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Evaluating the Fenton Process Efficiency in Removal of Reactive Red 2 from Aqueous Solution

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A R T I C L E I N F O

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ABSTRACT

Introduction: Dyes are visible materials and are considered as one of the hazardous components that make up industrial waste. Therefore it is removed from bodies of water, using various methods. In this regard, the Fenton oxidation process is one of the most effective ways to remove colored contaminants in aquatic environments, which has many applications today.

Materials and Methods: In this empirical study, the effect of the Fenton oxidation process in the removal of the soluble synthetic dye, Reactive Red 2 (RR2), has been studied. The color removal efficiency of the Fenton process in the presence of ferrous sulfate and hydrogen peroxide at different reaction variables were studied in the Jar Test when initial concentration of the dye was 10 mg/L at constant pH = 3 and lab temperature.

Results: The results showed that concentrations of hydrogen peroxide and iron ions influence the maximum removal efficiency.

Conclusion: According to the survey results, Fenton oxidation is an effective method for the removal of RR2 dye from aqueous solutions.

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Introduction

Textile and dyeing industries are major environment polluting industries with high pollutant content, which are considered as important and basic industries and indicators of development of countries. In addition to textile and dyeing industries, other industries such as cosmetics, leather, pharmaceuticals, and paper, and dye factories produce dyed wastewater. It has been estimated that annually approximately 800,000 tons of dyes are produced in the whole world; azo compounds form the largest group of synthetic organic dyes [1].

It has been estimated that 1–15% of dyes disappear during dyeing and polishing processes and enter the environment as wastewater. Dyes consume oxygen from water resources in the sewers through chemical and biological changes and endanger aquatic life due to their toxicities [2]. The addition of industrial wastewaters containing inorganic dyes to water bodies leads to deterioration of water quality, toxic effects, carcinogenicity, and mutagenicity, and causes irreparable damage to the environment[2]. Direct discharge of textile industry sewage into sewage ducts disrupts operations of the biological treatment. these wastewaters also lead to increasing the cost of treatment operations due to the existence of some compounds that need more biochemical oxygen starch and the release of large amounts of mineral salts, acids, and alkalis in the biological reactor [3]. These substances have very low biodegradability because of their complex molecular structure and large size [4]; therefore, it is necessary to remove these pollutants.

The most common methods of removing dye from textile sewage include physicochemical methods such as coagulation and flocculation, adsorption, ozonation, and reverse osmosis, using membrane filters and advanced oxidation[4]. The usual methods of physical and chemical treatment such as coagulation, flocculation, sedimentation, adsorption, flotation, and membrane processes (ultrafiltration–reverse osmosis) are not able to degrade these compounds and can only transfer them from one phase to another, leading to secondary environmental pollution. Aerobic biological treatment has limited effect in removing dye from these wastewaters due to the circular structure of dye compounds, low biodegradability, and toxicity of some dyes; also, they can be revived by dangerous intermediates such as aromatic amines under anaerobic conditions. Results obtained from researches indicated more than 90% of reactive dyes remain in wastewaters with activated sludge after conventional treatment [2].

Advanced oxidation process (AOP) such as the Fenton process is a method which has been used to treat hazardous materials from sewage since 1990. Fenton is considered a most effective process to remove organic pollutants from aqueous solutions due to its iron catalytic property and ease of exploitation and maintenance [5]. Fenton is a combination of divalent iron salts and hydrogen peroxide that can be used in acidic pH. The basis of the Fenton process is hydrogen peroxide decomposition in the acidic environment by divalent iron ion (as a catalyst) and the production of hydroxyl radicals. One of the major benefits of the Fenton process is that it is a combination of oxidation and coagulation that leads to the production of less sludge than the coagulation and flocculation processes [6,7,8].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^0 \qquad (1)$$

Hydroxyl radicals (OH^0) attack RH organic compounds and lead to decomposition of organic compounds.

$$OH^0 + RH \rightarrow H_2O + R^0 \qquad (2)$$

These organic radicals produce radical through reaction with O_2; intermediates of the obtained radicals begin some chain degradation reactions that eventually lead to change of the organic pollutants to carbon dioxide and other harmless substances.

$$R^0 + O_2 \rightarrow ROO^0 \text{ products} \qquad (3)$$

In a research that Panyaza et al. conducted in 2009, the results indicated that the Fenton system is effectively used for chemical oxidation of dye from industrial sewage. In this process, deep degradation of dye compounds is also conducted due to cracking of unsaturated bonds in the dye molecules [9]. Therefore, the goal of this research is to determining the effect of Fenton oxidation in the removal of reactive red dye. Given that the efficiency of a process is a function of the oxide concentration (H_2O_2), type and concentration of catalyst, and also time of the reaction, and environmental factors such as temperature and pH, their optimization is very important for the economic and strategic aspects of the process in action. Therefore, in this research, in addition to evaluating the efficiency of the process of optimizing the operation, the effective factors in the process and efficiency of the system will be evaluated under optimum conditions.

