



Removal of Anionic Brown 14 and Cationic Blue 41 dyes via Fenton Process

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Abstract

Textile wastewater contains a number of dyes which are known to be toxic and carcinogenic. In this study the results show that the Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) process is an efficient method for the removal of Acid Brown 14 (A.BR14) and Cationic Blue 41 (C.B41) dyes from textile wastewater. In this method, two reagents Fe^{2+} and H_2O_2 are used and do not require any additional energy. Several experiments showed that the pH level was an important parameter for this method. Fe^{2+} concentration was also an important factor in the experiment. The UV-Visible spectrophotometer analysis was used for verifying the results. Some of the important parameters were as follows. Initial dye concentration range: 50-500 mg/L, initial volume range: 50-500mL, initial pH: 3-5, concentration of Fe^{2+} as a catalyst: 4-18 mg/L, dose of H_2O_2 as an oxidant: 1.13, 2.26, 3.39g/L, and limitation time: 3-18 minutes. An efficiency of greater than 99% was observed for both dyes.

Keywords: Acid Brown 14, Cationic Blue 41, Textile wastewater, Fenton, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$.

Introduction

The huge production rate of synthetic dyes and their intensive usage in the textile and other industries produce large amount of colored wastewaters. There are more than 100000 commercially available dyes [1]. Approximately 15% of total world production of wastewater, or 150tons per day, is estimated to be released into the environment without

proper treatment [2]. Many dyes or their metabolites have toxic as well as carcinogenic, mutagenic and teratogenic effects on aquatic and human life [3]. Conventional process used to treat wastewater from textile industry includes chemical precipitation with alum or ferrous sulphate which suffers from drawbacks such as generation of a large volume of sludge leading to the disposal problem,

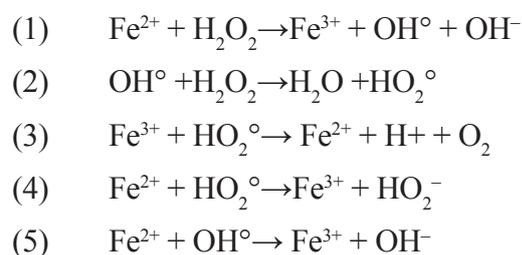
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the contamination of chemical substances in the treated wastewater, etc. Moreover these processes are inefficient in completely oxidizing dyestuffs and organic compounds of complex structure.

To overcome these problems advanced oxidation processes (AOPs) have been developed to generate hydroxyl free radicals by different techniques. There are several methods currently used to decolorize textile wastewater [4], but they are not universally applicable and they are not cost-effective for all dyes. AOPs include hydrogen peroxide (H_2O_2), Ozone (O_3) and UV irradiation, which have proven to be much efficient in treatment process [5]. The Fenton reaction [6, 7] is a catalytic process for the generation of hydroxyl radicals from hydrogen peroxide and is based on an electron transfer between H_2O_2 and iron ions acting as homogeneous catalyst. These radicals are a very strong oxidizing agent capable of reacting with a wide variety of organic compounds under ambient conditions. The advantage of the Fenton reagent is that no energy input is necessary to activate hydrogen peroxide [8]. Under acidic conditions hydrogen peroxide in the presence of ferrous ions undergoes a rapid decomposition [9]. The main advantage of Fenton's reaction compared to other AOPs is that this system offers a cost effective source of hydroxyl radicals and it is easy to operate and maintain. It is particularly advantageous in situation where textile wastewater contains

a high concentration of suspended solids due to the limited depth of photon penetration [10]. The Fenton process could be adopted readily in a textile wastewater treatment system, without the need for reconstructing the existing coagulation unit. The only changes in the process operation will be the addition of H_2O_2 and Fe (II) as well as pH adjustment. In addition, the rapid and slow mixing tanks can provide detention times, which are adequate for Fenton process to achieve the desired color removal [11].

The main reactions of Fenton process are shown in equation [12]:



In this study using Fenton catalyst was developed and applied to catalyze the oxidation reaction of textile dye in wastewater. Also, the effects of operating parameters such as initial pH, initial volume of wastewater, initial concentration of wastewater, dose of H_2O_2 as an oxidant, concentration of Fe^{2+} as a catalyst and contact time on the removal of dyes from synthetic wastewater was measured. The efficiency 99% was observed for anionic and cationic dye by acquiring optimal parameters.

