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Use of Fenton Reagent as Advanced Oxidative Process for Removal of Basic and Acid Red Dyes from Aqueous Solutions

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Abstract

In this study, the Fenton process was used to investigate the color removal efficiency of Acid Red 52 and Basic Red 18 dye solutions by direct chemical oxidation. Color and chemical oxygen demand (COD) was successfully removed more than 99% and up to 92% respectively. This article would provide an easy assessment of the viability of using Fenton reagent in acidic conditions, so it is a promising and easy method for the fairly degradation of the BR.18 and AR.52 dye in synthetic wastewater. Parameters such as dose of H_2O_2:1.5g/L, concentration of Fe^{2+}: 8 mg/L as a catalyst, initial pH:3, initial dye concentration (10-500mg/L) and reaction time (18min) have been studied. The proposed system was a viable alternative to some of the more conventional forms of chemical treatment of dye solutions.

Using UV-VIS spectra and COD analysis showed a good mineralization and fairly complete degradation of dye.

Key words: *Fenton, Basic Red18, Acid Red52, Degradation.*

Introduction

Textile industry is one of the most important industries in last few decades. It is broadcasted that more than 10,000 dyes are used in the textile industry and 280,000 tones of textile dyes are discharged every year worldwide. Textile dyeing and finishing processes create huge quantities of wastewater that are vastly colored and contain large concentration of organic matter, which is difficult to treat via conventional methods [1,2].For environmental protection, various techniques(chemical, physical and biological)have been employed for the treating of dyes from wastewaters[3,4]. Biological and physical treatment techniques are not satisfactory because they simply

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transfer the pollutants from one phase to another, and the equipment complicated in these processes is costly. In recent years chemical methods, have fascinated much attention. Among the treatment options, Fenton process appears to have a considerable potential for the removal of color from industrial effluents. The most popular and used chemical Advance Oxidation Process (AOP) is the Fenton method, where a mixture of Fe^{2+} and H_2O_2 (Fenton's reagent) is used for formation of nonselective hydroxyl radicals (OH•) and degradation of pollutants[5,6].This reaction allows the generation of hydroxyl radicals as shown in Eq (1) [7]:

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

These radicals are a very strong oxidizing agent capable of reacting with a wide variety of organic compounds under ambient conditions. The generation of hydroxyl radicals can be achieved by a variety of reactions, such as ozone/UV, hydrogen peroxide/UV, Fenton oxidation, photo-Fenton or titanium dioxide/hydrogen peroxide/solar radiation [8-13].In the Fenton (or Fenton like) reaction ferrous salts react with H_2O_2 to produce OH• as shown in Eqs.(2-4) [14]:

$$Fe^{2+}+H_2O_2+H^{+}\rightarrow Fe^{3+}+OH\bullet+H_2O \quad (2)$$
$$Fe^{3+}+ H_2O_2\rightarrow Fe^{2+}+OOH\bullet+H^{+} \quad (3)$$
$$Fe^{3+}+OOH\bullet \rightarrow Fe^{2+}+O2+H^{+} \quad (4)$$

This work attempts to treat wastewaters of two synthetic textile dyes by using low concentration of iron ions (≤10*mg/L*) to decolorize the wastewaters, and also to conform to the water effluent standards for iron levels. Such treatment can avoid creating a large volume of sludge. Experiments were conducted to examine the influences of various operating conditions on treatment system performance. The effects of experimental factors such as Fe^{2+}concentratin (as catalyst), dosage of H_2O_2 (as oxidizing reagent), the effect of initial pH, initial dye concentration and oxidation time on discoloration efficiency were examined.

The other aim of the present study was to evaluate Fenton's oxidation process to achieve complete mineralization of dyes and partial cleavage of aromatic amines to make them easily degradable. Under the optimized conditions, the chemical oxygen demand (COD) decreased by more than 90% in dye solutions. The absorption spectra of each dye solution before and after the process were illustrated.