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Materials and Methods

Materials

The dye (Reactive Red 2-RR2) is a product of Merck Company, Germany, in the group of acidic dyes and diazo water–soluble with the molecular formula $C_{19}H_{10}Cl_2N_6O_7S_2Na_2$, and molecular weight of 615,which has a molecular structure as shown in Figure 1. Hydrogen peroxide (purity percentage 30%, density 1.13, molecular mass 34.01-a product of Merck Company, Germany) and iron sulfate with chemical formula $FeSO_4.7H_2O$ (purity percentage 99.5%, molecular mass 278.02-a product of Merck Company, Germany) have been used as the main chemicals in this research.

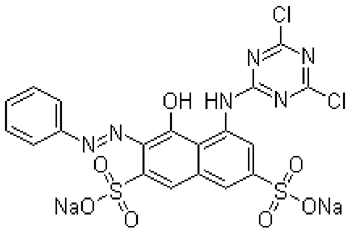

Figure 1: Molecular Structure of Reactive Red 2 (RR2) [10].

Methodology

This research was conducted to evaluate the efficiency of the Fenton process in the removal of the dye solution of RR2 through experimental method in laboratory scale in two stages. In the first stage, referring to researches in past years and also conducting a range-finding study, the concentration of the dye solution, concentration of the Fenton reagent, suitable time of reaction, and other effective parameters of the efficiency of the process, were determined. The results of the range-finding study on dye solution with concentration of 10 mg/L have provided a suitable range of concentrations of hydrogen peroxide and iron sulfate to conduct the research. Considering the number of concentrations of the oxidant (H_2O_2 $_{(mg/L)}$ = 10, 20, 30, 40, 50, 60, 70, 80, and 90), the catalyst (Fe^{2+} $_{(mg/L)}$ = 10, 30, 50, 70, and 90), and the reaction time (5, 10, and 15 minutes), samples were tested to determine the amount of the dye. The samples, synthetically with concentration of 10 mg/L with the primary pH (through meter model 537), were set on three through 1N sulfuric acid. The samples were put in the jar device (model Hatch) with speed of 100 revolutions per minute. During the mix, the intended values of oxidants and iron ion were added and effects of the reaction time and Fenton on the efficiency of decolorization of RR2 were evaluated in concentration of 10 mg/L of the dye. After oxidation, in order to remove the residual H_2O_2 and prevent formation of hydroxyl radicals through sodium, the pH of the samples was set on 9 [2]. After sedimentation of the samples, the supernatant was harvested to test and determine the dye concentration. The value of the dye concentration was determined by a spectrophotometer (model Jenway 6305). Some samples of the standard solution in the range of 20 mg/L to 100 mg/L were prepared in order to measure the concentration of RR2 and absorbance of the samples measured was 645 nm[11]. The dye removal efficiency (%R) has been calculated through Equation (4); in the equation, C_0 is initial dye concentration and C is dye concentration at various times.

$$R(\%) = \frac{C_0 - C}{C_0} \times 100 \qquad (4)$$

Results

The percentage of dye removal is shown in Figure 2. Based on Figure, the maximum removal efficiency of 10 mg/L of solution of synthetic dyes was achieved at concentrations of 90 mg/L and 50 mg/L of hydrogen peroxide and ferrous sulfate, respectively. Under optimum conditions, the removal efficiency in 15 minutes was 99%.