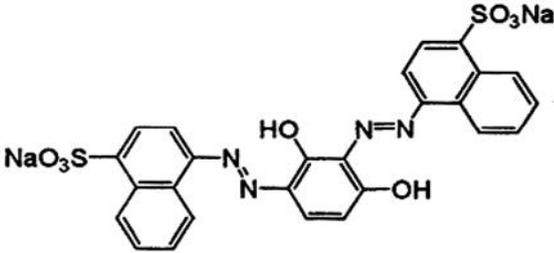
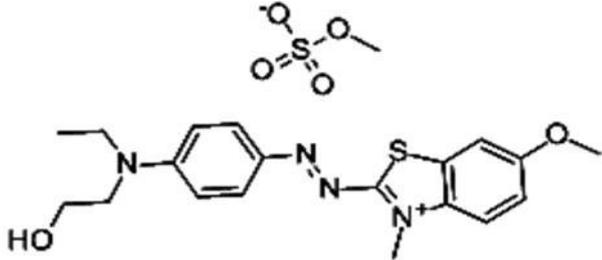
Experimental

Material

The dyes used in this study, Acid Brown 14 (A.BR14) and Cationic Blue 41 (C.B41) were supplied from Alvan-Sabet rang company-Iran. The dyes were used without further purification. The structures of dyes are shown

in table 1. All other chemicals used in this study were of analytical grade, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 30%hydrogen peroxide(H_2O_2) were supplied from Sigma–Aldrich. Solutions were prepared in deionized water. The initial pH was adjusted to the required value using NaOH or HCl solutions prior to addition.

Table1. Basic properties of investigated dyes.

Dye	Molecular Structure	λ_{max} (nm)
A.BR14		476
C.B41		610

Methods

All operations were performed in a batch system, at the 25°C temperature using dye solution with different concentrations of dye sample from 50 to 500 mg/L and 50-500 mL of volume of dye. The pH of the solution was adjusted using HCl and NaOH. After optimizing the pH condition, the effects of other parameters were investigated through changing one parameter and keeping the other ones constant [13].The reactor was run for several times under controlled pH condition

with amount of 30% H_2O_2 (1.13, 2.26, 3.39 g/L).Then, a measured amountof Fe^{2+} was added into the dyes solution (range: 4-18 mg/L).A magnetic stirrer was used to mix the solution continuously for a certain contact time at 100 rpm [14]. Following agitation, the samples were separated through filtration and dye content of the filtrate solution was determined using spectrophotometry. A high precision, double beam spectrophotometer (Hach-Longe Model: DR-2800) was used to measure the absorbance of dyes solution at

wavelengths between 200 and 800 nm.

The efficiency of removal of dye from textile wastewater was calculated by the following equation [15]:

$$\% \text{Removal of dye} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (6)$$

Where C_0 and C_e were the initial and final concentrations of the dyes in solution (mg/L), respectively.

Results and Discussion

The effects of different factors on removal of dye from textile wastewater using the Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) process were as follows:

Effect of initial pH (pHi)

The aqueous pH has a major effect on the efficiency of Fenton's treatment. Previous studies have established that the influent pH is an important parameter influencing the amount of OH° generation, and the preferable

condition for OH° generation was under acidic conditions [16]. Appropriate initial pH (pHi) would cause Fe^{2+} and H_2O_2 to react easily and to produce $\text{Fe}(\text{OH})_2$. Figure 1 demonstrates the effect of pH on the removal of the textile dye in wastewater. The results show that the oxidation rate increases as pH value decreases. A percentage of removal of anionic and cationic dyes of about 97-99% was achieved within 7 minutes at pH of 3-5. But the result shows that A.BR14 dye in the pHi: 3-5 was removed better than the C.B41 dye. Thus, an acidic pH will show better results in removal of dye from textile wastewater.

