Importance of H_2O_2/Fe^{2+} ratio in Fenton's treatment of a carpet dyeing wastewater

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Abstract

The effectiveness of the Fenton's reagent (H_2O_2/Fe^{2+}) in the treatment of carpet dyeing wastewater was investigated under different operational conditions, namely, H_2O_2 and $FeSO_4$ concentrations, initial pH and temperature. Up to 95% COD removal efficiency was attained using 5.5 g/l $FeSO_4$ and 385 g/l H_2O_2 at a pH of 3, temperature of 50 °C. The H_2O_2/Fe^{2+} ratio (g/g) was found to be between 95 and 290 for maximum COD removal. It was noteworthy that, keeping H_2O_2/Fe^{2+} ratio constant within the range of 95–290, it became possible to decrease $FeSO_4$ concentration to 1.1 g/l and H_2O_2 concentration to 96.3 g/l, still achieving nearly the same COD removal efficiency. The relative efficiencies of Fenton's oxidation and coagulation stages revealed that Fenton's coagulation removed organic compounds which were not removed by Fenton's oxidation, indicating that the Fenton's coagulation acted as a polishing step.
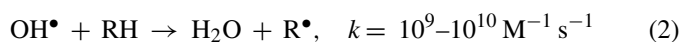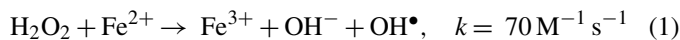© 2006 Elsevier B.V. All rights reserved.

Keywords: Carpet dyeing wastewater; Fenton's oxidation; Fenton's coagulation; H_2O_2/Fe^{2+} ratio
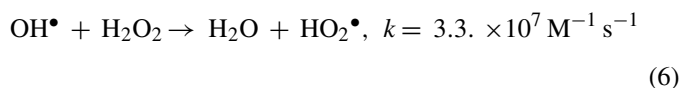
1. Introduction

A large portion of wastewater generated by the textile industry originates from dyeing operations and contains a wide range of contaminants that must be treated prior to disposal. The dyeing wastewater is known to have strong colour, chemical oxygen demand (COD), highly fluctuating pH and high temperature [1,2]. Fenton's treatment (H_2O_2/Fe^{2+} system), which is one of the advanced oxidation processes, was found to be effective in treating textile-dyeing wastewaters [3–7]. The Fenton's treatment has two distinct stages, namely Fenton's oxidation which is based on the formation of hydroxyl radicals ($OH^\bullet$) and Fenton's coagulation which is mainly simple ferric coagulation following the oxidation stage [5,6].

If H_2O_2 is added to an aqueous system containing an organic substrate and ferrous ions in a strong acid medium some complex redox reactions [6,8], as in Eqs. (1)–(4), will occur. The hydroxyl radical generated would attack the organic substrate RH like the unsaturated dye molecule used in this work:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^\bullet, \quad k = 70 \, \text{M}^{-1} \, \text{s}^{-1} \quad (1)$$

$$OH^\bullet + RH \rightarrow H_2O + R^\bullet, \quad k = 10^9 - 10^{10} \, \text{M}^{-1} \, \text{s}^{-1} \quad (2)$$

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

$$R^+ + H_2O \rightarrow ROH + H^+ \quad (4)$$

Additionally, many other reactions are also possible, which include the radical–radical reaction or the reaction of the OH radical with H_2O_2 [8]:

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2 \quad (5)$$

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet, \quad k = 3.3. \times 10^7 \, \text{M}^{-1} \, \text{s}^{-1} \quad (6)$$

The peroxide radicals ($HO_2^\bullet$) produced in the above case can further oxidize other species present in the solution [9]:

$$HO_2^\bullet + Fe^{2+} \rightarrow O_2 + Fe^{3+} + H^+, \quad k = 1.26 \times 10^6 \, \text{M}^{-1} \, \text{s}^{-1} \quad (7)$$
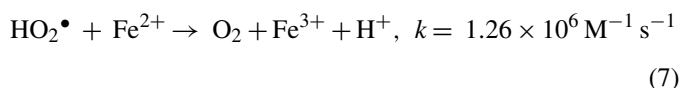
The rapid depletion of H_2O_2 that is often observed with Fenton's reagents is probably due to combined reactions (1), (2),

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(6) and (7). However, since reaction (2) has the highest rate constant, it is responsible for the degradation of the dye. Also, it is possible for Fe^{2+} to be auto-regenerated in this system, and act as a catalyst [8].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \qquad (8)$$
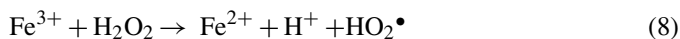
In spite of its desirable effectiveness, the Fenton's reagent dose required is an important factor to consider as it could determine the economic feasibility of the process. In fact, reported values for the required doses to treat synthetic wastewater containing 20–300 mg/l dyes are not so high and generally fall into the range of 17–584 mg/l H_2O_2 and 13–500 mg/l $FeSO_4$ [6,7]. However, it was also presented in the literature studies that treatment of real wastewaters by Fenton's reagent requires much higher doses than simulated wastewaters bearing same dye content to achieve the same treatment efficiency [5,6,10]. For example, Kuo [6] reported that the effective amount of H_2O_2 and $FeSO_4$ did increase from 292 to 2042 mg/l and from 333 to 666 mg/l, respectively, when dye auxiliaries and/or dispersants were present in wastewater containing 0.3 g/l dye (COD: 2000 mg/l). Regarding the higher amount of H_2O_2 and $FeSO_4$ needed, Kuo [6] suggested that the dye auxiliaries and/or dispersants may react with the active substances given from the decomposition of H_2O_2 and also may consume $FeSO_4$. Similarly, Guedes et al. [11] reported a very high dose of H_2O_2 (10.6 g/l) for the Fenton oxidation of cork cooking wastewater with a COD of 5000 mg/l. In another study, Perez et al. [3] applied Fenton–photo-Fenton oxidation to the real textile industry wastewater with a COD of about 1600 mg/l and emphasized the importance of light driven reactions. However, they still claimed that even for Fenton–photo-Fenton systems, large enough concentrations of Fe and H_2O_2 are essential (10,000 mg/l H_2O_2; 400 mg/l Fe^{2+}). They also stated that the use of large quantities of Fe has a negative effect from the applied point of view, since it implies the need of an additional treatment step for Fe removal. Hence, the major drawback of Fenton's treatment appears as the large concentrations of H_2O_2 and $FeSO_4$ required.

