed to be a function of time. For decolorization of the dye by Fenton's reagent, first order kinetic model has been suggested [25]. Hence, the kinetic data of few first minutes were fitted into the following equation:

$$\ln[C_0/C_t]= K.t \quad (10)$$

where C_0 and Ctare concentration of the dyes at time 0 and attime t. K is the first order rate constant in min^{-1} and t is the timein minutes. All of the values for the pseudo-first order reactionrate constant, K, were calculated from the linear regression ofthe pseudo-first order kinetic model (Table 2). The coefficient of correlation(R) was in the range of 92–98%. The rate constants for alltwo model dyes are summarized in Table 1.

Table 2. Pseudo-first order rate constant (*K*) for model dyes.

Dye	K(1/min)	Coefficient of correlation (*R*)
B.B3	1.2	0.98
D.B56	0.88	0.92

Kinetic results shows that maximum color removal percent of 99, and 90% was observed in B.B3 and D.B56, respectively, at pH 3, which is in agreement with the previous researchers [15, 19,26].

Conclusions

Low iron concentration (8 mg/L) of Fenton reaction was studied on the degradation of B.B3 and D.B56 dyes. It has been found that the solution pH, dose of H_2O_2 and concentration of Fe^{2+} in solution are the main factors that influence the degradation of B.B3and D.B56 dyes. More than 99% dye removal and 88% COD removal were obtained during 2-10 min, respectively for initial 10-100 mg/L dye solution in addition to Fenton's reagent at ambient conditions and pH: 3. Process of B.B3 and D.B56dyes was investigated and compared based on important operating parameters determination successfully. Removal of dye (%) in aqueous solution under various operational conditions was also investigated as follows: pH:3, T:25^{0}C, concentration of Fe^{2+}:8 mg/L, dose of H_2O_2:1.5 g/L, contact time: 2 min for 50mg/L of dye, %removal of dye:%99 for B.B3 and D.B56. The rate of Fenton oxidation of B.B3 and D.B56 is first fast (2min) and then is very slow.In this investigation Fenton oxidation can be described with a pseudo-first-order kinetic model.

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