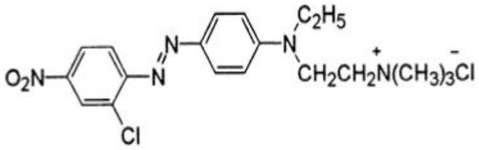
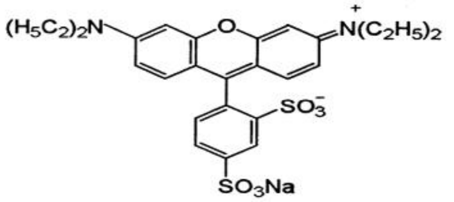
Experimental

Material

All chemicals were of analytical reagent grade and were used without any subsequent purification. Also, all of solutions were prepared using distilled water. Ferrous sulfate

($FeSO_4.7H_2O$) and hydrogen peroxide (30% w/w) were purchased from Sigma-Aldrich, Germany. In the present investigation, two dyes (BR.18and AR.52) were obtained from Alvansabetrang company-Iran and used without further purifications. The initial pH was adjusted to the required value using NaOH or HCl solutions prior to addition. The structure and general characteristics of dyes are shown in Table1.

Table1.General characteristicsofBR.18 and AR.52 dyes.

Dye	Chemical structure	Mw (gr/gr mol.)	Color index number	λ_{max}(nm)
BR.18		426.24	11085	526
AR.52		580.65	45100	565

All experiments were carried out in a 100mL glass reactor at room temperature. In order to make sure the reaction mixture homogenize, the experiments were performed in reactors equipped magnetic stirrer during reaction time. The appropriate concentration of Ferrous sulfate and H_2O_2 (30% (w/v)) was carefully dripped into the reactor to start the Fenton's reaction. The reaction time recorded as the H_2O_2 solution was added. Samples were taken from the reactor periodically during the reaction at different time interval for analysis and were immediately analyzed after filtration by a 0.25 μm syringe filter made of poly-(vinylidene fluoride).

Methods

The optical absorption of each dye solution was determined and recorded by a high precision, double beam spectrometer (Model:UV-IKON922) at wavelengths between 200 and 800 nm. The maximum absorbance wave length (λ_{max}) of BR.18 and AR.52 are 526 and 565nm from the spectra. Therefore the concentration of two dyes in water was determined by the absorption intensity at λ_{max}. All measurements are based on methods from standard method APHA-AWWA[15]. Dye removal efficiency percent was calculated by using Eq (5) as follows:

$$\text{Dye removal }(\%)=((C_i-C_e)/C_i)\times 100 \qquad (5)$$

Where C_i and C_e are the initial and final concentrations of dye in the solution at reaction time t and 0, respectively in mg/L.

Results and discussion

In this study, the removal of AR.52 and BR.18 were controlled by several operational parameters, such as, ferrous concentration, initial pH, dose of H_2O_2, initial dye concentration and oxidation time. In order to enhance the process performances, the influences of these parameters were studied as follows:

Effect of Ferrous (or Fe^{2+}) concentration

Figure 1 displays the effect of iron dose on the concentration of dyes under the following experiment conditions: pH fixed at 3, H_2O_2 dose of 1.5g/L, ferrous sulfate varied from 4 to 18 mg/L (as Fe^{2+}). The figure reveals the dye removal efficiency of AR.52 and BR.18 (as an example for 50mg/L dye solution) as a function of concentrations of Fe^{2+}. Thedata show that the dye removal efficiency of two dyes increases with increasingFe2+concentration from 4 to 8 mg/L, because iron activates the hydrogen peroxide to form hydroxyl radicals. However, ferrous ion can also be scavenger of hydroxyl radicals as shown in Eq. (6). In the excess amounts of ferrous ion, it can react with hydroxyl radical. Then, the hydroxyl radical in the system will decrease and the organic degradation efficiency will also reduce[16].

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe3^{+} + OH^{-} \qquad (6)$$

The results show that in the4 mg/L of Fe^{2+}, the dye removal efficiency were 99% and 97.5% forAR.52 and BR.18 respectively after 18 minutes of reaction time. However in 8 mg/L, the dye removal efficiency was maximized for two investigated dyes, over 99.9% for AR.52 and 98.5% for BR.18. Above this concentration of Fe^{2+} we observed that the dye removal efficiency was decreased for both dyes. We choose 8 mg/L of Fe^{2+} for the rest of the experiments. This is consistent with the results found in the literature [17, 18]. Moradianfard reported color removal more than 99 % in the pH: 3, at concentration of $FeSO_4$: 10-200 mg/L [19].

