

# Remediation of the Textile Dye Brilliant Blue FCF from Contaminated Water via a Fenton-Like Reaction: Influence of Aromatic Additives

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## Abstract

The oxidative decolorization of Brilliant Blue FCF (BBF) in aqueous solution was studied using a Fenton-like ( $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ ) reaction in a dark environment. The effects of operational parameters, such as  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{3+}$ , and initial dye concentrations, were investigated. Results indicated that by increasing the initial concentration of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{3+}$  the rate of BBF decolorization was enhanced; however, the rate of BBF decolorization decreased with an increase in the initial concentration of BBF. In addition, the influence of aromatic additives and Orange II on the efficiency of BBF removal was examined. The decolorization rate of BBF in the presence of various aromatic additives obeyed the following order: gallic acid > hydroquinone > salicylic acid > 2-nitrophenol > 1,4-dihydroxynaphthalene. The rate of BBF decolorization increased as the initial concentration of hydroquinone additive increased up to  $5 \times 10^{-5}$  M, but beyond this there was a decrease in the decolorization rate. Mineralization of the dye solution was determined by measuring the reduction of chemical oxygen demand (COD). For a dye solution with a COD of approximately 45 ppm and dye concentrations less than  $5 \times 10^{-5}$  M, complete color removal and 80% mineralization was obtained after a reaction time of 150 min under optimized conditions.

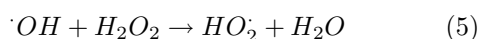
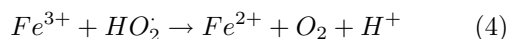
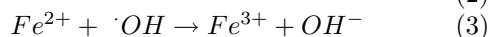
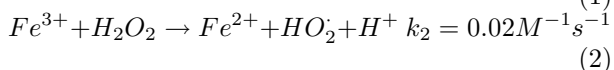
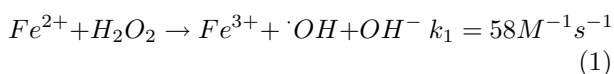
**Key Words:** Decolorization, Advanced oxidation processes (AOPs), Hydroquinone, Organic dyes.

## Introduction

Nowadays, among the serious problems that must be dealt with on a global level are toxic and carcinogenic environmental contaminate materials. A large portion of toxic pollutants is dyes, which are used for dyeing textiles and other industrial purposes. Many physical, chemical, and biophysical processes have been studied for their ability to remove environmental pollutants. In this respect the development of new technologies aimed at straightforward decolorization of such substances is of particular interest. In recent years, advanced oxidation processes (AOPs) have been used to remove toxic, resistant, and poorly biodegradable pollutants from water and wastewater. AOPs are based on the production of highly reactive hydroxyl radicals ( $\cdot\text{OH}$ ).

These radicals can completely decompose toxic and bioresistant compounds into harmless species ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , etc). Among the most promising AOPs for the treatment of contaminated water, the Fenton reaction (reaction of hydrogen peroxide with Fe(II) ion) has been proven to be an effective method for treating organic pollutants in wastewater (Spadaro et al., 1994; Spacek et al., 1995; Bandara et al., 1996; Kaptan and Kargi, 2000; Modirshahla et al., 2007; Wu, 2008; Khataee et al., 2009; Özcan et al., 2009).

Many investigations have been performed on the kinetics of the Fenton and Fenton-like reactions (Fenton, 1894; Barb et al., 1951; Walling, 1957; Daneshvar and Khataee, 2006; Ntampeglitis et al., 2006; Figueroa et al., 2009; Sun et al., 2009), which are summarized in Eqs. (1)-(5):



During reaction (2), Fe(III) ions are formed that can react by  $H_2O_2$  and  $HO_2$  to reproduce Fe(II) ions. The reaction of hydrogen peroxide with Fe(III) ions is referred to as a Fenton-like reaction.

Transformation of Fe(II) to Fe(III) ions, and vice versa, proceeds via reactions (1) and (2), which continually produce the active radicals  $\cdot OH$  and  $HO_2$ . The slow step of the above-mentioned mechanism [reaction (2)] is the rate-determining step of this process. One of the important advantages of a Fenton-like reaction, in comparison to the Fenton reaction, is that the cost of Fe(III) salts is lower than that of Fe(II) salts.

Any reaction capable of promoting the transformation of Fe(III) to Fe(II) ions would help accelerate the Fenton reaction. It has been reported that many kinds of inorganic and organic compounds can interact with Fe(III) or Fe(II) ions and, hence, considerably influence the kinetics of the Fenton reaction. Inorganic materials, such as  $Cl^-$ ,  $H_2PO_4^-$  (Bandara et al., 1996; Lu, 1997; Nadochenko and Kiwi, 1998) and  $Na_2C_2O_4$  (Balmer, and Sulzberger, 1999; Hislop and Bolton, 1999), and organic aromatic derivatives, such as hydroquinone and hydroquinone-like compounds, are promising candidate materials (Chen et al., 2002; Yingxum et al., 2006). Considering that aromatic derivatives are the main pollutants in most dye-contaminated wastewater, a comprehensive study on their effect on the Fenton reaction could generate important data. Hydroquinone efficiently catalyzed Fenton decolorization of organic compounds, which was attributed to the rapid reduction of ferric ions to ferrous ions and, hence, acceleration of the slow step of the Fenton reaction (Kerem et al., 1999; Zhao, 2002; Yingxum et al., 2006).

Brilliant Blue FCF, an acidic dye, is soluble in cold water and methanol. It can be found in thousands of textiles (as a dye for wool and silk), foodstuffs, and pharmaceutical wastewater. In addition, Brilliant Blue FCF is one of the ingredients in Aquashade and can be used as an aquatic algicide/herbicide in natural or manmade ponds,

lakes, fountains, fish farms, and fish hatcheries; it can be used both by professionals and homeowners. Aquashade is a blend of blue and yellow dyes specifically designed to block portions of the sunlight spectrum (red-orange and blue-violet wavelengths) required for underwater aquatic plant and algae growth. It can be dangerous in cases of ingestion, skin contact (irritant), eye contact (irritant), and inhalation (Daneshvar et al., 2006; Khataee and Khataee, 2008).

The present study investigated various operational parameters affecting the decolorization of a dye solution containing Brilliant Blue FCF using a dark Fenton-like reaction. The aim of this study was to investigate the effects of various aromatic additives and hydroquinone-like intermediates on the decolorization of Brilliant Blue FCF via a Fenton-like reaction. In addition, the effect of the addition of Orange II on decolorization was considered.

## Materials and Methods

### Reagents

Brilliant Blue FCF (C.I. Acid Blue 9) and Orange II (C.I. Acid Orange 7) were obtained from Shimi Keshavarz Company (Iran); their structures are given in Table 1. Other chemicals, including ethanol,  $HNO_3$  (65%),  $H_2O_2$  (30%),  $H_2SO_4$ , NaOH,  $Fe(NO_3)_3 \cdot 9H_2O$ , 2-nitrophenol, salicylic acid, hydroquinone, and gallic acid, were obtained from Merck (Germany). 1,4-Dihydroxynaphthalene was purchased from Fluka (Switzerland). The structures of the aromatic additives are given in Table 2.

### General procedure

Brilliant Blue FCF decolorization experiments were performed in a beaker maintained in a dark environment. Appropriate volumes of stock Brilliant Blue FCF and ferric sulfate solutions were poured into 100-ml Florence flasks and diluted with distilled water to 100 ml. The pH of the solutions was adjusted to 3.0 using a dilute solution of sulfuric acid while using a pH meter (Metrohm, Switzerland). The reactions were initiated by adding an appropriate predetermined amount of hydrogen peroxide to the beaker. All experiments were sampled using a pipette at regular time intervals. In order to retard the decolorization process, each 1-ml sample was mixed with 1 ml of ethanol. At the end of the reaction, all samples were analyzed spectrophotometrically.

**Table 1.** Characteristics of the 2 commercial dyes.

Dye	Color Index Number	$M_w$ (g mol <sup>-1</sup> )	$\lambda_{max}$ (nm)	Structure
Brilliant Blue FCF (C.I. Acid Blue 9)	42090	792.86	637	
Orange II (C.I. Acid Orange 7)	15510	350	483	

### Analysis method

UV-Vis spectra of Brilliant Blue FCF were recorded in the wavelength range of 200-800 nm using a UV-Vis spectrophotometer (WPA S2000, England). The maximum absorbance wavelength ( $\lambda_{max}$ ) of Brilliant Blue FCF can be found at 637 nm. The concentration of Brilliant Blue FCF at different intervals was determined by measuring the absorption intensity and constructing a calibration curve. Chemical oxygen demand (COD) was measured using the standard volumetric method (closed reflux, titrimetric method) (Clesceri et al., 1989).

### Results and Discussion

#### Effect of initial Fe<sup>3+</sup> concentration

To determine the desired conditions of the Fenton-like reaction for decolorization of Brilliant Blue FCF, variables such as the effect of Fe<sup>3+</sup> concentration, H<sub>2</sub>O<sub>2</sub> concentration, and dye concentration on color removal efficiency were investigated. Figure 1 (a) shows the relationships between decolorization of Brilliant Blue FCF as a function of time in the presence of various Fe<sup>3+</sup> concentrations. Figure 1 (b) shows the variation in color removal efficiency with different initial Fe<sup>3+</sup> concentrations at the end of the reaction. This figure indicates that increasing

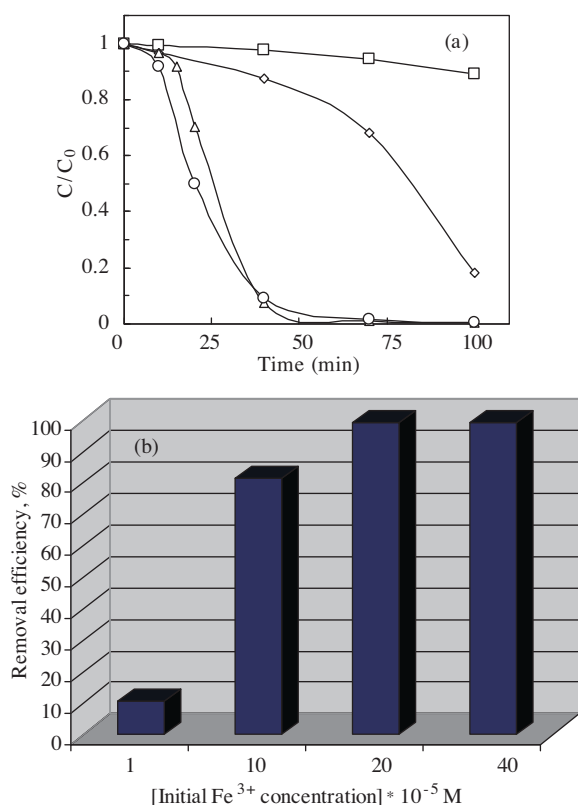
the Fe<sup>3+</sup> concentration led to an increase in Brilliant Blue FCF decolorization. When the Fe<sup>3+</sup> concentration increased to above  $2 \times 10^{-4}$  M, decolorization efficiency was more than 95% at the reaction time of 100 min; however, the extent of decolorization was negligible when the Fe<sup>3+</sup> concentration was less than  $10^{-5}$  M.

Decolorization of Brilliant Blue FCF in the initiation and termination phases fit the following pseudo-first-order kinetics. The results obtained from the fitting of  $\ln(C_o/C)$  versus reaction time date, based on the above-mentioned kinetic scheme, are reported in Table 3, where  $k_A$  is the pseudo-first-order reaction rate constant in the initiation phase and  $k_B$  is the pseudo-first-order reaction rate constant in the fast phase. The enhancement factor is  $k_B/k_A$ , which is an index for evaluating the acceleration of the decolorization process. The greatest enhancement factor was obtained at the  $2 \times 10^{-4}$  M Fe<sup>3+</sup> concentration. This indicates that by increasing the Fe<sup>3+</sup> concentration above  $2 \times 10^{-4}$  M the initiation phase accelerated more rapidly than the fast phase.

#### Effect of initial H<sub>2</sub>O<sub>2</sub> concentration

Figure 2 shows the effect of the initial H<sub>2</sub>O<sub>2</sub> concentration on Brilliant Blue FCF decolorization in a Fenton-like reaction. The extent of Brilliant Blue

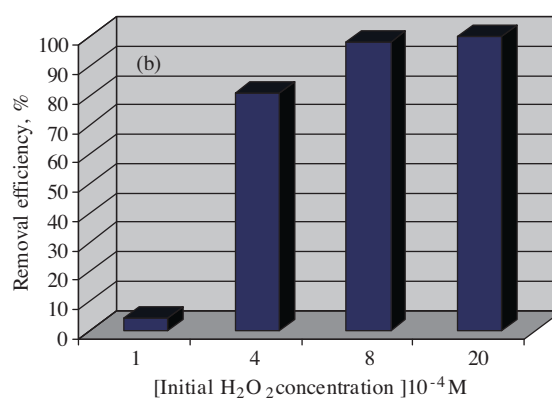
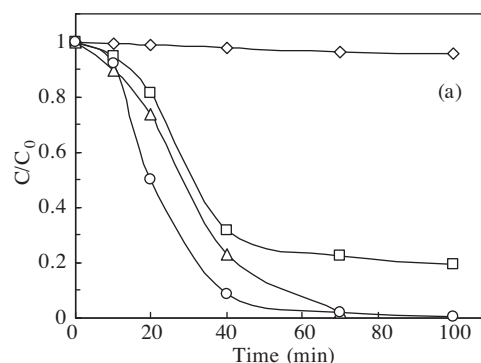
FCF removal increased as the  $H_2O_2$  concentration increased. The results indicate that when the  $H_2O_2$  concentration was  $2 \times 10^{-3}$  M, Brilliant Blue FCF decolorization was nearly completed at the reaction time of 100 min; however, when the  $H_2O_2$  concentration was  $10^{-4}$  M decolorization of Brilliant Blue FCF was minimal (5% at 100 min).



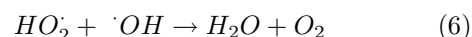
**Figure 1.** (a) The effect of various initial  $Fe^{3+}$  concentrations on Fenton-like decolorization of Brilliant Blue FCF. ( $\square$ )  $10^{-5}$  M; ( $\diamond$ )  $10^{-4}$  M; ( $\Delta$ )  $2 \times 10^{-4}$  M; ( $\circ$ )  $4 \times 10^{-4}$  M. (b) Variation in color removal efficiency (%) with different initial  $Fe^{3+}$  concentrations at the reaction time of 100 min.  $[BBF]_0 = 5 \times 10^{-5}$  M,  $[H_2O_2]_0 = 4 \times 10^{-4}$  M, pH = 3, in a dark environment.

The kinetic data scheme of Brilliant Blue FCF decolorization in various  $H_2O_2$  concentrations is shown in Table 4. According to this table, increasing the  $H_2O_2$  concentration up to  $8 \times 10^{-4}$  M had more of an effect on the initiation phase, whereas at concentrations above  $8 \times 10^{-4}$  M this enhancement declined. This shows that increasing further the  $H_2O_2$  concentration had no significant effect on decolorization in the fast phase. This is due to the fact that at higher  $H_2O_2$  concentrations scavenging of hydroxyl radicals

will occur, which can be expressed by Eqs. (5) and (6) (Lucas and Peres, 2006; Khataee et al., 2009):



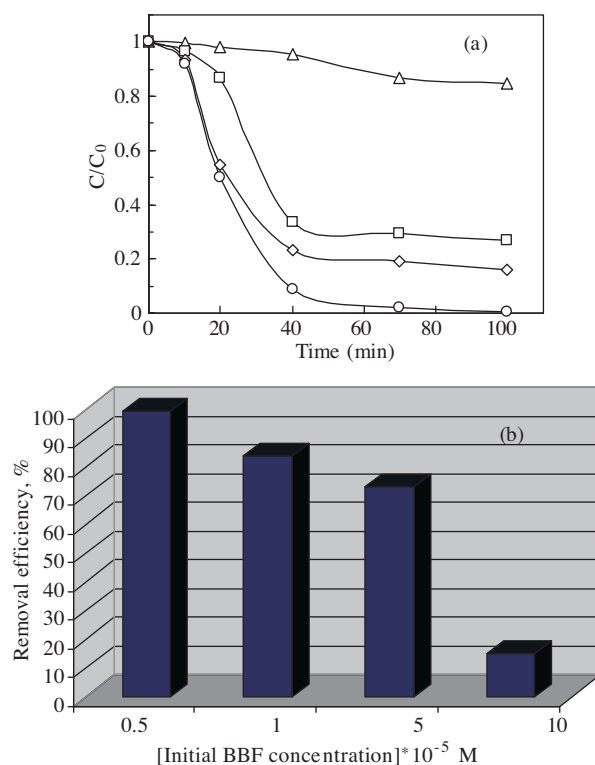
**Figure 2.** (a) The effect of various initial  $H_2O_2$  concentrations on decolorization of Brilliant Blue FCF. ( $\diamond$ )  $10^{-4}$  M; ( $\square$ )  $4 \times 10^{-4}$  M; ( $\Delta$ )  $8 \times 10^{-4}$  M; ( $\circ$ )  $2 \times 10^{-3}$  M. (b) Variation in color removal efficiency (%) with different initial  $H_2O_2$  concentrations at the reaction time of 100 min.  $[Fe^{3+}]_0 = 10^{-4}$  M,  $[BBF]_0 = 5 \times 10^{-5}$  M, pH = 3, in a dark environment.



### The effect of initial brilliant blue FCF concentration

The role of the initial Brilliant Blue FCF concentration on decolorization was tested and the results are reported in Figure 3. It can be seen that by increasing the initial concentration of BBF decolorization efficiency was decreased. More than 95% decolorization was achieved at the  $5 \times 10^{-6}$  M BBF concentration at the reaction time of 100 min, whereas at the BBF concentration of  $10^{-4}$  M less than 10% decolorization was observed at the same reaction time. The presumed reason is that when the initial concentration of the dye is increased hydroxyl radical

concentrations remain constant for all dye molecules and, hence, the removal rate decreases (Modirshahla et al., 2007). In other words, this is due to the fact that a lower concentration of the hydroxyl radical results from increasing the concentration of BBF, but the same concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{3+}$ , which led to a decrease in the decolorization efficiency of BBF (Sun et al., 2009).

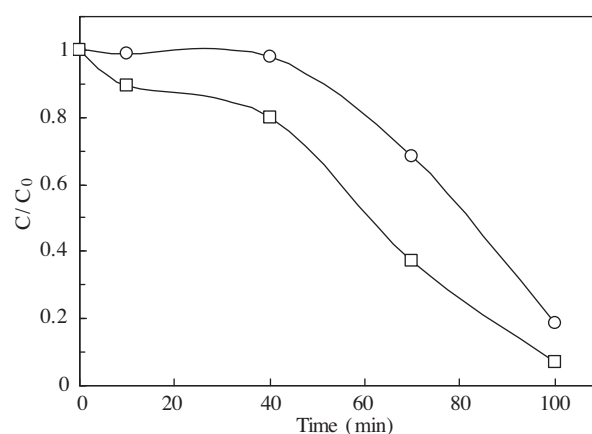


**Figure 3.** (a) The effect of various initial concentrations of Brilliant Blue FCF on decolorization efficiency. ( $\Delta$ )  $10^{-4}$  M; ( $\square$ )  $5 \times 10^{-5}$  M; ( $\diamond$ )  $10^{-5}$  M; ( $\circ$ )  $5 \times 10^{-6}$  M. (b) Variation in color removal efficiency (%) with different initial concentrations of BBF at the reaction time of 100 min.  $[\text{Fe}^{3+}]_o = 10^{-4}$  M,  $[\text{H}_2\text{O}_2]_o = 4 \times 10^{-4}$  M, pH = 3, in a dark environment.

### The effect of the presence of orange II

It has been reported that the presence of Orange II in a solution containing Malachite Green (MG) led to an increase in decolorization of MG (Chen et al., 2002). In consideration of the fact that Brilliant Blue FCF is a triphenyl methane dye, as is MG, we investigated whether this phenomenon also occurs with BBF. Figure 4 shows the effect of Orange II on decolorization of BBF. When we used only BBF,

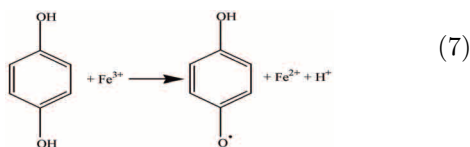
25% decolorization was achieved at the reaction time of 70 min, whereas when BBF was mixed with Orange II, 60% decolorization of BBF was achieved at the same reaction time. This was due to the formation of hydroquinone and hydroquinone-like intermediates during degradation of Orange II, which can accelerate the removal of BBF (Chen et al., 2002). Formation of hydroquinone-type compounds from the degradation of organic dyes such as Orange II has been reported. For example, Daneshvar et al. (2008) characterized hydroquinone-type compounds obtained from the degradation of Orange II. Özcan and co-workers (Özcan et al., 2008, 2009) identified hydroquinone as one of the by-products formed during electro-Fenton treatment of Orange II and Propam. In addition, hydroquinone has been identified as the degradation product of the azo dyes, such as azobenzene, *p*-methyl red, and methyl orange (Guivarch et al., 2003).



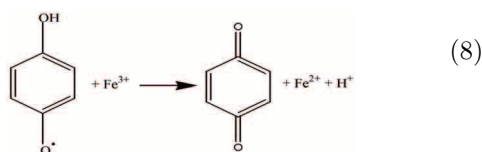
**Figure 4.** The effect of Orange II on decolorization of Brilliant Blue FCF.  $[\text{Fe}^{3+}]_o = 10^{-4}$  M,  $[\text{H}_2\text{O}_2]_o = 4 \times 10^{-4}$  M,  $[\text{Orange II}]_o = 10^{-5}$  M,  $[\text{BBF}]_o = 5 \times 10^{-5}$  M, pH = 3, in a dark environment. ( $\circ$ ) BBF only; ( $\square$ ) in the presence of Orange II.

The mechanism of acceleration of the Fenton-like reaction by hydroquinone-like intermediates is shown in Eqs. (7)-(9). According to this mechanism, hydroquinone efficiently reduces ferric ions to ferrous ions and, hence, accelerates the slow step of the Fenton reaction (Patel and Willson, 1973; Chen and Pignatello, 1997; Chen et al., 2002).

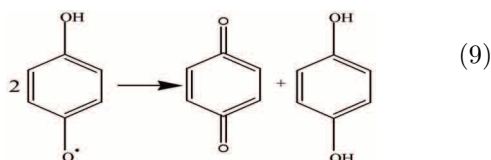
$$K = 4.4 \times 10^2 M^{-1} s^{-1}$$



$$K = 4.4 \times 10^4 M^{-1} s^{-1}$$



$$K = 1 \times 10^9 M^{-1} s^{-1}$$

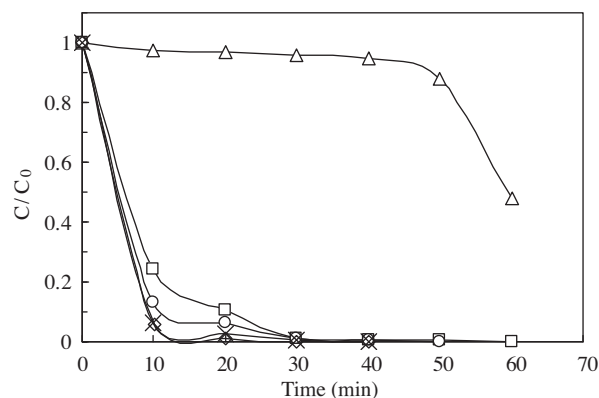


As such, Orange II itself, or some intermediates generated via its degradation could accelerate the removal of BBF by accelerating hydroxyl radical production. This observation is in good agreement with previous reports. Kerem et al. (1997) reported evidence that a hydroquinone-driven Fenton reaction was an important component of effective degradation of organic contaminants. Chen et al. (2002) reported degradation of MG by a Fenton-catalyzed process using aromatic compounds (hydroquinone, salicylic acid, quinine, carboxylic aromatic derivatives, and amido aromatic derivatives). Du et al. (2006) indicated that enhancement of the degradation of phenolic compounds by a Fenton-like reaction was due to the role of some hydroquinone-like intermediates, such as hydroquinone.

### The effect of different aromatic additives

Aromatic derivatives are the main pollutants in wastewater. Most dye-contaminated wastewaters contain various kinds of aromatic derivatives, such as phenol and hydroquinone. A detailed study on their effect on the Fenton reaction would provide a better understanding of the Fenton reaction mechanism and could be significant and useful in the application of the Fenton reaction to treating wastewater containing complicated components.

As previously mentioned, intermediate compounds generated by the degradation of organic dyes can include catechol, hydroquinone, benzoquinone, maleic acid, oxalic acid, and acetic acid. Such intermediates can affect the mechanism of Fenton-like reactions (Patel and Willson, 1973; Chen and Pignatello, 1997; Zhao et al., 2002; Lv et al., 2005; Yingxum et al., 2006). Decolorization of BBF in the presence of gallic acid, hydroquinone, salicylic acid, maleic acid, oxalic acid, and acetic acid was studied. The results depicted in Figure 5 confirm that each of these aromatic additives had a catalytic effect on the decolorization of BBF in a Fenton-like reaction. For example, the efficiency of BBF decolorization in the presence of gallic acid, salicylic acid, and 2-nitrophenol was 95%, 87%, and 75% at the reaction time of 10 min, respectively. The effect of aromatic additives depends on many parameters. The following are the most important possible parameters:



**Figure 5.** The effect of various aromatic additives on Brilliant Blue FCF decolorization.  $[\text{Fe}^{3+}]_0 = 10^{-4} \text{ M}$ ,  $[\text{H}_2\text{O}_2]_0 = 2 \times 10^{-3} \text{ M}$ ,  $[\text{Additive}] = 10^{-5} \text{ M}$ ,  $[\text{BBF}]_0 = 5 \times 10^{-5} \text{ M}$ ,  $\text{pH} = 3$ , in a dark environment. ( $\Delta$ ) 1,4-Naphthanol; ( $\square$ ) 2-nitrophenol; ( $\circ$ ) salicylic acid; ( $\times$ ) 1,4-hydroquinone; ( $\diamond$ ) gallic acid.

#### 1. Type of functional groups on the aromatic ring:

Functional groups can exist in electron-acceptor and electron-donor states. The electron-acceptor groups accelerate the attack of OH radicals on the aromatic ring. Aromatic additives were converted rapidly to hydroquinone and hydroquinone-like intermediates. It is obvious that by increasing the electrophilic effect of functional groups, the catalytic ef-

fect of intermediates increased. The electrophilic effect of the  $-\text{COOH}$  functional group was higher than that of the  $-\text{NO}_2$  functional group, which led to a stronger catalytic effect of gallic acid and salicylic acid, in comparison with 2-nitrophenol (Figure 5). In addition, it has been reported that amido aromatic additives tend to react with protons to generate ammonium in acidic solution under Fenton-like reaction conditions. They are less likely to undergo electrophilic attack by hydroxyl radicals and transform into hydroquinone-like compounds. As a result, amido aromatic additives do not exhibit catalytic effects in a Fenton-like reaction (Zhao et al., 2002).

### 2. Stereo-structure of aromatic additives:

Linkage of big groups such as phenyl can affect the activity of aromatic intermediates. When 1,4-dihydroxynaphthalene was used, the smallest effect on decolorization of BBF was observed (see Tables 2 and 5).

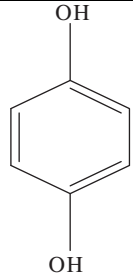
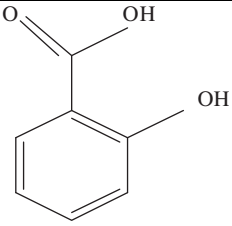
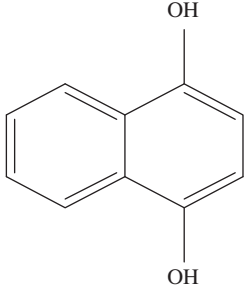
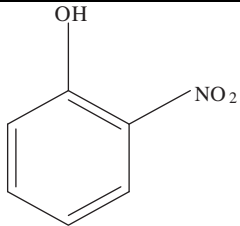
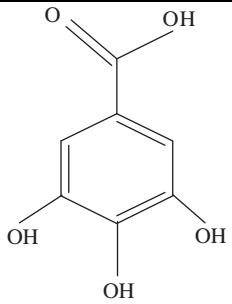
Kinetic data on the presence of different aromatic additives in decolorization of BBF by a Fenton-like reaction are reported in Table 5. According to this Table, the greatest catalytic effect was produced by gallic acid. The Fenton-like reaction rate of BBF after addition of various kinds of aromatic additives were in the following order: gallic acid > hydroquinone > salicylic acid > 2-nitrophenol > 1,4-dihydroxynaphthalene. As it is clear from Table 5, there is no indication of the termination phase ( $k_B$ ) for salicylic acid, gallic acid, hydroquinone, or 2-nitrophenol, which shows that these additives undergo reaction (7) at a very high speed. Therefore, a 3-phase Fenton-like reaction was converted to a 1-phase reaction, like the Fenton reaction. In other words, by adding aromatic derivatives, a 3-phase Fenton-like reaction was converted to a 1-phase reaction, like the Fenton reaction, except in the case of 1,4-dihydroxynaphthalene.

### The effect of varying the concentration of hydroquinone additive

The influence of different initial concentrations of hydroquinone additive was evaluated between  $0.2 \times 10^{-5}$  M and  $10^{-4}$  M, and the results are shown in Figure 6. At first, as the hydroquinone concentration increased from  $0.2 \times 10^{-5}$  to  $5 \times 10^{-5}$  M, the extent of BBF decolorization increased, whereas when the hydroquinone concentration was increased to  $10^{-4}$  M BBF decolorization decreased. With a high concentration of hydroquinone added, the extent of to-

tal organic material in solution increased and, consequently, required more OH radicals for decolorization.

**Table 2.** Characteristics of the aromatic additives.

Aromatic additives	Structure
Hydroquinone	
Salicylic Acid	
1,4-Dihydroxynaphthalene	
2-Nitrophenol	
Gallic Acid	

**Table 3.** Kinetic data on the influence of different  $\text{Fe}^{3+}$  initial concentrations on decolorization of BBF by a Fenton-like reaction.  $[\text{BBF}]_0 = 5 \times 10^{-5}$  M,  $[\text{H}_2\text{O}_2]_0 = 4 \times 10^{-4}$  M, pH = 3.

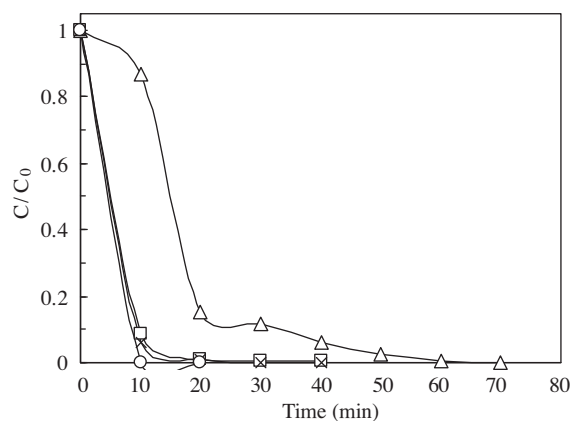
Initial concentration of $\text{Fe}^{3+}$	$k_A$ ( $\text{min}^{-1}$ )	$k_B$ ( $\text{min}^{-1}$ )	Enhancement factor
$[\text{Fe}^{3+}] = 10^{-5}$ M	0.0006 ( $R^2 = 0.999$ )	0.0016 ( $R^2 = 0.976$ )	2.67
$[\text{Fe}^{3+}] = 10^{-4}$ M	0.0053 ( $R^2 = 0.9511$ )	0.0259 ( $R^2 = 0.8639$ )	4.89
$[\text{Fe}^{3+}] = 2 \times 10^{-4}$ M	0.0052 ( $R^2 = 0.9133$ )	0.084 ( $R^2 = 0.9873$ )	16.15
$[\text{Fe}^{3+}] = 4 \times 10^{-4}$ M	0.0084 ( $R^2 = 0.999$ )	0.0666 ( $R^2 = 0.9883$ )	7.93

**Table 4.** Kinetic data on the influence of different  $\text{H}_2\text{O}_2$  initial concentrations on decolorization of BBF by a Fenton-like reaction.  $[\text{Fe}^{3+}]_0 = 10^{-4}$  M,  $[\text{BBF}]_0 = 5 \times 10^{-5}$  M, pH = 3.