The observed decolorization, i.e. > 99% at pH: 3-5 is also supported by previous studies by Meric et al. [17]. Also, Rodrigues et al. (2009) observed similar results as follows: "The optimal pH values were obtained at pH 3 with the highest decolorization of dye, which usually falls in the acidic range of pH in Fenton processes"[18].

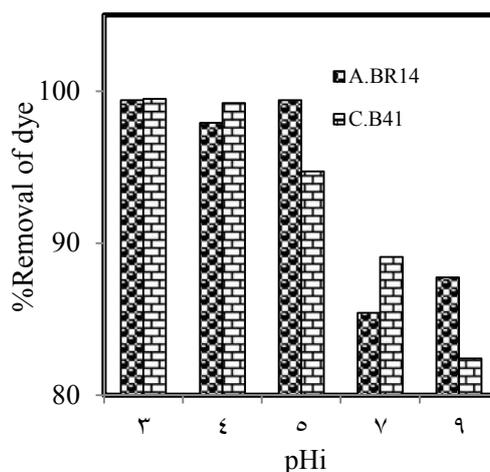


Figure 1. Effect of initial pH on the removal of dyes from wastewater.

Conditions: C_0 : 50 mg/L, $[\text{Fe}^{2+}]$: 8 mg/L, Dose of H_2O_2 (30%): 1.13 g/L, Initial volume of wastewater: 50mL, Contact time: 7min, mixing rate: 100 rpm.

Effect of contact time

Contact time was an important factor in the all experiments. All optimal testing conditions were assessed for several contact times (3, 7, 10, 18 minutes) in the optimal initial pH range. As Table 2 shows, Fenton oxidation process for removal of dyes from textile wastewater is optimized with a contact time of 7 minutes, with maximum removal efficiency of A.BR14 and C.B41 dyes. According to the results, at

the optimum conditions, A.BR14 dye has the best removal efficiency and lowest residual concentration.

Rezaei et al. (2013) have found that the maximum dye removal was achieved at 15 min and color removal remained unaffected for the reaction times between 30 and 120 min [19], but Hsing et al. (2007) reported the best results in less than 20 min of contact time [20].

Table 2. Effect of contact time on the removal of two dyes from wastewater.

Contact time (min)	C.B41		A.BR14	
	Ce (mg/L)	%Removal of dye	Ce (mg/L)	%Removal of dye
3	12.00	76>	1.00	97>
7	0.20	99>	0.30	99>
10	3.00	93>	0.80	98>
18	3.50	92>	0.80	98>

Conditions: C_0 :50 mg/L, $[Fe^{2+}]$:8 mg/L, Dose of H_2O_2 (30%):1.13 g/L, pH_{opt} : 3-5, Initial volume of wastewater: 50mL, mixing rate:100 rpm.

Effect of initial concentration of dye in wastewater

The effect of initial concentration of dye was investigated, since pollutant concentration is an important parameter in wastewater treatment [21]. With increasing dye concentration, (at fixed concentration of H_2O_2 and Fe^{2+}), the efficiency of discoloration was decreased. When the dye concentration is low, the concentration of H_2O_2 is in excess compared to the latter and traps the OH° radicals. On the other hand, intermediate products were increased [22]. Effects of initial concentrations

of 50, 100, 200, 300 and 500 mg/L of dyes on removal efficiency were investigated in this study. According to Figure 2, with increasing concentration of dyes, the removal of anionic and cationic dye is significantly reduced.

The reason is that the amount of hydroxyl radicals is identical for all samples. So the samples with lower concentrations of dyes will perform better [23]. Ghahramani [24], Hashemian [22] and Muruganandham [25] reported similar results. They proved that an increase in the dye concentration leads to an increase in the number of dye molecules; on

the other hand it did not alter the amounts of OH° radical concentration in the solution. Therefore, the decolorization rate of dyes exhibits a decrease with increasing dye concentration [25].