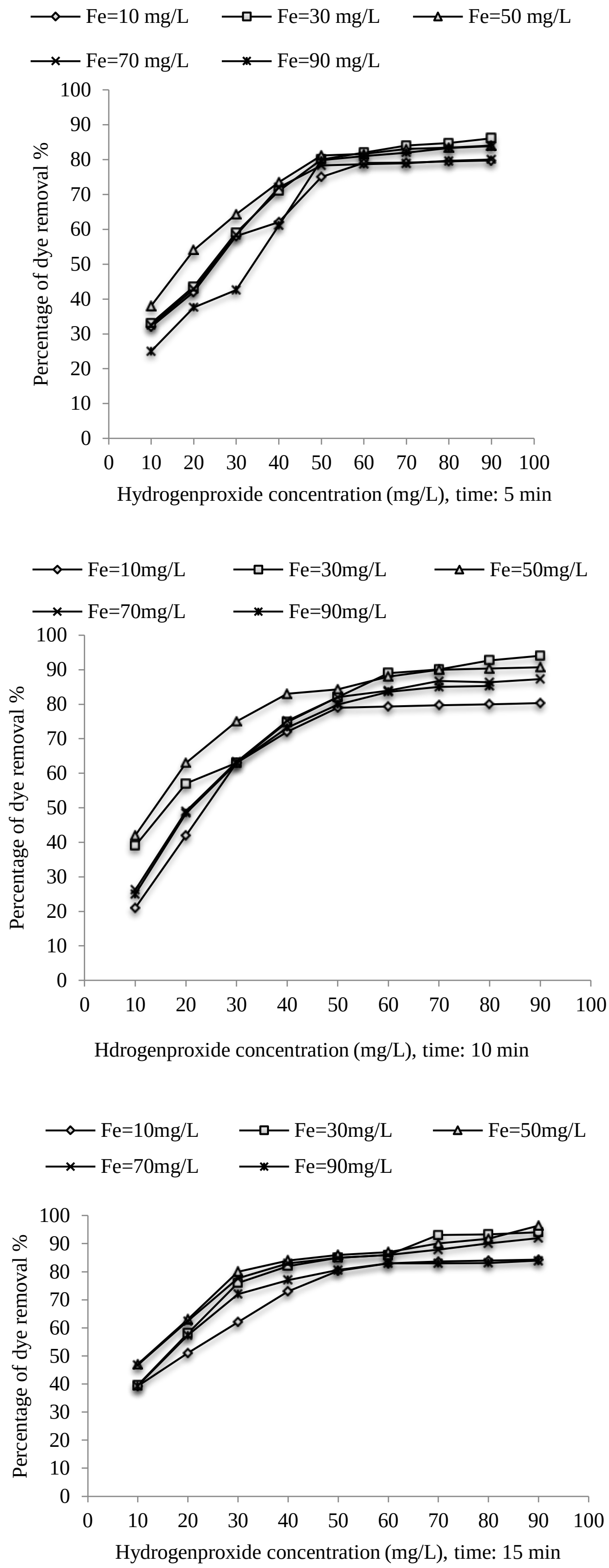

Figure 2: Diagrams about efficiency of Fenton process in removal of Reactive Red 2 (10 mg/L) in reaction times of 5, 10 and 15 minutes

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Discussion

In this research, the efficiency of the Fenton process in the removal of RR2 from aqueous solutions was conducted. Since pH is one of effective factors in the Fenton oxidation process, conducting the process in acidic pH is a major limitation of this method. According to the research by Pignatello et al. in 2006 on using advance oxidation processes in decomposition of organic materials, it has been indicated that in acidic pH the reaction occurs between hydrogen peroxide and ferrous ion which leads to decomposition of many organic compounds [12]. Therefore, in this research, the Fenton process was conducted in pH equal to three. The reason for selecting this pH as optimum is because in pH higher than three, due to the instability of ions of iron, and changing that to trivalent iron of these ions sediment as $Fe(OH)_3$ in the environment and reduce solubility of iron ions. As a result, a lower hydroxyl radical is formed and removal efficiency of the dye is reduced; while in the acidic mode, the stability of iron ions and hydrogen peroxide is increased in the environment and iron sulfate in the environment changes to form iron hydroxide, which is completely soluble leading to increased production of hydroxyl radicals and consequent increase in the removal efficiency. Studies of researchers also indicate that in pH lower than three, iron hydroxide with hydrogen peroxide is formed slowly, which causes reduction of OH radicals and the removal efficiency is reduced [5]. The results obtained from the research of Barbosinski et al. in 2003 indicated that the removal efficiency of the dye (Acid Red 18) is higher than 90 percent in the initial concentration of 100 mg/L in pH equal to three, and with increase or reduction of pH from this value, the removal efficiency is reduced [13].

Effect of Various Concentrations of H_2O_2 on the Fenton Process

Considering the obtained results, it is observed in figure 2 that the value of the dye removal rises with increase in the concentration of hydrogen peroxide. This increase in the removal efficiency is an effective factor in the Fenton oxidation process due to the high production of hydroxyl radicals caused by the increased concentration of hydrogen peroxide; this issue has also been considered by researchers in previous studies [14, 15, 16]. In Figure 3, the slope of the diagram has been approximately fixed from concentration of 70 mg/L to 90 mg/L so that no considerable difference is observed in the removal efficiency. This observation is supported by the research of Meric et al. in 2005, in which hydrogen peroxide decomposes into water and oxygen at high concentrations and may be combined again with hydroxyl radical, as shown in Equations (5) and (6) [17].

$$2H_2O_2 \rightarrow 2\,H_2O + O_2 \quad (5)$$

$$H_2O_2 + OH^0 \rightarrow H_2O + HO_2^0 \quad (6)$$

Considering the results obtained in this research, the maximum removal efficiency of the dye is 99 percent in 15 minutes in optimum concentrations of 50 mg/L of iron sulfate and optimum concentration of 90 mg/L of hydrogen peroxide.