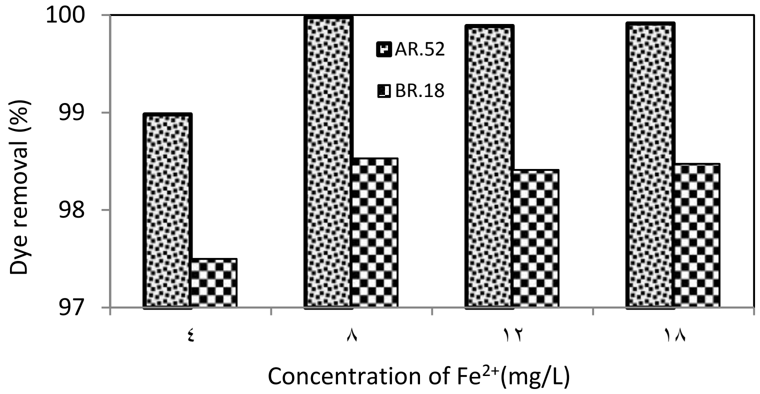


Figure1. Comparative curve - Effect of Fe^{2+} concentration on the dye removal efficiency percent of BR.18 and AR.52.
Conditions: Initial Concentration of dye: 50mg/L, Initial volume of wastewater:50mL, Dose of H_2O_2:1.5g/L, Mixing rate :200rpm, Oxidation time:18 Min.

Effect of initial pH

Initial pH plays a significant role in the discoloration of dyes by Fenton process. Figure.2 demonstrates the effect of initial pH on the dye removal efficiency percent (as an example for representative 50mg/L concentration of dye). Concentration of 50mg/L of dye was used because it corresponded to the level of pollution found in strongly colored polluted waters located close to textile manufacturing sites. Observations demonstrated that increasing the initial pH from 3 to 9leads to a decrease in the removal efficiencyfrom99% to 59% for AR.52.Also at initial pH:3 maximum dye removal efficiency was observed in both of dyes. According to the data, it seems that the value of decolorization efficiency of dyes varies with the type of dye. It may be explained by the hydrolysis of Fe^{2+} in the solution to reduce $OH^{\bullet}$ producing rate. From the literature it revealed that for all dyes, Color removal efficiency by Fentons reaction was achieved at initial pH about 3.0 [20-25].

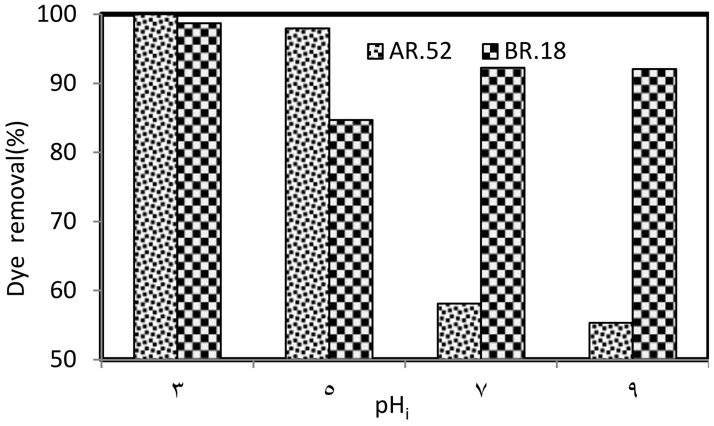


Figure 2.Comparative curve -Effect of initial pH on the dye removal efficiency percent of BR.18 and AR.52.
Conditions: Initial Concentration of dye: 50mg/L, Initial volume of wastewater:50mL, Dose of H_2O_2:1.5g/L, Concentration of Fe^{2+}:8mg/L, Mixing rate:200 rpm.

Effect of H_2O_2 dose

The initial concentration of H_2O_2 plays an important role in the fenton process. Oxidation of dyes by Fenton process is carried out by $OH^{\bullet}$ radicals that are directly produced from the reaction between H_2O_2 and Fe^{2+}. To determine the concentration of H_2O_2 giving the maximum dyes (AR.52 and BR.18) removal efficiency, experiments were conducted, and results obtained are represented in Figure 3. The dye removal efficiency according to the variation of dose of H_2O_2 from 1 to 3.5 g/L, shows that the degradation yield increases with increasing concentration of H_2O_2. For the Fenton process, the addition of H_2O_2 from 1 to 1.5 g/L increases the declorization from80% to 99.5% for AR.52, and 69% to 98.5% for BR.18 respectively at 18 min of contact time. Increasing in the decolorization is due to the increase in hydroxyl radical concentration by the addition of H_2O_2 [26]. The degradation rate of organic compounds will decrease as a result of the so-called scavenging effect [27]. The reaction of H_2O_2 and $OH^{\bullet}$ in aqueous solution can be expressed by the following equation [28].