Initial Concentration of $\text{H}_2\text{O}_2$	$k_A$ ( $\text{min}^{-1}$ )	$k_B$ ( $\text{min}^{-1}$ )	Enhancement factor
$[\text{H}_2\text{O}_2] = 10^{-4}$ M	0.0005 ( $R^2 = 0.999$ )	0.0006 ( $R^2 = 0.999$ )	1.2
$[\text{H}_2\text{O}_2] = 4 \times 10^{-4}$ M	0.0102 ( $R^2 = 0.9276$ )	0.0383 ( $R^2 = 0.9578$ )	3.75
$[\text{H}_2\text{O}_2] = 8 \times 10^{-4}$ M	0.0153 ( $R^2 = 0.976$ )	0.0741 ( $R^2 = 0.9915$ )	4.84
$[\text{H}_2\text{O}_2] = 2 \times 10^{-3}$ M	0.0346 ( $R^2 = 0.8397$ )	0.0653 ( $R^2 = 0.9809$ )	1.89

**Table 5.** Kinetic data on the presence of different aromatic additives on decolorization of BBF by a Fenton-like reaction.  $[\text{Fe}^{3+}]_0 = 10^{-4}$  M,  $[\text{H}_2\text{O}_2]_0 = 2 \times 10^{-3}$  M,  $[\text{Additive}] = 10^{-5}$  M,  $[\text{BBF}]_0 = 5 \times 10^{-5}$  M, pH = 3.

Additives	$k_A$ ( $\text{min}^{-1}$ )	$k_B$ ( $\text{min}^{-1}$ )	Enhancement factor
Gallic acid	0.2318 ( $R^2 = 0.9878$ )	-	-
Hydroquinone	0.1555 ( $R^2 = 0.9381$ )	-	-
Salicylic acid	0.1393 ( $R^2 = 0.9844$ )	-	-
2-Nitrophenol	0.1162 ( $R^2 = 0.9692$ )	-	-
1,4-Dihydroxynaphthalene	0.0012 ( $R^2 = 0.9357$ )	0.0339 ( $R^2 = 0.8339$ )	28.25

**Figure 6.** The effect of different initial concentrations of 1,4-hydroquinone on decolorization of Brilliant Blue FCF.  $[\text{Fe}^{3+}]_0 = 10^{-4}$  M,  $[\text{H}_2\text{O}_2]_0 = 2 \times 10^{-3}$  M,  $[\text{BBF}]_0 = 5 \times 10^{-5}$  M, pH = 3, in a dark environment. ( $\Delta$ )  $2 \times 10^{-6}$  M; ( $\square$ )  $10^{-4}$  M; ( $\times$ )  $2.5 \times 10^{-5}$  M; ( $\circ$ )  $5 \times 10^{-5}$  M.

By considering Figure 1 (a) it can be concluded that decolorization of Brilliant Blue FCF via a Fenton-like reaction was a 3-phase reaction:

1. The first step or initiation phase: The Fenton-like reaction was performed according to reaction (2) with slow speed, resulting in  $\text{Fe}^{2+}$  generation;
2. The second step or fast phase:  $\text{Fe}^{2+}$  generated at the initiation phase followed reaction (1), but this reaction was very fast. The consumption rate of  $\text{H}_2\text{O}_2$  and the formation rate of  $\text{Fe}^{2+}$  both increased rapidly;
3. The last step or termination phase:  $\text{H}_2\text{O}_2$  concentration decreased rapidly due to consumption at the initiation and termination phases (Yingxum et al., 2006).



### Mineralization of the dye solution

Mineralization of the dye solution was followed by measurement of COD, before and after treatment of the dye solution. COD of the initial dye solution was measured using the standard volumetric analytical method (Clesceri et al., 1989). Then subsequent to decolorization by a Fenton-like reaction under optimized conditions ( $[BBF]_o = 5 \times 10^{-5}$  M,  $[Fe^{3+}]_o = 4 \times 10^{-4}$  M,  $[H_2O_2]_o = 4 \times 10^{-4}$  M, pH = 3, reaction time of 150 min), COD of the treated solution was measured again and COD was reduced by about 80%.

### Conclusion

This study considered the influence of experimental parameters and aromatic additives on the Fenton-like treatment of Brilliant Blue FCF. From the experimental results it can be concluded that the Fenton-like reaction completely decolorized the solutions containing BBF and is, therefore, a suitable process for removing color from dye-polluted solutions. It is necessary, however, to continue the process until the complete removal of the different intermediates

produced during degradation of the dye. In all the experiments of BBF decolorization without aromatic additives, kinetic data showed that Fenton-like decolorization proceeded through 3 phases: the initiation phase, the fast phase, and the termination phase; however, by adding aromatic derivatives, a 3-phase Fenton-like reaction was converted to a 1-phase reaction, like the Fenton reaction, except in the case 1,4-dihydroxynaphthalene. The results show that aromatic additives effectively catalyzed the Fenton-like degradation of BBF in a dark environment. The catalytic ability of the aromatic additives followed the order: gallic acid > hydroquinone > salicylic acid > 2-nitrophenol > 1,4-dihydroxynaphthalene. Addition of Orange II to BBF solution increased BBF decolorization. This finding can be attributed to the fact that one of the intermediates generated in Orange II degradation probably accelerated the regeneration of  $Fe^{2+}$  via the reduction of  $Fe^{3+}$  and, therefore, accelerated BBF degradation.

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