Effect of Various Concentrations of iron ion (II) in Fenton process

The obtained results in Figure 2 show that the value of the dye removal rises with increased concentration of ferrous iron from 10 mg/L to 50 mg/L. However, the removal efficiency is reduced with increased concentration of iron to more than 50 mg/L. The way iron sulfate works in the Fenton process is that with increasing iron sulfate in the environment the iron ions convert to trivalent iron and lead to the production of strong hydroxyl from hydrogen peroxide in the process; Therefore, hydroxyl radicals are not formed without the presence of iron sulfate in the environment. Thus, it can be said that divalent iron has remarkable effect as a catalyzer in the Fenton process [18]. Increasing the iron concentration from 10 mg/L to 50 mg/L is justified as the value of hydroxyl radical's increase due to the reaction of iron ions with hydrogen peroxide which causes rapid decomposition of the dye; as a result, the value of the dye removal is increased, too. Results obtained from research of Lin et al. in 2007 indicated that the removal efficiency of the dye will improve with increased iron concentration. Results obtained from the research indicated that iron increased the speed of decomposition of hydrogen peroxide because it performs the catalyst role in the Fenton process and, as a result, high amounts of hydroxyl radicals are produced and the removal efficiency is increased [19].The removal efficiency is reduced with increased iron concentration to higher than 50 mg/L, as shown in Figure 3. This is because with excessive increase of iron ions, these ions combine with hydroxyl ions (OH°) to form complex substances and, as a result, more hydroxyl radicals are freed that eventually reduces the removal efficiency [15]. In other words, this can be described as the tendency of hydroxyl radicals to react through oxidation–reduction with H_2O_2 and Fe^{2+} [16]. The increase of the iron value to higher than 50 mg/L increases the opacity value due to the formation of iron hydroxide and this factor can be effective in reducing the removal efficiency. In a research which Santana et al. conducted in 2009, the obtained results indicated that the maximum removal efficiency is in concentrations of iron ion of 0.27 moles and, with the increase of the iron concentration from this value, the removal efficiency is reduced due to the effect on hydroxyl radicals in the environment [20]. In the research by Hsuehet al. in 2005 on the topic of removal and degradation of dye with the Fenton process, it has been reported that excessive increase of concentration of iron ion prevents production of hydroxyl radicals and also leads to reduction of the removal and speed [21]. Therefore, concentrations equal to 50 mg/L can be selected as optimum in this research.

Effect of Reaction Time on Fenton Process

Figure 2 shows that the dye removal trend has increased with the increase of the reaction time from 5 minutes to 15 minutes so that the removal efficiency is equal to 94 percent in 5 minutes with concentration of 90 mg/L of H_2O_2 and optimum concentration of ferrous iron (50 mg/L), while the removal efficiency has increased to 99 percent in the same concentration from H_2O_2 and in 15 minutes, which is higher than the efficiency obtained in 10 minutes with concentration of 90 mg/L of H_2O_2 and 50 mg/L of iron ion. The reasons for these reactions can be explained as over time, the value of intermediate products has increased because of hydrogen peroxide decomposition and hydrogen peroxide decomposition has increased due to the reaction of iron ions with intermediate products and, as a result, the production of hydroxyl radical has increased in the environment; so, the removal efficiency is increased [22].This issue has been emphasized by researchers in previous studies [13,18].

Conclusion

Results obtained from this research indicated that the Fenton oxidation process is an effective method in the removal of Reactive Red 2, as more than 95 percent of the dye was removed in optimum conditions with concentrations of 90 mg/L of hydrogen peroxide and 50 mg/L of iron sulfate in 15 minutes. Furthermore, the results indicated that this process is affected by two main variables including the concentration of hydrogen peroxide and concentration of ferrous iron and the increase or reduction of these two factors have a direct effect on the removal efficiency. According to the results of this research, concentration of 50 mg/L of ferrous iron as the optimum concentration showed a suitable efficiency in removal of the dye. This concentration is very important due to the reduction of the reactor volume, economic issues such as reduction of cost of treatment operation, and reduction of the sludge amount.

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Conflict of interest

We affirm that this article is the original work of the authors and have no conflict of interest to declare.

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