$$H_2O_2 + OH\bullet \rightarrow H_2O\bullet + H_2O \qquad (7)$$

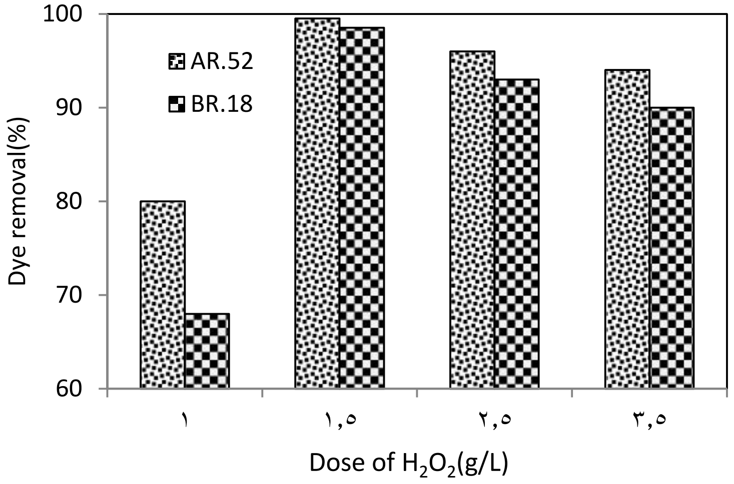


Figure 3. Comparative curve -Effect of H_2O_2 dose on the decolorization percent of BR.18 and AR.52. Conditions: Initial Concentration of dye: 50mg/L, Initial volume of wastewater: 50mL, Initial pH:3, Concentration of Fe^{2+}: 8(mg/L), Mixing rate :200rpm.

Effect of oxidation time

The effect of time was investigated on dye degradation. The reaction time required for dye removal using H_2O_2 varies according to the type of dyes. Figure 4 shows the dye removal efficiency percentage increased with increasing contact time (from 0 to 20 min) for all the dyes. At the end of 18 min, maximum removal efficiency of 99.5% and 98.5% was obtained for AR.52 and BR.18 respectively.

The treated samples were colorless and showed no absorbance in the visible range. Some results were carefully approved with the literatures [29-30].

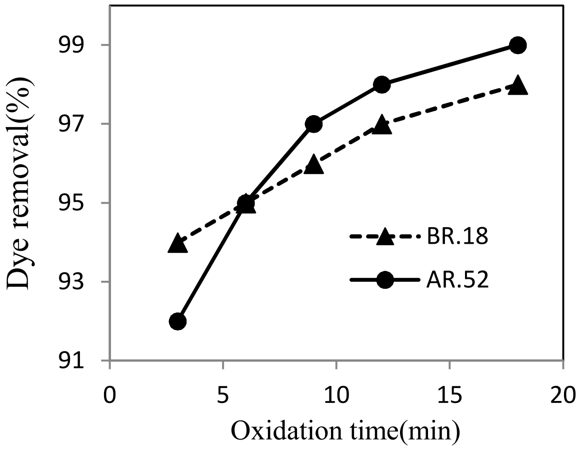


Figure 4. Comparative curve - Effect of time on the decolorization of BR.18 and AR.52 by Fenton process. Conditions: Initial volume of wastewater:50mL, Initial Concentration of dye: 50mg/L, Dose of H_2O_2:1.5g/ L, Concentration of Fe^{2+}:8mg/L, Mixing rate:200rpm.

Effect of dye initial concentration

The dye solutions with different initial concentrations in the range of 10-500 mg/L were treated by Fenton oxidation in optimized pH, dose of Fenton reagent and time of oxidation values. The effect of dye initial concentration was investigated for AR.52 and BR.18 dyes using the same amount of Fenton's reagents, since pollutant concentration is an important parameter in wastewater treatment. This phenomenon can be explained by the fact that an increase in the initial dye concentration leads to increasing the number of dye molecules. The number of hydroxyl radicals remains the same. Concentrations of H_2O_2 and Fe^{2+} were kept constant, which causes a decrease in efficiency of discoloration. When the dye concentration is low, the concentration of H_2O_2 is in excess compared to the latter and traps the OH• radicals [31]. Decolorization of both dyes was measured at several different concentrations (10,50,100,200,300,500mg/L) of dyes and dose of H_2O_2 and concentration of Fe^{2+} were fixed. The results were shown in Figure. 5. According to Figure.5 the decolorization of both dyes decrease with an increase in dye concentration, decreasing for BR.18 was very significant. The same results were reported in some literatures [32-33].