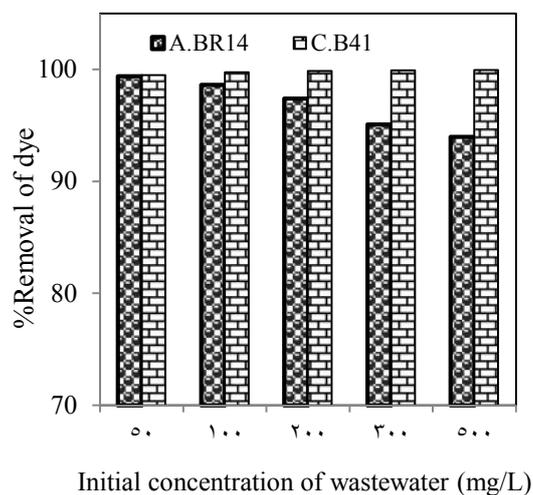


Figure 2. Effect of initial concentration of wastewater on the removal of dyes from wastewater. Conditions: $[\text{Fe}^{2+}]$:8 mg/L, Dose of H_2O_2 (30%):1.13 g/L, pH_{opt} :3-5, Initial volume of wastewater: 50mL, mixing rate:100 rpm.

Effect of initial volume of wastewater

Initial volume of wastewater is an important parameter on the removal of dye from wastewater. The effect of volume was tested on 50, 100, 300 and 500 mL (other conditions represented in Figure 3). Based on the results, the initial volume of dyes has no significant effect on the removal efficiency of cationic

and anionic dyes. So given the same volume of wastewater, increasing the volume of A.BR14 and C.B41 dyes does not significantly influence removal efficiency.

The measurement of this parameter is a new contribution and had not been considered in previous studies.

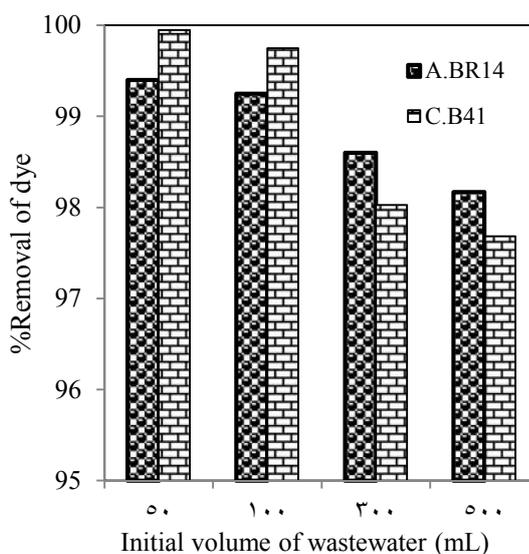


Figure 3. Effect of initial volume of wastewater on the removal of dyes from wastewater. Conditions: C_0 : 50 mg/L, $[Fe^{2+}]$: 8 mg/L, Dose of H_2O_2 (30%): 1.13 g/L, pH_{opt} : 3-5, Initial volume of wastewater: 50 mL, Contact time: 7 min, mixing rate: 100 rpm.

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

Fe^{2+} concentration was effective at decreasing the concentration of dyes by producing hydroxyl radical and creating the phenomenon of coagulation. Figure 4 displays the effect of iron concentration on the removal of wastewater. Concentrations of 4, 8, 12 and 18 mg/L of Fe^{2+} as a catalyst in this study were tested for the removal of dyes by Fenton reagents. Finally, it was observed that the percentage removal of dyes increases with increasing iron concentration, but according to the iron permissible concentration amount 10 mg/L has been reported in previously [26]. This is due to the fact that Fe^{2+} plays a critical role in initiating the decompositions of H_2O_2 to generate the OH^\bullet in the Fenton process. When the concentrations of Fe^{2+} and OH^\bullet are

high, Fe^{2+} can react with the OH^\bullet (see equation 5). The lower degradation capacity of Fe^{2+} at small concentration is probably due to the lowest OH^\bullet radicals' production of variable for oxidation [21]. Therefore in this study, for removal of A.BR14 and C.B41 dyes from textile wastewater by optimal parameters, the optimal amount of iron was selected to be 8 mg/L.

Ghahramani (2013) has found that, 50 mg/L (0.33 mM) of $FeSO_4$ ion and 300 mg/L (8.82 mM) of H_2O_2 dose at pH: 3 was required for > 95% of decolorization [24]. Also, Moradianfard et al. (2013) reported color removal was more than 99% in the pH: 3, at concentration of $FeSO_4$: 10-200 mg/L by keeping H_2O_2 concentration constant [27].

