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Investigation of color and COD removal by Fenton reagent from aqueous solutions containing acid and reactive dyestuffs

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ABSTRACT

Textile industry is one of the most important industrial activity areas for our country. Because this industry has various production processes, it contains high pollution load and wastewater volume, dissolved substance concentration and different structure dyestuffs. If not treated by appropriate methods, this wastewater with excessive amounts of color and toxicity properties causes serious environmental problems. Compared with other advanced oxidation processes, Fenton process, one of the advanced oxidation processes, has many advantages as being simple, economical and requiring short reaction time. In this study, it was aimed to determine color and chemical oxygen demand (COD) removal efficiencies using Fenton's reagent from aqueous solutions of reactive and acid dyestuffs prepared as synthetic and commercial names CI Reactive Yellow 176 and CI Acid Red 266, respectively. Color and COD removals were investigated for two different dyestuffs by using variable values for five basic factors such as pH, concentration of Fe^{+2}, concentration of H_2O_2, temperature and slow mixing times affecting the efficiency of Fenton process. Optimum values were determined and decolorization efficiency above 98% and COD removal above 89% for CI Acid Red 266 and decolorization efficiency above 95% and COD removal above 81% for CI Reactive Yellow 176 were reached.

Keywords: Fenton; Decolorization; COD removal; CI Reactive Yellow 176; CI Acid Red 266

1. Introduction

Dyes used in textile industries can originate color in water courses that receive discharges of their liquid effluents, generating important environmental impacts, among which is the decrease of the solar light penetration [1]. Direct discharge of these effluents can cause formation of toxic aromatic amines under anaerobic conditions in receiving media and contaminate soil and groundwater, necessitating proper treatment before discharge into the environment [2]. The most frequently used physicochemical method of textile wastewater treatment is coagulation, which is used mainly in wastewater decolorization and reduction of the total load of suspensions and organic pollutants [3]. Because chemical coagulation is not effective for the removal of dissolved reactive dyestuffs, there is a need for advanced treatment processes to further remove color and COD from textile wastewater [4]. Moreover, more stringent requirements of wastewater discharge standards have promoted recent research efforts to identify other more efficient and economic chemical treatment methods in an attempt to meet these demands [5]. In recent years, advanced oxidation processes using ozone, titanium dioxide (TiO_2), ultra violet (UV), and Fenton's reagent (H_2O_2 and ferrous ion) have received considerable

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attention as effective pretreatment processes of less biodegradable wastewater. Among them, Fenton's reagent has been widely used because it is cost effective, easy to treat, reacts well with organic compounds and does not produce toxic compounds during oxidation [6]. As a result, several research have been developed on decolorization of textile wastewater, Fenton's oxidation's mechanism was determined and found that hydroxyl radicals ($^{\bullet}OH$) were generated by catalytic decomposition under acidic conditions [7]. At pH values ≤4.0, ferrous ions decompose H_2O_2 catalytically yielding hydroxyl radicals most directly. However, at pH values >4.0, ferrous ions easily form ferric ions, which have a tendency to produce ferric hydroxo complexes. H_2O_2 is unstable and easily decomposes itself in the basic (Ph > 10) solutions [2]. The major advantage of Fenton process is that the reagent components are safe to handle and environmentally benign [8].

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + OH^- + H_2O \quad (1)$$

$k_1 = 76\ M^{-1}s^{-1}$

$$Fe^{3+} + H^2O^2 \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^+ \quad (2)$$

$k_2 = 0.01 - 0.02\ M^{-1}s^{-1}$

$$^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet} \quad (3)$$

$k_3 = 10^7 - 10^{10}\ M^{-1}s^{-1}$

$$R^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + R^+ \quad (4)$$

$$R^{\bullet} + H_2O_2 \rightarrow ROH + {}^{\bullet}OH \quad (5)$$

In the past few years, many experiments have been carried out to remove COD and color from industrial wastewater by Fenton's reactions. The efficiency of Fenton process depends on the properties of the wastewater like the pH value, the Fe^{2+} concentration, the H_2O_2 concentration and the reaction time [9]. In oxidation applications, hydroxyl radical, one of the most important oxidizing agents was produced and used [10].

All dyes used for dyeing in textile industry created the problem which is not the same, so the structure of dyestuffs determine behavior toward treatment operations. Furthermore, amount of remaining dye in wastewater also depends strongly on dyestuff properties [11]. The aim of this study is to determine removal efficiencies in terms of the COD and color removal from synthetic wastewater containing CI Reactive Yellow 176 (RY176) and CI Acid Red 266 (AR266) by Fenton's oxidation (Fe^{+2}/H_2O_2) and also optimization experiments for Fe^{+2} and H_2O_2 dose, temperature, pH were carried out.

In literature, there are no studies that investigate the removal of CI acid Red 266 and CI Reactive Yellow 176 dyestuffs by using Fenton process. Consequently, this study will contribute to literature by presenting on efficient process for treating these kind of dyestuffs.

2. Materials and methods

Commercially available RY176 (Sum-pa Textile Co. Ltd.) and AR266 (Alfa Chemistry Co. Ltd.) dyes were obtained from Istanbul in Turkey. Synthetic dye solutions of dyestuff were prepared as 200 mg/l with distilled water. Synthetic wastewater characteristics are presented at Table 1.

2.1. Fenton process

The Fenton process experiments were conducted by jar test (Velp FC6S) according to Kuo's (1992) and Kang et al. (2002) methods with a modification of 2 min rapid mixing at 120 rpm and then 20 min slow mixing at 30 rpm and subsequently settling for 1 h [4,12]. Operating parameters included concentrations of H_2O_2 and $FeSO_4$, pH value, temperature and slow mixing time (SM). Each beaker was first filled with 250 ml of wastewater sample, and pH was adjusted to the designed value with 0.1N H_2SO_4 solution. Then $FeSO_4$ and H_2O_2 (35%, w/w) were added and the process was proceeded. Fenton process serves both oxidation and coagulation functions. In the oxidation step, hydrogen peroxide was added to a water sample, then the water sample was mixed rapidly for 2 min. In the coagulation step, the above oxidized water sample was mixed slowly for 20 min and then allowed to stand still for sedimentation to take place. The pH for both Fenton oxidation and coagulation experiments was controlled with 0.1 N

Table 1
Main characteristics of dyestuff solutions

Dye solution	Parameters					
	pH	Conductivity (μs/cm)	TDS (mg/l)	COD (mg/l)	Maximum Absorbance (nm)	Concentration (mg/l)
RY176	4.95	66.2	34.2 (at 19.3 °C)	70.84	419	100
AR266	5.88	28.4	12.5 (at 19.3 °C)	40.94	499	100

H_2SO_4 and NaOH. After rapid and slow mixing, and settling period, pH of the supernatant was readjusted up to 7.5 and it was left to settle for 1 h. Finally, supernatant was centrifuged for 10 min at 4000 rpm for COD and color analyses.

2.2. Analytical methods

The color measurements were carried out by a spectrophotometer based on absorbance measurement. For maximum absorbance measurements, Hach Lange DR-5000 spectrophotometer was used and dye solutions were measured at three different wavelengths (436, 525, 620 nm) in terms of Germany Textile Discharge Standarts. COD experiments were carried out in accordance with the Standard Methods by APHA, AWWA and WEF (1998) [13]. The pH measurements were performed by using a portable pH meter (Consort C931).