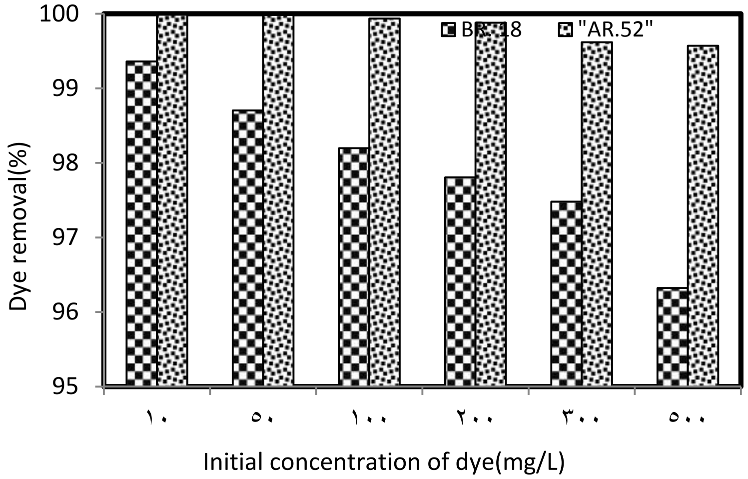


Figure 5.Comparative curve- Effect of initial dye concentration on the decolorization of BR.18 and AR.52. Conditions: Initial volume of wastewater: 50mL, Dose of H_2O_2:1.5g/L, Initial pH: 3, Concentration of Fe^{2+}:8 mg/L, Mixing rate: 200rpm.

Mineralization of synthetic colored solutions-absorption spectra of AR.52 and BR.18

The mineralization of the two dyes solution with an initial concentration of 50 mg/L was carried out by Fenton oxidation in this study. This is a powerful process for degradation of dye since OH• has the ability to selectively react with chromophores, leading to high color removal. In the present work, all the dye solutions were effectively decolorized after 18min. reaction periods. Blank experiment (before removal) and oxidation experiment (after removal) were carried out for comparative purposes in Figures 6 and 7. In order to clarify the changes in the molecular characteristics of the species resultant from this advanced oxidation process, the evolution of the UV-Vis spectra of solution at initial (t0) and final state(t=18 min) was recorded as a function of wavelength from 200 to 800 nm. In Figure.6, the UV-vis absorption spectra of AR.52 characterized by one main band in the visible region with the maximum absorption at 565 nm, which is associated with the chromophores of the dye molecules, also in Figure.7, the UV-vis absorption spectra of BR.18 characterized by one main band in the visible region with the maximum absorption at 526 nm.

In addition to the rapid bleaching effect, the decay of the absorbance in the UV region is considered an evidence of the degradation of the aromatic fragments of the dye molecules and their oxidation intermediates. Particularly, the absorbance at 254 nm is commonly associated with the presence of aromatic moieties. These observations are in agreement with the previous researchers for oxidation (catalytic ozonation) of dyes and textile effluents [34-35].

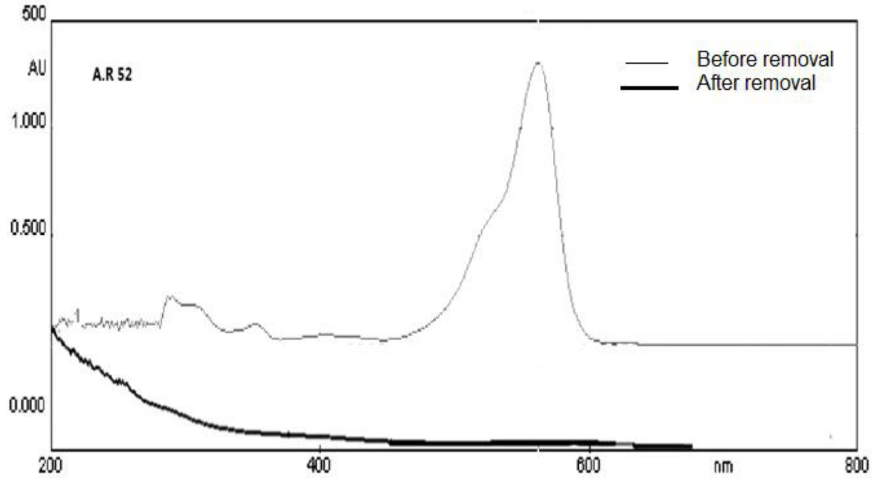


Figure 6. UV–vis absorbance spectra of A.R52 (Comparative curve for before and after removal). Conditions: Initial concentration of dye solution: 50mg/L, Initial volume of wastewater:50mL, Volume of H_2O_2:1.5g/L, Concentration of Fe^{2+}: 8(mg/L), Mixing rate :200rpm, Reaction time:18 min.

