Removal of Reactive Blue 19 Dye Using Fenton From Aqueous Solution

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Abstract
The discharge of wastewater containing reactive dyes into water sources leads to health hazards. Colors can adversely affect the natural environment due largely to some qualities like carcinogenicity, being mutagenic, toxicity, and coloration of water. Environmental degradation can be attributed to the destruction of living organisms and the increased biological oxygen demand (BOD). The aim of this study was to evaluate the removal of Reactive Blue 19 dye using the Fenton process from aqueous solution. This research was an experimental study, in which the effectiveness of Fenton in color removal was investigated. The factors influencing this process were: pH, color concentration, the ratio of Fenton reagent (H2O2/Fe2+), and contact time. Finally, after determining the optimum concentration of color, pH, the ratio of Fenton reagent, and contact time, the residual adsorption rates in the samples were measured using direct photometry by spectrophotometer in a wavelength of 594 nm. The results showed that the highest removal efficiency was obtained under the conditions of pH = 3, the color concentration of 2 mg/L, the ratio of Fenton reagent = 1:5, and the contact time equal to 10 minutes. The Fenton process is able to remove the Reactive Blue 19 under different concentrations. This process achieved the best removal efficiency in acidic pH.

Keywords: Reactive Blue 19, Color, Oxidation process, Fenton

1. Introduction
The entry of industrial sewage into the environment has raised concerns about surface water and groundwater, because this sewage contains different types of pollutants with varying quantities and qualities (1-3). Discharge of colored wastewater not only affects the aesthetic aspects of receiving water, but also prevents the aquatic environments from access to sunlight, causes the loss of photosynthesis, and disrupts biological processes. Many dyes are also toxic to some living organisms and can damage their health (4). The effluent from the textile industry is infinitely colored due to the use of a variety of dyes in various processes including dyeing, finishing, and processing the sewage treatment products, and thus they should be treated before entry to the environment (5-7). Reactive dyes are a series of water-soluble and anionic dyes which have been widely used in the textile industry for their variety, ease of use, brilliant colors, and low energy consumption (8). Azo dyes are one of the largest dye groups (70%) among all types of dyes (9). Studies have found that dyes have carcinogenic and mutagenic effects (10,11). Dyes also cause genetic changes in microbes and some fish (12). Due to having complex structures, toxic compounds, resistance to chemical and degradation, and carcinogenic potential, Azo dyes disturb the ecosystem; hence, in the produced wastewater of these industries, dyes should be removed before discharge into the environment in order to avoid environmental health hazards (13). Approximately 50% of consumed reactive dyes in the industry are converted to sewage; and the concentrations of these dyes reach 10-200 mg/L in the industrial wastewater (14). The conventional biological sewage treatment systems are not suitable for dye removal due largely to the low biodegradation of synthetic dyes. Furthermore, it is difficult to remove dyes by conventional processes such as the coagulation and deposition due to their high solubility in aqueous environment (15). Reactive Blue 19 is among the anthraquinone dyes in terms of dye factor and is highly resistant to chemical oxidation (16,17). Fig. 1 shows the chemical structure of Reactive Blue 19 (18).