3. Results and discussions

3.1. Fenton process results of synthetic textile wastewater

3.1.1. Effect of pH on color and COD removal efficiencies

pH was a significant factor effecting the Fenton process performance. It affects directly the mechanism of oxidation dye, because a change in pH of the solution, involves a variation of the concentration of Fe^{2+}, and therefore the rate of production of $^{\bullet}OH$ radicals responsible for oxidation dyes, will be restricted [14]. Fig. 1 demonstrates the pH effect on the color and COD removal of RY176 and AR266 treated by Fenton process with a fixed amount of 2.94 mm H_2O_2 and 0.90 mm $FeSO_4$. As the pH increased from 2.5 to 4, the COD removal remained in the range of 46–52%, and the maximum value of COD removal was 52% at pH 4 for RY176. In addition to this, color removal efficiency changed in the range 84–91% and maximum color removal was determined as 91% for RY176 at pH 4. In the same pH range for AR266, COD removal changed in the range of 58–64%, and the maximum value of COD removal was 64% at pH 3.5. In addition to this, color removal efficiency was obtained above 99% at all pH values and maximum color removal was observed 99% at pH 3.5. The COD removal started to decrease slightly at pH 4, due to the increasing rate of autodecomposition of H_2O_2, deactivation of iron ion into iron oxyhydroxides, the increased scavenging effect of $HO^{\bullet}$ resulting in the decreased oxidation potential of $HO^{\bullet}$ [9].

3.1.2. Effect of Fe^{+2} concentration on color and COD removal efficiencies

Ferrous sulphate concentration also affected color and COD removals (Fig. 2). Increasing Fe^{+2} concentrations provided positive effect on removal efficiencies. Fig. 2 shows the Fe^{+2} effect on the color and COD removal of RY176 and AR266 treated by Fenton process. After optimum pH values were determined for two dye wastewater, Fe^{+2} concentrations were changed in the range of 0.09–1.34 mm for RY176 and 0.45–1.79 mm for AR266 with a fixed amount of 2.94 mm H_2O_2. According to the results of $FeSO_4$ optimization, maximum color and COD removals were obtained as 91% color and 72% COD removal with 0.18 mm Fe^{+2} for RY176 and 99% color and 58% COD removal with 0.90 mm Fe^{+2} for AR266. This can be explained as production of $^{\bullet}OH$ radicals increased with increased iron dose, but further increases in the amount of Fe^{+2} did not result in increases in the rate of degradation [15].

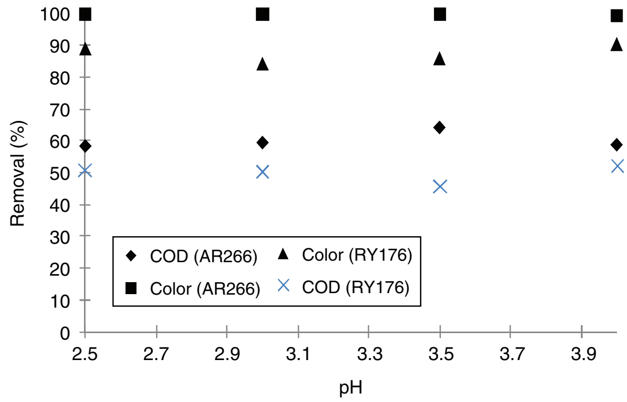

Fig. 1. Effect of pH on the COD and color removal during Fenton's process. $C_{Fe^{+2}}$ = 0.90 mm[1], $C_{H_2O_2}$ = 2.94 mm and SM = 20 min for both dyes.

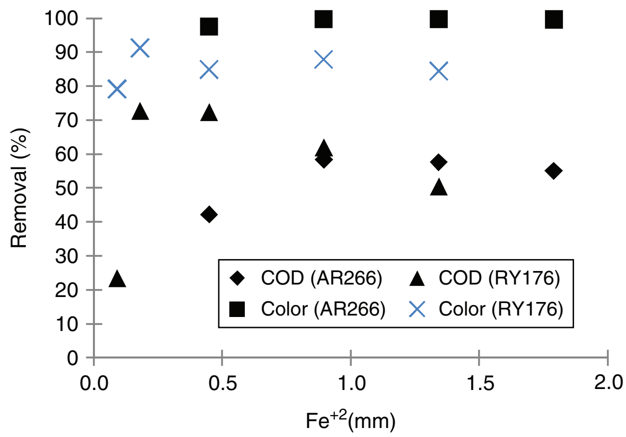

Fig. 2. Effect of Fe^{2+} on the COD and color removal during Fenton's process. $C_{H_2O_2}$ = 2.94 mm and SM = 20 min for both dyes, pH 3.5 for AR266, pH 4.0 for RY176.

