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**Research Article** 

# Removal of Azo Dyes From Aqueous Solution Using Fenton and Modified Fenton Processes

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**Background:** Fenton ( $Fe^{2+}$  and  $H_2O_2$ ) and modified Fenton ( $Fe^{3+}$  and  $H_2O_2$ ) are two popular methods used in advanced oxidation processes (AOP) and degradation of persistent organic pollutants (POPs), such as dye compounds. In these processes,  $Fe^{2+}$  and  $Fe^{3+}$  as catalysts and  $H_2O_2$  as the oxidizing agent are added to the reactor.

**Objectives:** The aim of the current study is to assess the abovementioned methods for removal of Reactive Red 198 and Blue Reactive 19 from aqueous solutions.

**Materials and Methods:** This research was carried out using lab-scale. After preparation of RB-19 and RR-198 stock solutions (1000 ppm), optimum pH and temperature were determined within the range of (3-11) and (15°C - 40°C) respectively, and specific amounts of Fe<sup>2+</sup> and Fe<sup>3+</sup> (0.8, 1, 3, 7, 14 and 32 mM) were prepared by adding FeSo<sub>4</sub>. 7H<sub>2</sub>O and FeCl<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub> 30% W/W (2, 5, 11, 23, 47 and 94 mM) were added to the solutions to establish the H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>, Fe<sup>3+</sup> molar ratios. Standard jar tests were conducted using jar test apparatus. After sedimentation time, samples were filtered through a 0.45 µm fiber membrane, and then final dye concentrations were measured using a UV/VIS spectrophotometer.

**Results:** The highest dye removal efficiency in both Fenton and modified Fenton methods were obtained at the optimum pH=3, optimum reaction time of 10 minutes, optimum temperature at 25°C and  $H_2O_2/Fe^{2+}$  and  $H_2O_2/Fe^{3+}$  concentrations of 11.3 and 5.1 mM, respectively. In the Fenton reaction the maximum efficiency was obtained at 94.70% and 99.31% for reactive red 198 and reactive blue 19, respectively. Moreover, by the modified Fenton method the maximum removal efficiency for reactive red 198 and reactive blue 19 was 94.8% and 99.43%. **Conclusions:** Fenton and modified Fenton processes could be used as very effective methods for removal of reactive red 198 and blue reactive 19 from aqueous solutions.

Keywords: Fenton's reagent; reactive red 198; Adsorption; Waste Water

## 1. Background

Textile and dyeing industrial are considered as the major sources of water consumption. According to the production rate, water consumption varies between 25 - 250 m<sup>3</sup>/ton of product. The resulting wastewater contains BOD, COD and synthetic dyes (1, 2), and discharge of contaminated effluent without any treatment into the environment creates depressed photosynthesis and aquatic plant demise which characteristics are considered as environmental threats (3). Dyes are substances with complex structures which contain atoms: electron acceptors such as chromophore or electron donors such as ecsocrimium, which determine its strength and solubility in water (4, 5). Based on the application, dyes are categorized as Watt, reactive, direct, cation, acidic and disperse, of which Azo dyes are found in more than 50% of dyes (6, 7). Azo reactive dyes are anionic and soluble in water. Because of their variety of colors, easy utilization, good stability during washing and low energy consumption, Azo dyes are applied more frequently in the textile industry (5, 8). These dyes have strong resistance to photolysis and chemical decomposition, and in some cases there are special components in their structures that have carcinogenic and mutagenic consequences (5, 9). Even the presence of a small quantity of dye (less than 1 ppm) in water has adverse effects. Synthetic dyes are used in abundance by textile (60%), paper making (10 %) and plastics industries. Now, over 10000 varied types of commercial pigments and dyes are produced annually, about  $7 \times 10^5$  tons (10). Their absorption into biological masses are very weak and there is no decomposition in aerobic conditions. Reactive red 198 and blue reactive 19 are mono Azos which are used in textile plants in Iran

Implication for health policy/practice/research/medical education:

Fenton and modified Fenton are effective methods in advanced oxidation. These processes can be used for dye removal from textiles and industrial wastewater. Moreover, they are highly economical in removing such dyes. This study can be used by experts, researchers, environmental students and industrial managers.

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(3, 11, 12). Different technologies are applied to decrease absorption of these dyes into the environment such as ion exchange, chemical sedimentation, electrochemical reduction, advanced oxidation, membrane process and absorption (13-15).

The limitations of the available technologies include dense solution disposal, high energy consumption, high operation costs, excessive production of sludge, expensive facilities (16-18). Therefore, finding new and effective alternatives is necessary to remove contaminants from aquatic environments. One effective technique is advanced oxidation which can be used to remove toxic and resistant chemicals and reprocess them into mineral form to release carbon dioxide and oxygen. Advanced chemical oxidation processes such as chemical, photochemical, photocatalytic methods and electrochemical methods (UV/O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>, Fenton, modified Fenton, and ultrasound) are decrepitating and produce hydroxyl radicals. In this process, hydroxyl radicals using Fe(II) and Fe(III) catalysts are generated easily as follows (19-21):

Fenton reactions:

1.  $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{\bullet}$ 2.  $Fe^{3+} + H_2O_2 \rightarrow Fe \cdot OOH^{2+} + H^{+}$ 3.  $Fe \cdot OOH^{2+} \rightarrow Fe^{3+} + O_2H^{\bullet}$ 4.  $Fe^{3+} + O_2H^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+}$ 5.  $Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{\bullet}$ 6.  $H_2O_2 + OH^{\bullet} \rightarrow H_2O + O_2H^{\bullet}$ 7.  $OH^{\bullet} + Reactive dye production$ Reactions related to modified Fenton process: 1.  $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+}$ 2.  $HO_2^{\bullet} \rightarrow O_2^{\bullet} + H^{+}$ 3.  $HO_2^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^{+}$ 

Efficiency of the advanced oxidation process is ds on the oxidation rate of hydroxyl radical. These radicals have high reaction rates, oxidation potential, low selectivity for organic components and will destroy contaminants in four ways: (i) addition of OH<sup>-</sup> to structure of contaminant (ii) hydrogen absorption (iii) electron transmission (iv) reaction between free radicals that can lead to the formation of stable compounds. Among the various processes of advanced oxidation, using the Fenton  $(H_2O_2)$ Fe<sup>2+</sup>) and modified Fenton (H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup>) methods have greater advantages, such as simple operation, low reaction time, using of coagulation and flocculation processes, non-toxic compound production, economic viability, and possibility of utilization at different scales. Disadvantages include costly treatment processes and disposal of sludge, ferrous ions are consumed faster than produced, the process is limited to low pH range, and deactivation of iron ions due to bonding of iron ions with various reagents such as anion phosphate, oxidation of the product as well as further water pollution due to existence of catalysts such as iron salt. The main steps involved in the Fenton process are (i) oxidation, (ii) neutralization, (iii) flocculation and (iv) sedimentation (22-24). Research shows that modified Fenton is very effective in treating colored wastewater but so far little research has been done using this method.

## 2. Objectives

This paper presents a brief review on the role of Fenton and modified Fenton reactions in the removal of contaminants (blue reactive 19 and reactive red 198) from aqueous solutions.

## 3. Materials and Methods

Reactive dyes were bought from Alvan Sabet Company (Iran); other chemical material was obtained from Merck Company (Germany). The chemical structures and a number of the physicochemical properties of the dyes used are listed in Table 1.

This research was carried out using lab-scale in chemistry laboratory of Zahedan University of Medical Sciences. The advanced oxidation experiments were started in a Plexiglas reactor (1 L) as batch system. Ranges of experimental parameters are given in Table 2. After preparation of RB-19, RR-198 Stock solutions (1000 ppm), working solutions were made by dissolving stock solution in deionized water. After determination of optimum pH within range of (3-11) and temperature (15°C - 40°C), specific amounts of  $Fe^{2+}$  and  $Fe^{3+}$  (0.8, 1, 3, 7, 14 and 32 mM) were prepared by adding FeSo<sub>4</sub>.7H2O and FeCl<sub>3</sub>, and determined amounts of H<sub>2</sub>O<sub>2</sub> 30% W/W (2, 5, 11, 23, 47 and 94 mM) were added to the solution to create the  $H_2O_2/Fe^{2+}$ and H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup> molar ratios. Standard Jar Tests were conducted using jar test apparatus (model OSK8996). After sedimentation time, supernatant samples were collected from the solution using a 50 mL pipet. Collected samples were filtered through a 0.45 µm fiber membrane, then final dye concentrations were measured using a UV/VIS spectrophotometer (optima SP-3000 plus) at 590 nm for RB-19 and 518 nm for RR-198. The dye removal percentage (R%) was calculated as follows (Equation 1):

Equation 1. 
$$R\left(\%\right) = rac{C_0 - C}{C_0} imes 100$$

Where  $C_0$  is the initial concentration (mg/L) and C is the final dye concentration (mg/L).

#### 4. Results

It has been established that pH has a significant influence on the performance of oxidation processes. In the present study the effect of pH (3-11) on removal of two dyes, reactive red 198 (RR198) and blue reactive 19 (RB 19), were investigated. Figure 1 shows that the highest removal efficiency for the dyes studied occurred at pH 3 for both processes, modified Fenton and Fenton. Final values of pH samples at the end of the experiments are presented in Figure 2. Optimum reaction time for Fenton and modified Fenton methods depends on the initial concentration and variance of catalyst dosage. Dye removal efficiency was investigated at fixed pH and  $H_2O_2/Fe^{2+}$ ,  $Fe^{3+}$  ratio conditions. As it can be seen in Figure 3, optimum reaction time for both processes was obtained at 10 minutes.

Temperature has a positive effect on treatment efficiency; hence, six temperatures were investigated in this study. As shown in Figure 4, the best removal efficiency for both methods was obtained at 25°C. In addition, this effect was studied in various molar ratios. Maximum dye removal in optimum molar ratios in Fenton and modified Fenton methods were obtained at  $H_2O_2/Fe^{2+}$  = 11.3 and  $H_2O_2/Fe^{3+}$  = 5.1, respectively (Figures 5 to 8). To determine the effect of dye concentration on removal efficiency, mentioned dyes were examined at three concentrations (10, 50 and 500 mg/L). Figures 5 to 8 reveal dye removal efficiency in various concentrations. As can be seen, removal efficiency was increased by increasing dye concentration.

Characteristics	Reactive Red 198	Reactive Blue 19
Chemical structure		NH <sub>2</sub> SO <sub>3</sub> Na U H S CH <sub>2</sub> CH <sub>2</sub> OSO <sub>3</sub> Na
Molecular formula	C <sub>27</sub> H <sub>18</sub> C <sub>1</sub> N <sub>7</sub> Na <sub>4</sub> O <sub>15</sub> S <sub>5</sub>	$C_{22}H_{16}O_{11}N_2S_3Na_2$
Molecular weight, g/mol	967.5	626.5
λmax, nm	520	592
Table 1. Characteristics of Dyes Used		
Table 2. Ranges of Experimental Parameters <sup>a</sup>		
Parameters		Ranges of Experimental
Mixing speeds, rpm		
1 min		80
80 min		30
Temperatures, 'C		15, 20, 25, 30, 35, 40
Sampling Times, min		10, 20, 40, 80
Initial dyes concentrations, Mg/L		10, 50, 500
$H_2O_2$ concentrations, mM		2, 5, 11, 23, 47, 94
Fe <sup>3+</sup> ,Fe <sup>4+</sup> concentrations, mM		0.8, 1, 3, 7, 14, 32
<u>pH</u>		3, 5, 7, 9, 11
<sup>d</sup> Abbreviation: rpm_revolutions per minute		

Figure 1. Effect of pH on Reactive Red 198 and RB-19 Removal Percentage in Fenton and Modified Fenton Methods



Temperatures 25°C, reaction time of 20 minutes, dyes concentrations 50 mg/L,  $H_2O_2/Fe^{2+}$ ,  $Fe^{3+} = 11.3$ .









Temperatures 25°C, pH = 3, dye concentration 50 mg/L,  $H_2O_2/Fe^{2+}$ ,  $Fe^{3+}$ =11.3.

pH = 3, reaction time of 10 minutes, dyes concentrations 50 mg/L,  $H_2O_2/Fe^{2+}$ ,  $Fe^{3+} = 11/3$ .

40

Figure 5. Removal Percentage and Residue Concentration of reactive red 198 in Different Dye Concentrations and Molar Ratios of H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> in Fenton Method



Temperatures 25°C, pH = 3, reaction time of 10 minutes.

Figure 6. Removal Percentage and Residue Concentration of Reactive Blue 19 in Different Dye Concentrations and Molar Ratios of H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> in Fenton method





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**Figure 7.** Removal Percentage and Residue Concentration of Reactive Red 198 in Different Dye Concentrations and Molar Ratios of H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup> in Modified Fenton Method

**Figure 8.** Removal % and Residue Concentration of Reactive Blue 19 in Different Dye Concentrations and Molar Ratios of H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup> in Modified Fenton Method



Temperatures 25 °C, pH = 3, reaction time of 10 minutes.

Temperatures 25 °C, pH = 3, reaction time of 10 minutes.

#### 5. Discussion

The present study has evaluated a number of parameters such as pH, contact time, temperature, initial hydrogen peroxide  $H_2O_2$  concentration and iron (II), iron (III) concentrations.

## 5.1. Effect of pH

pH is one of the effective parameter on dye removal efficiency in Fenton and modified Fenton processes. pH plays an important role in production of radicals that are effective in increase of oxidation efficiency. It has been proven that the Fenton reactions in acidic pH are more effective than neutral pH (25); On the other hand, oxidation reactions are slower in neutral pH due to hydroxylation of iron (26). Figures 1 and 2 show that the maximum removal percentage reached is 95% in pH = 3, thus the optimum pH was obtained as 3 for all of samples. In pH > 3, because of Fe(III) sedimentation, Fenton efficiency decreases, the synthetic hydroxide produced can hydrolyze the available hydrogen peroxide to other products (O<sub>2</sub> and H<sub>2</sub>O) that subsequently cause oxidation and hydroxyl ions decline. Moreover in pH > 3, the Fe(II) [Fe(II)  $(H_2O)_6]^{2+}$  substance can react with hydrogen peroxide peroxide better than the Fe(II) [Fe(II) (OH)  $(H_2O)_{\epsilon}^{2+}$ ] substance (27, 28). In lower pH, the additionally droxide ions react in reverse which leads to further Fe(III) production. As shown in Figure 8 below (27).

8.  $Fe^{3+} + H_2O_2 \rightarrow Fe - OOH^{2+} + H^+$ 

As shown above, the generation of Fe(III) to Fe(II) is prohibited and as a result the available Fe(II) concentration producing hydroxyl radical was declined. These results are in accordance with other reported research (29). In the Fenton method, iron ions will become sediment in higher pH in the form of ferric hydroxide. In low pH iron ions can form a stable substance with hydrogen peroxide leading to the inactivation of the catalyst and subsequently removal efficiency decreases. Acidic solutions have a propensity to produce hydrogen peroxide (Equation 9), but according to equation 10, in low pH, the number of active sites for hydrogen peroxide is declined. In pH < 3 hydrogen peroxide forms ecsoniumion and remains constant. According to other research, pH = 3 because of renewed production of Fe(II) via reaction between Fe(III) and hydrogen peroxide, the Fenton process has less effect (10, 22, 23).

9.  $O_2 + 2H^+ + 2^{e_-} \rightarrow H_2O_2$ 10.  $H_2O_2 + 2H^+ + 2^{e_-} \rightarrow 2H_2O$ 11.  $H_2O_2 + H^+ \rightarrow H_2O_2$ 

$$\Pi_{2}\Pi_{2}\Pi_{2} \to \Pi_{3} \Pi_{2} \Pi_{2}$$

Figure 5 shows the final pH of the solution and it can be concluded that by increasing the iron concentration, the pH decreases from 4 to 2.5; this may be due to the hydrolysis of water and production of further H<sup>+</sup> ions (28). Yuang et al. obtained optimum pH = 2 - 4 for treatment of pharmacy wastewater; also the optimum pH for dye removal was 3 - 4 (30, 31).

## 5.2. The Effect of Contact Time

To study the optimum time and its effect in the Fenton and modified Fenton processes, experiments were performed for 10 to 80 minutes to determine optimum time of the Fenton and modified Fenton efficiency in dye removal. As shown in Figure 3, maximum efficiency was attained at 10 minutes for both of the processes which was more than 94%. It is clear that removal efficiency increase was linear and slow thereafter. Linear increase of dye removal efficiency can be related to chemical oxidation of dye by OH. In advanced chemical oxidation, with methods other than the Fenton process, OH production in the environment is continuous, but in the Fenton process high concentrations of OH are produced n the first minutes of the process (29). Fenton oxidation of organic compounds showed that in the early stages the initial rate of mineralization was fast with Fenton reagents, due to the immediate formation of hydroxyl radicals, where the color could obviously be reduced. It demonstrated that the recalcitrant organic compounds which were in the wastewater had been oxidized by HO• after reaction time of 60 minutes, resulted in the curve slightly ascending (21). In the Fenton oxidation system, the hydroxyl radicals made, which had extremely high oxidizing ability, could oxidize into hardness with the decomposition of organic compounds in a short time. Also after the rapid and slow mixing, large amounts of pinpoint flocs were consistently observed and took a very long time to settle down. These tiny amounts of floc frequently interfered with color and measurement. The majority of color was generally removed after rather short oxidation times: one minute (26), 10 minutes (18), and 15 minutes (27).

#### 5.3. The Effect of Temperature

Although temperature has a positive effect on treatment efficiency in the Fenton process, it has a less effect than other factors. Very low or high temperature has adverse results on the efficiency process (28). Figure 5 shows the highest removal efficiency at 25°C. Goi et al. (32) reported that 30°C is as an optimum temperature for decomposition of silicicacid. Also it has been proven that temperatures between 20°C - 30°C can be used as the best temperature because of high efficiency (32). Zhang et al. concluded that COD removal efficiency was increased gradually by varying temperature from 15°C -35°C (28). Weng et al. reported that dye decomposition rate was less at lower temperatures (33). The optimum temperature was estimated to be 45°C (31). During the process, temperature hadtwo effects on accumulation of hydrogen peroxide peroxide: a) when temperature is increased, dissolving of oxygen decreased; b) peroxide had a low solubility in higher temperature. When temperature increased to more than 30°C, dye decomposition declined because of decomposition of hydrogen peroxide. Also the negative effect of temperature on contaminant removal can be described as low concentration of dissolved oxygen (DO) and spontaneous decomposition of peroxide in high temperatures (20). Usually when temperature increases, hydrogen peroxide concentration decreases, because increasing the temperature reduces DO to wastewater. Devi et al. reported that by increasing temperature from 30 to 50°C, Alizarin Red decomposed very well (34). Ayodele et al. (19) showed that phenol decomposition increased with varving the temperature from 22°C to 27°C: it also proved that by increasing the temperature, oxidation and mineralization rates improved by decreasing the hydrogen peroxide and Fe(II). This phenomenon can be due to the increasing reaction between hydrogen peroxide and any sort of iron ions that finally lead to generation of hydroxyl radicals or a high capacity of iron species (19).

## 5.4. The Effect of $H_2O_2$

In the Fenton process, hydrogen peroxide plays an essential role in contaminant removal efficiency. Figure 3 shows the effect H<sub>2</sub>O<sub>2</sub> concentration on reactive dye removal percentage from colored solutions. An increase in  $H_2O_2$  concentration from 2 to 5 mM causes an increasing in the dye removal percentage. Improvement in dye removal can be attributed to increase of hydroxyl radicals as a result of growing growth (31). When H<sub>2</sub>O<sub>2</sub> concentration increases, the reaction time gets shorter. Minimum removal efficiency was observed in higher concentrations of  $H_2O_2$  (> 5 mM). The slow decomposition of reactive dye at higher concentrations of  $H_2O_2$  was due to the conversion of the generated hydroxyl radicals to hydroxyl ions, reaction of hydroxyl radicals, prohibition of its formation and H<sub>2</sub>O<sub>2</sub> dissociation with oxygen and H<sub>2</sub>O that change precipitate Fe<sup>3+</sup> ions. The sequences above are in accordance with the following equations (35):

 $12. \text{H}_2\text{O}_2 \rightarrow \text{HO}^{\bullet} + \text{HO}^{\bullet}$ 

13.  $Fe^{2+}$  + HO<sup>-</sup> →  $Fe^{3+}$  + OH<sup>-</sup>

14.  $[Fe^{3+}][OH^-] \rightarrow Ksp Fe(OH)^3$ 

In other words, the deactivation of Fe<sup>2+</sup> takes place at higher dosages of  $H_2O_2$ , thus giving a brownish yellow precipitate at higher dosages (29). Zhang et al. (28)reported that efficiency of hydrogen peroxide for removing organic materials in the leachate decreased with the increase of Fenton's reagent dosage. At a high dosage of  $H_2O_2$ , the decrease in removal efficiency was due to the hydroxyl radical scavenging effect of  $H_2O_2$  (Equations 15 and 16) and the recombination of the hydroxyl radical (Equation 17) (10):

15.  $HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$ 16.  $HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2$ 17.  $2HO^{\bullet} \rightarrow H_2O_2$ 

According to the 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  $H_2O_2$ , according to reaction 18 (36):

18.  $OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O_2$ 

Reaction 18 contends better with reaction seven at higher concentrations of  $H_2O_2$ , reducing the oxidation rate of the target dye compound. Hydroxyl radical concentration increased when the  $H_2O_2/Fe^{2+}$  ratio increased that led to greater oxidation of dye. In this study,  $H_2O_2$  dosage in the Fenton and modified Fenton processes were chosen as 11 and 5 mM as the optimum dosage, respectively.

#### 5.5. The Effect of Iron Concentration

There are no hydroxyl radicals devoid of ions, so the iron ion concentration is essential because increasing the hydroxyl radicals and the coagulation phenomenon lead to a decrease of contaminants. Fenton efficiency can be enhanced by increasing the Fe(II) and Fe(III) concentration, since hydroxyl radical concentration [the same key oxidant] was increased by increasing the Fe(II) concentration. Hydrogen peroxide is not strong enough to oxidize big molecules such as pigments in wastewater dye without the presence of Fe(III) (37). By adding a quantity of Fe(III), removal efficiency will increase. Wang et al. reported that Fe(II) ions reduce COD amount by increasing Fe(II) (0.33 mM), where COD removal efficiency reached 43% from 19% (38). Zhou et al. found that methylene red removal was increased from 45% to 75% in presence of Fe(II) at 10 minutes (39). The effect of ferric and ferrous dosage on removal efficiency is shown in Figures 3 and 4; the plots illustrate that an increase in iron ion concentration, results in a decrease in the percentage of dye removal. The use of high concentrations of Fe<sup>2+</sup> (for a given hydrogen peroxide concentration) accelerated the rate of decomposition of the hydrogenperoxide generated perhydroxyl radicals [HO<sub>2</sub>•] which is considered to be the rate limiting step, while lower doses of Fe<sup>2+</sup> favored the reaction to generate OH\* which is mor ereactive than HO<sub>2</sub><sup>•</sup> radicals. Beyond the dosage, 2 mM inactivation of the Fe<sup>2+</sup> occurred owing to instantaneous formation of hydroxyl ion in accordance with the following reaction (33):

19. OH• + Fe<sup>2+</sup> →OH + Fe<sup>3+</sup>

This takes place at a faster rate than the formation of hydroxyl radical from  $Fe^{2+}$  and peroxide. In conclusion, more reduction in dye removal was observed as more catalyst was added earl in the reaction. The Fenton reaction occurred during the first 10 - 40 minutes. Then, the rate of Fenton reaction due to production of  $Fe^{+2}$  by  $Fe^{+3}$  became slower and decolorization stopped (37). By increasing the iron ions above these values, removal efficiency did not increased because of the tendency of the hydroxyl radicals to react with  $Fe^{2+}$  and  $H_2O_2$  in the oxidation-reduction reaction (29). In this paper,  $Fe^{2+}$  and  $Fe^{3+}$  dosage of 3 and 1 mM were selected as the optimum dosage respectively.

#### 5.6. The Effect of Dye Concentration

Dye concentration is effective on dye removal percentage. Figure 8 shows the effect of various dye concentrations (10, 50, 500 mg/L) on removal efficiency [pH = 3,Fe(II) and Fe(III) concentration 50 mg/L, contact time of 10 minutes]. The line reveals that an increase in the dye concentration from 10 to 500 mg/L, reduces the percentage of dye removal, because by increasing the concentration and keeping the H<sub>2</sub>O<sub>2</sub> value stable, the hydroxyl radicals produced also become stable, thereby the removal percentage will reduce (29, 36). RR-198 and RB-19 removal percentage was determined in 50 mg/L of dye. The Present study was performed with the aim of evaluating the Fenton and modified Fenton processes in removal of reactive red 198 and Reactive Blue 19 from aqueous environments. The effect of various operating parameters such as H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>, H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup>, pH, reaction time, temperature and initial concentration of dye was investigated. The results of this study showed that the most effective dye removal agents are  $H_2O_2/Fe^{2+}$ ,  $H_2O_2/Fe^{3+}$ , equal to 11/3 and 5/1 mM at pH = 3 respectively. Dye removal efficiency for reactive red 198 and Reactive Blue 19 utilizing the Fenton and modified Fenton processes were 99.43, 99.31, 94.8 and 90.98%, respectively (initial dye concentration 50 mg/L and reaction time of 10 minutes). The findings of this study showed that removal efficiency reduced with increase of dye concentration in fixed conditions for other parameters. Finally, it can be concluded that the modified Fenton process is superior to the Fenton process for dye removal from aqueous solutions.

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## **Authors' Contribution**

The overall implementation of this study including design, experiments and data analysis, and manuscript preparation which were the results of joint efforts by individuals who are listed as co-authors of this paper. All authors have made extensive contribution in the review and finalization of this manuscript.

## **Financial Disclosure**

There were no conflicts of interests.

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