In recent years, various methods have been proposed for the treatment of industrial sewage including the aerobic digestion, anaerobic digestion, coagulation, advanced
oxidation, chemical and biochemical combinations, adsorption and membrane filtration, all of which have different advantages and disadvantages, as well as removal efficiency (19-21). Since 1990, extensive advanced oxidation processes (AOPs) including Fenton and Pseudo-Fenton processes, chemical and photochemical oxidation, ozonation, and ultrasound have been applied to treat hazardous substances in wastewater (22,23). Using the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, Fenton process is among the most effective processes for the removal of organic pollutants due to the high oxidation power, rapid oxidation, reduced energy consumption for the presence of iron catalyst and ease of operation and maintenance (22-24). Hydroxyl radicals generated in AOPs and the hydroxyl radicals generated in the process can degrade organic pollutants via dehydrogenation, redox reaction, and electrophilic addition reaction (25). Fenton process is widely accepted because it is one of the most efficient AOPs in removing various pollutants (26-28). In Fenton process, the reaction between ferrous ion and hydrogen peroxide ($\text{H}_2\text{O}_2$) leads to the production of hydroxyl radicals under acidic conditions as in Eq. (1). Ferric ion generated via Fenton reaction reacts further with $\text{H}_2\text{O}_2$ and regenerates ferrous ions as in Eqs. (2) and (3). Even though the Fenton process is efficient, the factors like $\text{H}_2\text{O}_2$ requirement, low rate of ferrous ion regeneration, sludge generation, the increment in solution pH along with reaction time, and so on lead to the invention of extended Fenton processes (29).

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}^+ \quad (1)$$

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}^- \quad (2)$$

$$\text{Fe}^{3+} + \text{HO}^- \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad (3)$$

Inability to regenerate the catalyst is the main difficulty of conventional Fenton process, which is overcome by using heterogeneous catalyst instead of ferrous salts (28,30).

Therefore, the Fenton process is a good option for the treatment and removal of textile dyes. The present study aimed to evaluate the removal of Reactive Blue 19 dye from aqueous environment using the Fenton process.

### 2. Materials and Methods

In this study, 4 variables of pH (3, 5, 7, 12), contact time (5, 10, 15, 20, 25, 30 minutes), dye concentration (0.5, 1, 1.5, 2 mg/L), and ratio of Fenton reagent (1:1, 1:5, 1:7, 1:10) were considered (31). This process was carried out at ambient temperature in the following four steps:

1. **Materials and Methods**
   - **Range of pH:** 3, 5, 7, 12
   - **Contact Time (min):** 5, 10, 15, 20, 25, 30
   - **Dye Concentration (mg/L):** 0.5, 1, 1.5, 2
   - **Ratio of Fenton Reagent:** 1:1, 1:5, 1:7, 1:10

   In the first step, we studied the optimum dye concentration through different color concentrations at fixed pH=5 and contact time of 5 minutes and the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of 1:5. Different concentrations of dye (0.5, 1, 1.5, 2 mg/L) were prepared in this step. After adjusting the pH value with pH meter and obtaining the fixed pH of 5, the specimens were placed in a centrifuge for 5 minutes. Afterward, the specimens were transferred to a spectrophotometer with a fixed wavelength of 594 to read the residual dye concentration.

   In the second step, to assess the pH effects, four different pH values (3, 5, 7, and 12) were studied in order to achieve an optimized pH value. Given the optimum dye concentration (2 mg/L from the previous step), 2 variables, namely the contact time (5 minutes) and the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio (1:5) were kept constant like the first step. In this step, the optimum pH was determined 3.

   In the third step, we studied different ratios of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ (1:1, 1:2, 1:5, 1:7) under the optimum concentration of dye (2 mg/L), the optimum pH of 3, and contact time of 5 minutes, in order to determine the optimum $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio. After centrifugation for 5 minutes, specimens were transferred to the spectrophotometer and the optimal ratio of 1:5 was obtained for $\text{H}_2\text{O}_2/\text{Fe}^{2+}$.

   In the fourth step, the contact time was studied at 6 different time points (5, 10, 15, 20, 25, 30 minutes) under the optimum concentration of dye equal to 2 mg/L and optimum pH of 3, as well as the optimum $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of 1:5. It should be noted that the experiments were performed in triplicate. As the other steps, the specimens were placed in a spectrophotometer after centrifugation (Table 1). Finally, the results and shapes were analyzed and drawn in Excel.

### 3. Results and Discussion

To determine the optimum pH, pH tests were performed at different values of 3, 5, 7, 12. The total mean and standard deviation of total samples for pH was 0.61 ± 0.08. The results showed that higher pH values resulted in reduced removal rate and the highest removal efficiency was observed at pH 3. The removal efficiency at this pH was 70% (Fig. 2). Fig. 3 shows the effect of Fenton on dye removal at initial dye concentration of 2 mg/L. The total mean and standard deviation of total samples for $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was 0.58 ±0.07. According to Fig. 3, under the ratio of Fenton reagent from 1:1 to 1:5, the removal efficiency increased from 55% to 65%, after which the removal rate

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**Table 1. Studied Variables and Their Ranges**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
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<tbody>
<tr>
<td>pH</td>
<td>3, 5, 7, 12</td>
</tr>
<tr>
<td>Contact Time (min)</td>
<td>5, 10, 15, 20, 25, 30</td>
</tr>
<tr>
<td>Dye Concentration (mg/L)</td>
<td>0.5, 1, 1.5, 2</td>
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<tr>
<td>Ratio of Fenton reagent</td>
<td>1:1, 1:5, 1:7, 1:10</td>
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decreased and the efficiency reached to 50% in the ratio of 1:10. Fig. 4 shows the effect of different reaction time points (5, 10, 15, 20, 25, 30 minutes) on dye removal under the optimum pH of 3. The total mean and standard deviation of total samples for contact time was 0.58 ± 0.08. The figure shows that increasing the time from 10 minutes onwards causes the reduction of the removal efficiency and the highest removal efficiency at 10 minutes was observed to be 69%. The total mean and standard deviation of total samples for color was 0.79 ± 0.08.

3.1. The Effect of pH in the Color Removal Process
According to the obtained results from dye removal at different pH values, the experiment indicated that a decrease in pH led to the ascending trend of removal; and the highest amount of removal was seen in the acidic pH. The pH value is an effective parameter in the Fenton process (32). Based on the obtained results, the optimum pH was equal to 3 (Fig. 2). Under these conditions, ferrous (Fe²⁺) ion was often insoluble, and thus the oxidizing power of hydroxyl radical was high. In fact, acids are partially responsible for stability of H₂O₂. Studies indicate that the pH of about 3 to 4 is suitable for Fenton tests, because the higher or lower pH values discharge the iron ion as sludge from the reaction medium (32,33). At pH values greater than 3, Fe²⁺ precipitates as Fe(OH)₃ and decomposes H₂O₂ down into H₂O and O₂. Higher pH values reduce concentration of iron ion in reactions (34). On the other hand, higher pH values may be due to the precipitation of ferric ions as hydroxide. In this case, iron decomposes H₂O₂ down into H₂O and O₂ (35), and the oxidation rate decreases because less hydroxyl radical is available (36). In alkaline pH, the ferrite ion is converted to ferric ion, and ferric ion produces a sediment, which prevents the penetration of hydroxyl radicals to remove the color (37). The pH value of specimens was set to 3 for investigating the effects of other factors in the experiment. Similar results were observed in the study of Miri et al (38). In order to examine the effect of pH on the amount of dye removal and chemical oxygen demand, Malakoutian et al tested dye specimen at different pH values of 4, 7, and 10. Based on the results, the efficiency of process was higher at acidic pH (pH=4) than the alkaline pH (39). According to the study by CHiuo et al on the removal of Reactive Black 5 by Fenton process, the optimum pH was 3 and an increase in pH led to the reduced efficiency, and that the process efficiency was higher at acidic pH than that in the alkaline pH (40). As Fig. 4 shows an increase in the contact time enhanced the removal rate, so that the removal of 69% was seen at the time of 10 minutes (40).

3.2. The Effect of Time on the Color Removal Process
According to the studied effect of time on the removal efficiency of color at acidic pH, the removal efficiency showed the first ascending trend with increasing the time from 5 to 10 minutes, and then it showed descending trend because increasing the reaction time led to the production of intermediate compounds which reacted with hydroxyl radicals, reduced the performance, and eliminated hydroxyl (28). In the Fenton reaction, a high concentration of hydroxyl free radicals is produced in the first few minutes of the reaction (41,42). But over time, as a result of the production of hydroxyl radicals, the amount of color removal is greatly reduced (43). These results are consistent with the results of a study by Xing et al in China in 2009 regarding the fermentation sewage treatment using composite processes of coagulation, Fenton, and sedimentation (44). As a result, the time of 10 minutes was considered as the appropriate time for the reaction. According to studies, an increase in the time enhances the
rate of decomposition and degradation of pollutants, but this decomposition rate is very high at the first minutes, and then it is reduced, so that the efficiency of process will be descending after the optimum time. Results of the study by Malakoutian et al are consistent with the results from this test (39). The results are also in line with those of Bahmani et al. The removal percentage of Reactive Blue 19 was reduced by increasing the time (45).

3.3. Effect of $\text{H}_2\text{O}_2$/Fe$^{2+}$ Ratio in the Removal Process
According to the results of tests for determining the optimum ratio of $\text{H}_2\text{O}_2$/Fe$^{2+}$, the removal rate initially had ascending trend from 1:1 to 1:5 ratios and then descending trend in the ratio of 1:7. Fig. 3 shows that the highest removal percentage was found in the ratio of 1:5 of Fenton reaction; and higher ratios reduced the removal of Reactive Blue 19 dye, because $\text{H}_2\text{O}_2$ could not alone oxidize organic compounds which are resistant to biodegradation, and the presence of ferrous ion led to the formation of very little hydroxyl radical. Removal of Reactive Blue 19 dye was increased by rising the concentration of iron ion in the solution. However, the excessive ferrous ion reacted with hydroxyl radical which was subsequently associated with the reduced oxidation of organic compounds including color, and reduced rate and efficiency of chemical degradation. Consequently, it is very influential and vital to control ferrous ion concentration in the Fenton reaction. In the study of Eslami et al, the removal efficiency increased from 15.5% to 47.4% based on the increased concentration of ferrous ion; and an increase in the amount of ferrous ion was associated with the increased efficiency. The efficiency of process was decreased by exceeding this concentration, and this was consistent with the results of the present study (46). Mousavi et al also found similar results in their study (47). Moreover, increasing the concentration of hydroxyl peroxide to some extent increased the removal efficiency and then the reduction of removal was observed (48). While, ferric ion increased the production of hydroxyl radical (49).

3.4. Effect of Color Concentration
Fig. 5 shows that the removal of color at higher concentrations was accordingly higher, and with increasing color concentration, the removal percentage increased. In this figure, the highest removal percentage was observed at a concentration of 2 mg/L. The concentrations of 0.5 and 2 mg/L corresponded to 17% and 66% removal, respectively (Fig. 5). Bahmani et al also achieved such results (45).

4. Conclusion
Effective parameters for the removal of Reactive Blue 19 dye were investigated by the Fenton process. In this experiment, the optimum conditions viz pH =3, H$_2$O$_2$/Fe$^{2+}$ ratio of 1:5, contact time= 10 minutes, and the Reactive Blue 19 concentration of 2 mg/L were obtained for the removal of Reactive Blue 19. In addition, the results showed that the initial concentration of dye directly influenced the selection of the suitable concentration of H$_2$O$_2$ and iron sulfate. Therefore, selecting the appropriate concentration to reduce the cost of treatment, environmental issues, and the amount of sludge production is of particular importance. Reactive Blue 19 removal percentage was 70%. The results of this study showed that the Fenton process was able to remove various concentrations of the Reactive Blue 19 dye from aqueous solution.

Conflict of Interest Disclosures
The authors declare that they have no conflict of interests.

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References


Malakotian M, Rezaei SH, Nasiri A, Amir Mahani N. Removal of methylene blue from aqueous environments by activated escape of Zarand power plant in Kerman. Water and 54 | Avicenna J Environ Health Eng, Volume 5, Issue 1, 2018