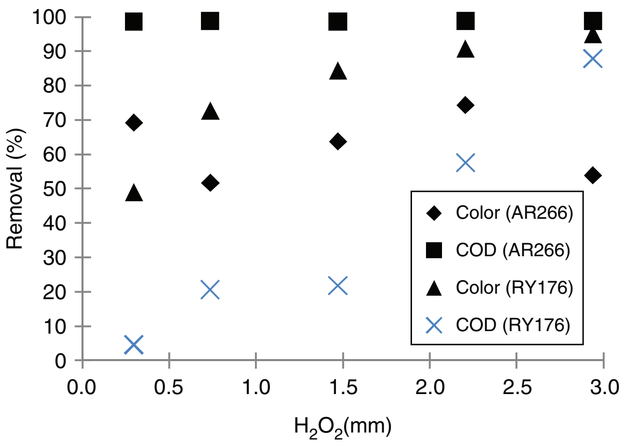

Fig. 3. Effect of H_2O_2 on the COD and color removal during Fenton's process. $C_{Fe^{+2}}$ = 0.90 mm, pH 3.5 for AR266, $C_{Fe^{+2}}$ = 0.18 mm, pH 4.0 for RY176 and SM = 20 min for both dyes.

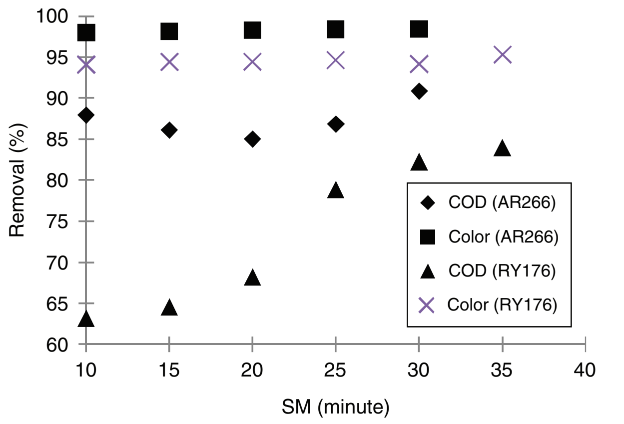

Fig. 4. Effect of slow mixing time on the COD and color removal during Fenton's process. $C_{Fe^{+2}}$ = 0.90 mm, $C_{H_2O_2}$ = 2.20 mm, pH 3.5 for AR266, $C_{Fe^{+2}}$ = 0.18 mm, $C_{H_2O_2}$ = 2.94 mm, pH 4.0 for RY 176.

3.1.3. Effect of H_2O_2 concentration on color and COD removal efficiencies

Fig. 3 shows the relation between color and COD removals at different H_2O_2 concentrations. The pH was controlled at 4 and 3.5, $FeSO_4$ concentrations were fixed at 0.18 and 0.90 mm for RY176 and AR266, respectively. When the concentration of H_2O_2 increased from 0.29 to 2.94 mm, color removals increased from 49% to 95% and maximum color removal was determined as 95% with 2.94 mm H_2O_2 for RY176. At all H_2O_2 concentrations above 98% color removals were obtained for AR266, but maximum color removal was observed as 99% with 2.20 mm H_2O_2 concentration. In addition to this, COD removals increased from 4.6% to 88% for RY176 and from 52% to 74% for AR266 with increasing H_2O_2 concentrations from 0.29 to 2.94 mm. Maximum COD removals were determined as 88% with optimum 2.94 mm H_2O_2 concentration for RY176 and 74% with optimum 2.20 mm H_2O_2 concentration for AR266. Sun et al. (2009) reported that there is a critical concentration of H_2O_2 in the Fenton oxidation process, and when the concentration of H_2O_2 is beyond the critical value, the scavenging of •OH by excessive H_2O_2 will became more significant and cause the degradation efficiency and rate of pollutants to decrease [16].

3.1.4. Effect of slow mixing time on color and COD removal efficiencies

Fig. 4 shows the results of optimization of SM time. When the SM times changed in the range of 10–35 min, it was observed that color removal increased from 98% to 99% and COD removal increased from 85% to 91% for AR266. Optimum SM time in terms of maximum 99% color removal and 91% COD removal were determined as 30 min. During the investigation of variable slow mixing times for RY176, it was observed that color removal increased from 94% to 95% and COD removal increased from 63% to 84%. Optimum SM time in terms of maximum 95% color removal and 84% COD removal was determined as 35 min for AR266. Although, Meriç et al. (2004) reported that 20 min SM time was optimum for COD removal for Reactive Black 5 because of floc destabilization at higher SM times but color removal higher than 99% for all SM time, in this study COD and color removal increased with increasing SM times [17].

3.1.5. Effect of temperature on color and COD removal efficiencies

Decolorization and COD removals were affected with temperature. Fenton's reactions can be accelerated at high temperature and more •OH is formed [16]. In Fig. 5 the effect of temperature on the COD and color removal is presented. In this step, temperature was changed in the range of 20–60 °C and it was observed that color removal change from 93% to 95% for RY176 and from 96% to 99% for AR266. In addition, COD removal changed from 63% to 82% for RY176 and from 13% to 89% for AR266. It can be deduced from Fig. 5 that optimum temperature was determined as 50 °C for RY176 in terms of maximum 82% COD and 95% color removal, on the other hand optimum temperature was found 30 °C for AR266 in terms of maximum 89% COD and 99% color removal. Decolorization at high temperatures is usually better than that at low temperatures. The redox reaction and decolorization can be accelerated by

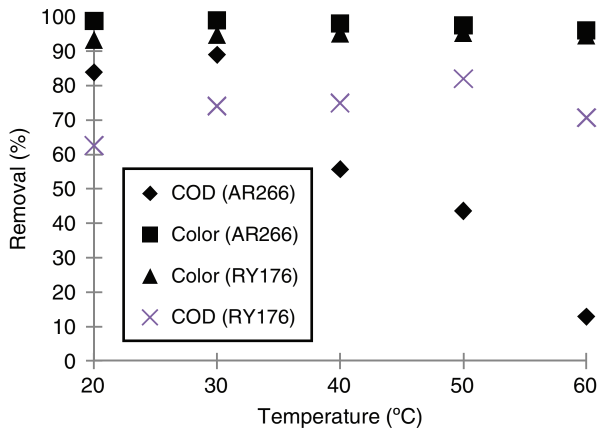

Fig. 5. Effect of temperature on the COD and color removal during Fenton's process. $C_{Fe^{+2}}$ = 0.90 mm, $C_{H_2O_2}$ = 2.20 mm, pH 3.5, SM = 30 min for AR266, $C_{Fe^{+2}}$ = 0.18 mm, $C_{H_2O_2}$ = 2.94 mm, pH 4.0, SM = 35 for RY176.

increasing the temperature. Likewise, the temperature of the wastewater discharged from dyeing and finishing mills is usually equal to or lower than 50 °C, all experiments were conducted with wastewater at a temperature of 50 °C [12].

4. Conclusions

In this study, optimum values were determined for 5 main factors (pH, Fe^{+2} concentration, H_2O_2 concentration, SM time and temperature) affecting Fenton process performance. Results showed that maximum removal efficiencies and optimum conditions in terms of color and COD removal with Fenton oxidation of dye solutions can be sorted in the following way: 99% color and 89% COD removal with pH 3.5, 0.90 mm Fe^{+2}, 2.20 mm H_2O_2, 30 min SM time and 30 °C temperature for AR266, and 95% color and 82% COD removals with pH 4.0, 0.18 mm Fe^{+2}, 2.94 mm H_2O_2, 35 min. SM time and 50 °C temperature for RY176.

The present study demonstrated that two commercial dyes, AR266 and RY176 could be decolorized by Fenton's process. The experimental results indicated that during Fenton's process, decolorization results were better than COD removal.

Based on these findings, it could be concluded that the Fenton oxidation process would find large application area for the treatment of this type wastewater in the future.

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