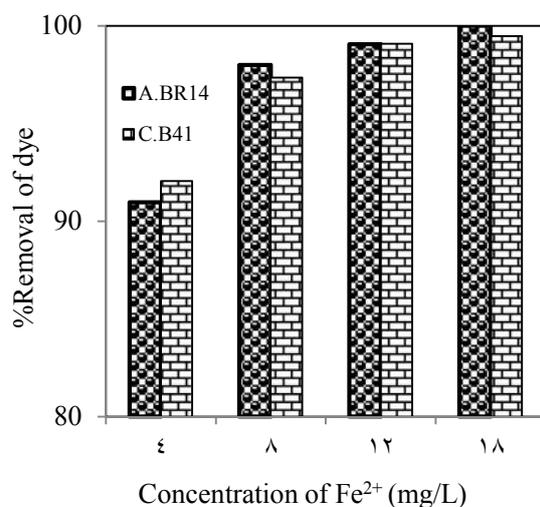
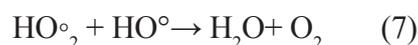


Figure 4. Effect of concentration of Fe²⁺ on the removal of dyes from wastewater. Conditions: C₀: 50 mg/L, Dose of H₂O₂ (30%): 1.13 g/L, pH_{opt}: 3-5, Initial volume of wastewater: 50mL, Contact time: 7min, mixing rate: 100 rpm.

Effect of dose of H₂O₂ as an oxidant

Choosing appropriate value of reagent in the Fenton process is crucial; hence the H₂O₂ in the oxidant role is a very significant parameter. Figure 5 (comparative curve for two dyes) shows the percentage removal of dyes based on the amount of H₂O₂. Experiments were performed in optimal conditions; dose of applied H₂O₂ was in the range of 1.13 to 3.39 mg/L.

The result shows the increase in the decolorization is due to the increase in hydroxyl radical concentration by the addition of H₂O₂ [28]. However, at high H₂O₂ concentration, efficiency of dye removal showed no significant improvement, which is due to the recombination of hydroxyl radicals, and scavenging of OH[•] radicals, as shown in equation 7 [28]:



According to the recent studies, the results show that additional H₂O₂ does not provide a significant improvement in the decolorization rate and amount of residual dye [29]. According to the reports from Hsueh et al. (2005) and Lodha (2007) the decolorization rate of dye increases as the H₂O₂ concentration increases until H₂O₂ concentration reaches a critical value [30, 31]. Moradianfard et al. (2013) observed that color removal efficiency increased by raising H₂O₂ concentration from 25 mg/L (65%) to 400 mg/L (99.99%) [27]. According to other results at a lower optimization of FeSO₄ ion and H₂O₂ dosage, operating cost of the treatment can be lowered and the amount of sludge generation can be minimized [26].

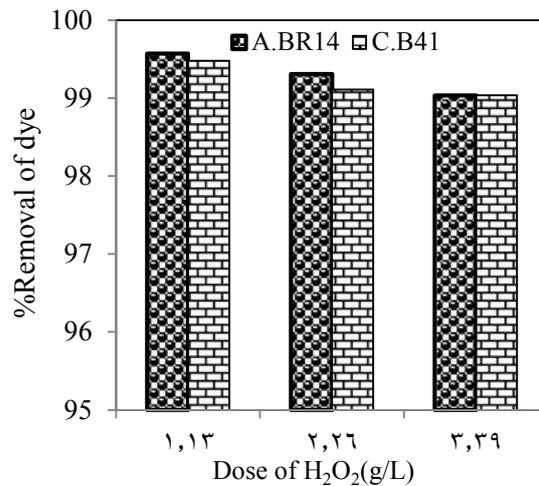


Figure 5. Effect of H₂O₂ dosage on the removal of dyes from wastewater. Conditions: C₀: 50 mg/L, [Fe²⁺]: 8 mg/L, pH_{opt}: 3-5, Initial volume of wastewater: 50mL, Contact time: 7min, mixing rate: 100 rpm.