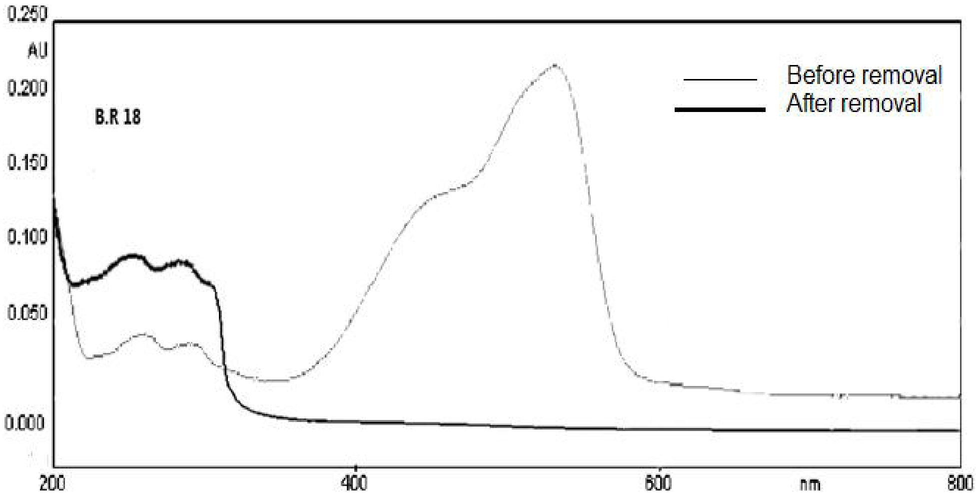


Figure 7. UV–vis absorbance spectra of B.R18 (Comparative curve for before and after removal). Conditions: Initial concentration of dye solution: 50mg/L, Initial volume of wastewater:50mL, Volume of H_2O_2:1.5g/L, Concentration of Fe^{2+}: 8(mg/L), Mixing rate :200rpm, Reaction time: 18 min.

COD reduction

Extent of mineralization of the AR.52 and BR.18 by Fenton oxidation process can be evaluated by measuring Chemical Oxygen Demand (COD) measurement. In this study COD measurements were conducted. From the aforementioned sections it is clear that pH: 3 seem to be the optimum pH for this oxidation process. The degradation of two dyes was evaluated for COD reduction of treated samples. To determine the change in the COD of reaction medium, initial COD (pure dye solution) and the COD of a sample at different intervals during the reaction were measured and COD reduction was determined as follows:

$$\%\text{COD removal} = \frac{(1-C_t)}{C_0} \times 100 \qquad (8)$$

Where COD_t and COD_0 are COD (mg/L) values at time (*t*) and at time (*0*), respectively. COD was measured according to standard method, (APHA-AWWA), [15]. 92% and 85% COD reduction is achieved in AR.52and BR.18respectively, in 18 min, which indicates the fairly mineralization of dyes. Kuo [22] reported approximately 90% chemical oxygen demand (COD) removal in 30 min by Fenton oxidation. Malik [36] observed that at the optimal pH: 3, 70% of COD removal can be achieved in 60 min.

Conclusions

From the present study, it can be concluded that degradation and mineralization of organics in synthetic textile wastewater was possible by Fenton process. Results indicate that using Fenton oxidation, the optimum operating conditions of initial pH: 3, Fe^{2+} concentration: 8mg/L, H2O2 dose: 1.5g/L, temperature: 25°C, and 18min reaction time for Basic Red18 & Acid Red52 at atmospheric pressure, giving maximum color removals of 98.5% and 99.5%, respectively. This work attempts to treat wastewater of two synthetic dyes by using low concentration of iron ions to decolorize the wastewaters, and also to conform to the water effluent standards for iron levels (the maximum limit for total iron in effluent is 10 mg/L). However, the best performance was recorded by AR.52 in the same situation. It has been found that direct oxidation with Fentone reagent yielded acceptable decolorization and almost total mineralization of AR.52 solutions due to the UV-vis spectra and COD removal percent (92%) and synergistic action of hydroxyl radicals as a stronger oxidizing agent. This investigation has demonstrated the Fenton process is a useful application to drainage of an actual textile factory is supposed to perform as further study.

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