On the other hand, it is also supported by several studies in the literature that the H_2O_2/Fe^{2+} ratio is the key to improve the efficiency of the Fenton's treatment. According to the studies conducted by Tang and Huang [12–15], both H_2O_2 and Fe^{2+} can also react with $OH^{\bullet}$ and therefore both can inhibit the oxidation reactions if either of them is not in the optimal dosage. Parallel to their findings, Tang and Tassos [16] and Kochany and Lugowski [17] pointed out that optimal H_2O_2/Fe^{2+} has to be maintained to achieve the maximal degradation efficiency since both components can scavenge the radicals generated (Eqs. (1), (2), (6) and (7)) and reduce the amount of radicals available to substrates. At this point, one should think if it is possible to reduce the quantities of Fe and H_2O_2 as long as their ratio is kept constant.

Therefore, the purpose of this research is to find out the H_2O_2/Fe^{2+} ratio needed for maximum COD removal in a real carpet dyeing wastewater and to find out the level up to which the concentrations of H_2O_2 and $FeSO_4$ added to the

Table 1
Dyes present in the wastewater

Dye	Type
Tectilon Red 599EU	Azo dye
Tectilon Orange 4G	Azo dye
Tectilon Blue 608	Anthraquinone dye
Tectilon Yellow 2G	Azo dye
Tectilon Red 2B	Azo dye
Tectilon Blue 4R-01	Anthraquinone dye

system can be decreased on the condition that the ratio is kept constant. The relative efficiencies of Fenton's oxidation and Fenton's coagulation stages were also examined through the treatment of carpet dyeing wastewater by Fenton's reagent and the operational parameters that could affect the efficiency of Fenton's treatment, namely the H_2O_2 and $FeSO_4$ concentrations, initial pH and temperature of the wastewater, were studied.

2. Materials and methods

2.1. Wastewater

The wastewater used in this study was obtained from a carpet mill (Ankara, Turkey). The wastewater of carpet dyeing mill includes acidic, basic and disperse dyes, acetic acid, several dye stuffs like levelling agents. The wastewaters used in this study were sampled from the acidic (300 m^3/day), basic (200 m^3/day) and disperse (300 m^3/day) dyeing wastewater lines. The dyes present in the wastewater and the wastewater characteristics are given in Tables 1 and 2, respectively. The wastewater samples taken as 24 h composite from these three individual wastewater lines (about 30 l of each sample) are composited in terms of their flow rates (i.e. in a volumetric ratio of 3:2:3) and the obtained composite sample was used in this study. This composite sample had a COD of about 2400 mg/l, a biochemical oxygen demand (BOD_5) of about 890 mg/l, a total organic carbon (TOC) of about 2000 mg/l and pH of 4.8. Following the preparation of composite sample, sodium azide (5 mg/l) was added to inhibit the biological activity during the storage at room temperature.

Table 2
Dyeing wastewater characteristics

Parameter	Basic	Acidic	Disperse
BOD_5 (mg/l)	580	890	1100
COD (mg/l)	2576	2770	2150
Suspended solids (mg/l)	52	27	16
NH_4-N (mg/l)	0.896	1.568	5.824
Free Cl (mg/l)	–	–	–
Oil-gres (mg/l)	109	133	157
Total Cr (mg/l)	0.302	<0.3	<0.3
Sulfur, S^{2-} (mg/l)	<0.008	<0.008	0.249
pH	4.49	4.83	4.76
Phenol (mg/l)	<0.001	0.0259	0.0320
Conductivity (μmhos/cm)	820	530	550

2.2. Experiments

The following steps were taken during this study:

(1) A temperature range of 25–70 °C was studied in order to observe the effect of temperature on Fenton's treatment when initial concentrations of $FeSO_4$ and H_2O_2 were 5.5 and 385 g/l, respectively, at a pH of 3.

(2) The effect of initial pH on treatment efficiency was investigated within the pH range of 2–5.5 when initial concentrations of $FeSO_4$ and H_2O_2 were 5.5 and 385 g/l, respectively, at a temperature of 50 °C.

(3) In an attempt to determine the effect of $FeSO_4$ and H_2O_2 concentrations on Fenton's treatment, the amount of $FeSO_4$ added was changed between 1.1 and 10.9 g/l when H_2O_2 concentration was kept constant at 385 g/l; the amount of H_2O_2 added was changed between 19.3 and 577.5 g/l when $FeSO_4$ concentration was kept constant at 5.5 g/l. Temperature and pH of the wastewater were kept at 50 °C and 3, respectively, as determined during the first and second step of this study. The H_2O_2 and $FeSO_4$ dose ranges studied were selected based on the results of the preliminary experiments for which the data are not presented here.

The experiments were conducted in batch reactors containing 100 ml of wastewater sample heated up to a set temperature. The pH adjustment was carried out with diluted sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH). Required amounts of $FeSO_4 \cdot 7H_2O$ and H_2O_2 were added to the sample and stirring was applied. Then, 30 min were allowed for the completion of the reaction (the equilibration time is reported to be in the range of 10–30 min by Kuo [6], