Decolorization of Cationic and Anionic Textile Blue Dyes from Aqueous Solution with Advanced Oxidation Process Using H2O2 and Various Catalysts

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Abstract

In this study, we used advanced oxidation process (AOP)for the removal of a cationic and anionic blue dyes, namely Basic Blue 3 (BB3) and Acid blue 62(AB62), from aqueous solutions. Fenton reactions are mixture of H_2O_2 and Fe^{2+}. However this paper investigates the application of twelve different catalysts such as: FeCl2 , FeSO4, $(NH_4)Fe(SO_4)_2$, $FeCl_3$, Nano iron (Fe_0), $Fe(NO_3)_3$, K2FeO4, Nano Silver (Ağ), Nano ZnO, $Zn(NO_3)_2$, Nano Al2O3 and$Al_2(SO_4)_3$, with the H_2O_2. The formed hydroxyl radicals led to the oxidative degradation of BB3& AB62. The results show that the optimum amounts of reagent was 5.6 mg/L as a metal catalyst and 30mM of H2O2 for an initial dye concentration at 50 mg/L. The percentremoval of dye were found to be strongly influenced by the increasing of the oxidant and metal catalyst up to a certain value. It was found that the maximum removal of dye (up to 99.9%.) was enhanced using pH = 3.The best catalyst for the decomposition of AB62 dye was $FeCl_2$ and for BB3 dye wasNH4Fe$(SO_4)_2$.The correlation coefficient (R^2) obtained from first order reaction model were found to be higher than 0.98 for both investigated dyes. Comparing the results shows that the removal of AB62 is more feasible compare with BB3.

Keywords: *Advanced oxidation process, Various catalysts, Removal of dye, AB62, BB3.*
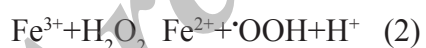
Introduction

Textile industry wastewater is considered as one of the major pollutant to the environment due to high discharge volume, organic/ inorganic content and concentration of color consume large quantity of water and chemicals for various operations such as washing, drying, rinsing and finishing [1-3]. Colored

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agents hinder the transmission of light through water and consequently the photosynthesis, resulting in ecological imbalance [4]. On the one hand, many dyes or their metabolites have toxic as well as carcinogenic and mutagenic effects on aquatic life and humans [5, 6]. In recent years, the Advanced Oxidation Processes (AOPs) are being widely studied because of their efficiency in removing non-biodegradable industrial wastewater. Heterogeneous catalysis, employed by advanced oxidation processes have emerged as a potential destructive technology leading to the total mineralization of most of organic pollutants [7-9]. The resource to AOP, like homogenous Fenton reaction (Fe^{2+}/H_2O_2) is one of the most important processes to generate hydroxyl radicals •OH[10] in an acidic aqueous solutions as follows[11]:

$$Fe^{2+}+H_2O_2+H^+ \quad Fe^{3+}+^{\bullet}OH+H_2O \quad (1)$$
$$Fe^{3+}+H_2O_2 \quad Fe^{2+}+^{\bullet}OOH+H^+ \quad (2)$$
$$Fe^{3+}+^{\bullet}OOH \quad Fe^{2+}+O_2+H^+ \quad (3)$$

The generated free hydroxyl radical attacks to the unsaturated bond in the dye molecule, thus decolorization the wastewater is occurred. In this study the decolorization of two different blue dyes solutions (AB62 and BB3) by advanced oxidation process has been investigated. By using AOP process, this paper investigates the application of twelve different catalysts such as: $FeCl_2$, $FeSO_4$, (NH_4) $Fe(SO_4)_2$, $FeCl_3$, Nano iron (Fe^0), $Fe(NO_3)_3$, $K2FeO_4$, Nano Silver (Ag̊), Nano ZnO, $Zn(NO_3)_2$, Nano Al2O3 and $Al_2(SO_4)_3$, with the H_2O_2. Study on chemical oxidation of BB3 and AB62 was investigated by introducing some important operating parameters such as initial pH, dose of oxidizing agent, type of catalyst, dose of catalyst and time of decolorization. The detrimental effects of optimize catalyst and oxidizing agent warrant a process to be developed in which the dye contaminants could be brought down to the levels below the permissible limits. The first and second orders kinetics have been analyzed.

Experimental

Materials

All the chemicals were of analytical grade. Two dyes acid blue 62 (AB62) and basic blue 3 (BB3) were selected for this study that was purchased from Alvansabet company and used without further purification, also all the catalysts reagents were purchased from Merck or Sigma-Aldrich and nano-reagents were purchased from nanopusheshfelez - Iran. Deionized water was used for preparation of various solutions. pH of the solution was adjusted with 1N HCl or 1NNaOH. Hydrogen peroxide (30% w/v, density 1.11 g/mL) was obtained from Merck. The chemical structure of the two dyes is shown in Figures 1 and 2.
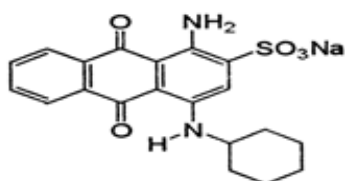
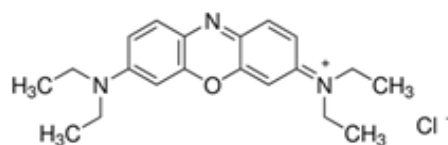**Figure 1.** Chemical structure of anionic, Acid blue 62.

Figure 2. Chemical structure of cationic, Basic blue 3.

Methods

Dye concentration of aqueous solution was selected as 50 mg/L to represent actual textile wastewater. All tests were conducted in 100 mL capacity glass beakers and volume of waste water was selected 50 mL. The reaction was initiated by adding different catalyst and hydrogen peroxide to the reactor after the pH was adjusted. Samples were periodically taken out from the reactor and then absorbance measurements of the reaction solutions were immediately performed. Color measurement of two dyes was recorded from 400 to 800 nm wavelengths using a UV/VIS spectrophotometer (Model: UV-IKON922). The concentration of the AB62 & BB3 in the reaction mixture at different reaction times were determined by measuring the absorption intensity at λ max = 637 & 654 nm respectively. Prior to the measurement, a calibration curve was obtained by using the standard solution with known concentrations of two dyes. Each experiment lasted 60 min. The percent removal of dye was determined as follows:

Removal of dye (%) = (1 - C_0/C_e) × 100   (4)

Results and discussion

Effect of pH

pH is one of the effective parameter on dye removal efficiency in Fenton and Fenton-like processes. pH plays an important role in production of radicals that are effective in increase of oxidation efficiency. The optimal pH in the range of 2.5-4 was represented to be a highly important factor for effective Fenton oxidation [12-14]. In the present study, the effect of initial pH= 3, 5, 9 on removal of two dyes, acid blue 62 (AB62) and basic blue 3(BB3), were investigated. The best results and visual decolorization were achieved in the pH =3. Tang stated that if the pH value dropped to 2, a significance decrease in removal of color was occurred as follows [15]:

$$^{\cdot}OH + H^+ + e^- \rightarrow H_2O \quad (5)$$
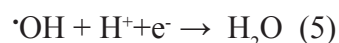
Because high excess of H^+, behaves as an $^{\cdot}OH$ scavenger. Therefore pH= 3, was used for oxidation in this study. The evolution of pH= 3, 5, 9 followed in non similar trend for two dyes with H_2O_2 and collection of catalysts (Table 1 and Table 2). AB62 was decolorized fast (under 10 sec) with $FeCl_2/H_2O_2$ at maximum removal efficiency ,99.9%, however BB3 was decolorized after 15 min with $(NH_4)Fe(SO_4)_2/H_2O_2$ at 99.5% removal efficiency. It is postulated that, favors uptake of anionic AB62 dye due to increased electrostatic force of attraction. It has been proven that the Fenton reactions in acidic pH are more effective than

neutral pH [16].All the results are tabulated in   Tables 1 and 2.

Table 1. Important operating parameters for decolorization of AB62.

Oxidation reagent	Catalyst (Metal)	Dye: Acid Blue 62					
		pH=3		pH=5		pH=9	
		η (%)	Time (min)	η (%)	Time (min)	η (%)	Time (min)
H_2O_2	**FeCl$_2$**	**99.9**	*	0	60	-	60
	FeSO$_4$	99.9	20	7	60	-	60
	(NH$_4$)Fe(SO$_4$)$_2$	99.9	10	14	60	-	60
	FeCl$_3$	97	50	60	60	-	60
	Nano iron(Fe$^\circ$)	80	35	26	60	10	60
	Fe(NO$_3$)$_3$	99.9	15	94	35	-	60
	K$_2$FeO$_4$	-	60	-	60	-	60
	NanoSilver(Ag$^\circ$)	95	50	-	60	-	60
	Nano ZnO	85	60	-	60	-	60
	Zn(NO$_3$)$_2$	42	60	-	60	-	60
	Nano Al$_2$O$_3$	31	60	-	60	-	60
	Al$_2$(SO$_4$)$_3$	50	60	40	60	45	60

[Conditions: Initial dye concentration=50mg/L, [H_2O_2] =30 mM, Volume of wastewater=50mL, Mixing rate=200rpm,Catalyst (Metal) concentration=5.6mg/L as metal].-: No recommended, *: Instantaneous or rapid reaction, under 10 sec, η: Removal of dye (%).

Table 2. Important operating parameters for decolorization of BB3.

Oxidation reagent	Catalyst (Metal)	Dye: Basic Blue 3					
		pH=3		pH=5		pH=9	
		η (%)	Time (min)	η (%)	Time (min)	η (%)	Time (min)
H_2O_2	FeCl$_2$	99.7	30	55	60	85	60
	FeSO$_4$	99.7	30	42	60	86	60
	(NH$_4$)Fe(SO$_4$)$_2$	**99.5**	**15**	52	60	52	60
	FeCl$_3$	26	40	24	60	26	60
	Nano iron(Fe$^\circ$)	27	60	27	40	34	40
	Fe(NO$_3$)$_3$	99.6	45	90	60	97	60
	K$_2$FeO$_4$	40	60	30	60	49	60
	NanoSilver(Ag$^\circ$)	30	60	31	60	87	40
	Nano ZnO	27	60	33	60	39	60
	Zn(NO$_3$)$_2$	25	60	30	60	56	60
	Nano Al$_2$O$_3$	30	60	27	60	57	60
	Al$_2$(SO$_4$)$_3$	27	60	27	60	40	60

[Conditions: Initial dye concentration=50mg/L, [H_2O_2] = 30 mM, Volume of wastewater=50mL, Mixing rate=200rpm, Catalyst (Metal) concentration=5.6mg/L as metal].
η: Removal of dye (%)

Effect of H₂O₂

H_2O_2 plays the role of an oxidizing agent in this process. The selection of an optimal H_2O_2 concentration for the decolorization is important from practical point of view due to the cost of H_2O_2 [17]. AOPs process is carried out by •OH radicals that are directly produced from the reaction between H_2O_2 and metal catalysts like iron ions.At a high dosage of H_2O_2, the decrease inremoval efficiency was due to the hydroxyl radical scavenging effect of H_2O_2, (Equations 6 and 7) and the recombination of the hydroxyl radical(Equation 8) [18]:

$$HO^• + H_2O_2 \rightarrow HO_2^• + H_2O \qquad (6)$$
$$HO_2^• + HO^• \rightarrow H_2O + O_2 \qquad (7)$$
$$2HO^• \rightarrow H_2O_2 \qquad (8)$$
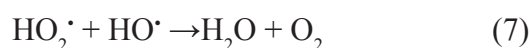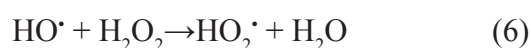
Following literature, stepwise H_2O_2 addition could be more effective than applying a large initial dose. This could be due to scavenging of OH• by H_2O_2 [19]. In this study, as the H_2O_2 dosages increases from 0 to 30mM, the decolorization of two dyes is enhanced because more Fe^{2+} (or other catalytic metal) and •OH are formed at higher H_2O_2 dosage in the solution. The results indicated that the dye removal efficiency increases as the dosage of the oxidant increases in each dye concentration up to 30 mM in Figure 2 as an example for initial dye (BB3) concentration of 50 mg/L with $FeSO_4$ and H_2O_2. Saeedeh applied 50 mM H_2O_2 for removal of methyl violet dye (time of reaction= 15 min, dye removal efficiency=99.5%) [10].
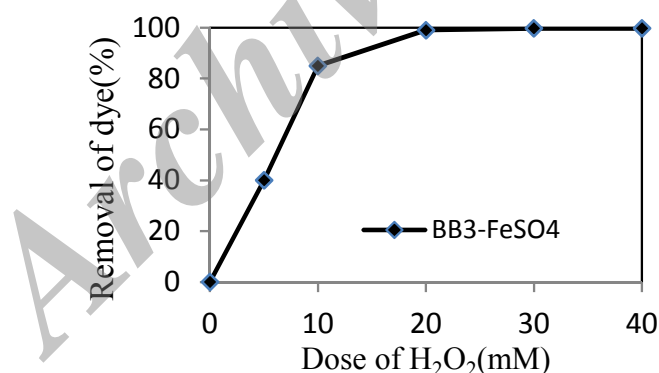

Figure 3. Effect of the H_2O_2 on the decolorization of BB3 by fenton process.
[Conditions: Initial dye concentration=50mg/L, pH=3, Volume of wastewater=50mL, Mixing rate=200rpm, Fe^{+2} concentration=5.6mg/L as metal]

The Effect of catalyst Concentration

The concentration of Fe^{2+} (or other catalytic metals in this study) is one of the critical parameters in fenton and similar oxidation processes. Hydrogen peroxide is not strong enough to oxidize big molecules such as pigments in coloric wastewater without the presence of catalyst. In the present study the effect of different iron concentrations (0-15 mg/L) is tested. The concentration of hydrogen

peroxide is fixed (30mM), and each dye concentration (AB62 or BB3) is 50mg/L. It can be seen from results, each dye degradation increased with increasing Fe^{2+} concentration as we mentioned before(equations1 to 3), for example by adding a quantity of Fe(II), removal efficiency will increase. Zhou et al. found that methylene red removal was increased from 45% to 75% in presence of Fe (II) at 10 minutes [20]. Barbusinski used Fe^0=1000mg/L for removal of acid red 18 from aqueous wastewater [21]. In this study according to the results, up to the concentration of 5.6 mg/L, the rate of color removal was relatively constant; however we apply several catalysts for removal of two dyes. Dosage of each metal catalyst were fixed and chosen as 5.6 mg /L as metal catalysts (see Tables 1 and 2).Therefore two textile dyes were oxidized by H_2O_2/ metal catalyst and the results of effectiveness of these catalysts on the oxidation process has been compared in each experiment. The optimized amount of oxidizing agent and catalyst have been used which was below the permissible limit of chemical reagent were used. The results in Table 1 indicate that the best catalyst is $FeCl_2$ because of instantaneous dye removal (under 10seconds) for AB62, but $FeSO_4$ and $(NH_4)Fe(SO_4)_2$ can also considered as effective catalyst for the oxidation process of AB62.Hencethe results in Table 2 indicate that the best catalyst is $(NH_4)Fe(SO_4)_2$ because of short time reaction(under 15 min) for BB3

but $FeSO_4$ and $FeCl_2$ can also considered as effective catalyst for the oxidation process (Each experiment lasted 60 min).

Comparing the results in Tables 1 and 2 shows that the removal of AB62 from the synthetic textile wastewater is more feasible compare with BB3.To the best of our knowledge there is no report on our search of literature, indicated that there is no report on application of other metallic catalysts (such as Al, Zn, Ag,…. That was used in this study) for removing textile dye.

Kinetics studies for the removal of AB62&BB

Kinetic models and oxidation rate are important for describing and image the mechanism for the interaction of dye molecules on oxidizing agent and catalyst in the oxidation process such as fenton. The decolorization kinetics of AB62 & BB3 by (AOP_s) process was studied for various contact times. Kinetics models are established to perform such studies and then occurred by the first and second order kinetics as described by the equations 9 and 10 [22].

$$Ln (C_e)= Ln (C_0)-K_1t \qquad (9)$$
$$1/C_e-1/C_0=K_2t \qquad (10)$$

Where C_0 is initial concentration ofAB62 & BB3, C_e is concentration of the dyes at time t, K1 (min^{-1}) and K_2(mg. L^{-1}. min^{-1}) are the rate constants of the first order and second order kinetic equations. Values of K_1 and K_2

were determined respectively by the plot of the curves of Ln (C_e/C_0) versus time (Figure 4) and $1/C_e$ versus time. All data found were presented in Table 3. The kinetic study was discussed in the first time by using the first and second orders models. In the light of these results and in order to fit the best experimental data, we compare the correlation coefficient of the both models [23, 24].
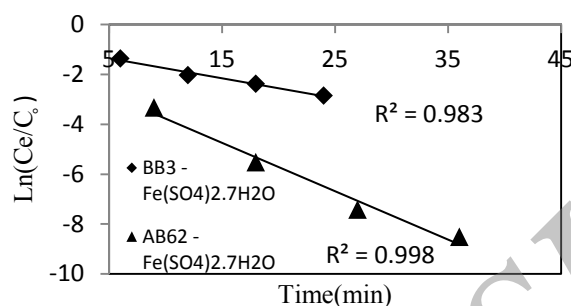

Figure 4. First-order model for Fenton- oxidation of AB62 & BB3.

As seen in Table 3 or Figure 4, the correlation coefficient (R^2) obtained from first order reaction model were found to be higher than 0.98 for both investigated dyes , which were larger than those of the second order reaction model. Hence the results indicated that the AB62followed the first order reaction model well. Also the calculated values of K1 (rate of first order reaction constant) obtained for two investigated dyes.

Table 3. Data of the first and second orders kinetics.

Reactions	First order model		Second order model	
	K_1 (min^{-1})	R^2	K_2 (L.min^{-1}mg^{-1})	R^2
AB62-fenton	0.19	0.9982	1.82	0.8496
BB3- fenton	0.08	0.9835	0.01	0.9715

[Conditions: Initial concentration of dyes: 50 mg/L, pH: 3, Initial volume of waste water: 50mL]

Conclusion

This work has shown that advanced oxidations process is good method for color removal of AB62 & BB3 in synthetic textile wastewater. In acidic conditions all reagents have a high efficiency of removal dye. $FeCl_2.4H_2O$ and $NH_4Fe(SO_4)_2$ are the best reagents for AB62 & BB3 dye respectively. The effect of system

parameters such as pH, H_2O_2, metal catalyst concentration and 12 types of different catalysts on dye removal efficiency were performed. The kinetics of AB62 & BB3 decolorization could be described by a model of first order kinetics in fenton process. The values of the coefficient (R_2) obtained from first order reaction model were higher than 0.98 for both dyes. Comparing the results shows that the removal of AB62 from the synthetic textile wastewater is more feasible compare with BB3.

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