The absorption spectra of A.BR14 and C.B41 dyes

The mineralization of the A.BR14 and C.B41 solutions with an initial concentration of 50mg/L was carried out by Fenton process in this study. Blank experiment (before removal) and Fenton oxidation experiment (after removal) were carried out for comparative purposes in Figures 6 and 7. In order to clarify the changes in the molecular and structural characteristics of the species resultant from this advanced oxidation process, the evolution of the UV-Vis spectra of solution

at initial (t₀) and final state (t=7min) was recorded as a function of wavelength. The absorption spectra of A.BR14 and C.B41 are characterized by one main band in the visible region with the maximum absorption at 476nm and 610nm, respectively, which is associated with the chromophores of the dye molecules. The evolution of the UV-Vis spectra during Fenton followed a similar trend for all dyes, i.e. the spectrum of each dye solution and its disappearance changed over time. The disappearance of the band in the visible region is due to the H₂O₂ attack on the chromophore.

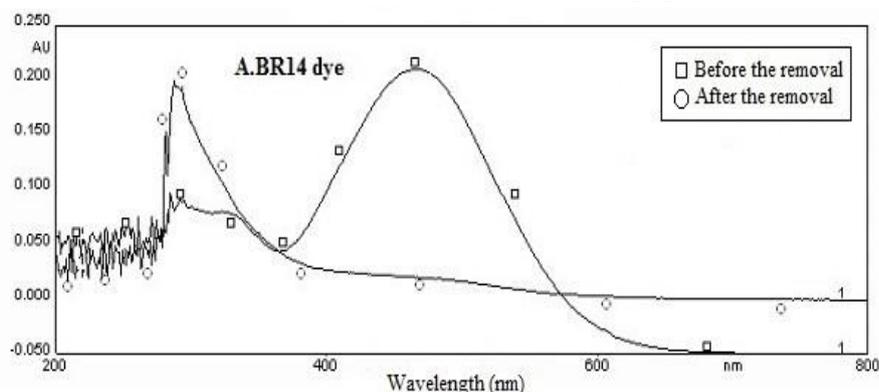


Figure 6. UV-Visible Adsorption spectrum of A.BR14, Before and After the removal of dye by Fenton process.

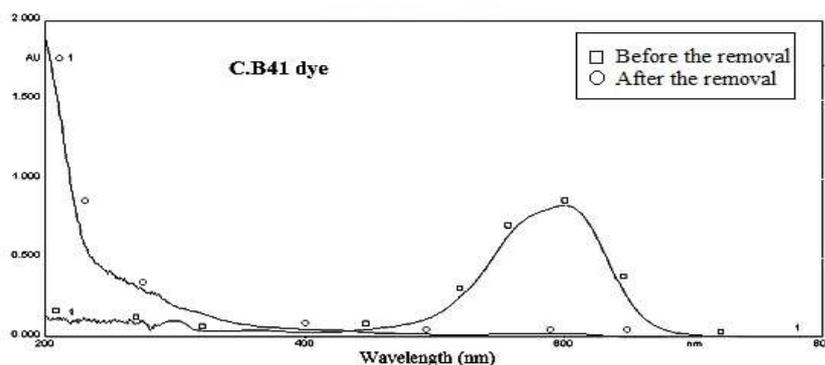


Figure 7. UV-Visible Adsorption spectrum of C.B41, Before and After the removal of dye by Fenton process.

Conclusion

The results of the experiments showed that the Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) process is an effective and efficient manner for the removal of anionic and cationic dyes from textile wastewater. Removal of textile dyes from wastewater is due to generated hydroxyl radicals. The tests determined that the removal efficiency of A.BR14 and C.B41 dyes depends on the initial pH, initial concentration of dyes, and concentration of Fe^{2+} and contact time. Optimal conditions for removal of A.BR14 and C.B41 dyes in textile wastewater were as follows: Concentration of Fe^{2+} as a catalyst: 8 mg/L, Dose of H_2O_2 (30%) as an oxidant: 1.13 g/L, Contact time: 7 minutes, Optimum initial pH: 3-5. Even though the percentage removal of the two dyes by Fenton process for A.BR14 and C.B41 were above 99%, the process was better suited for Acid Brown 14 dye.

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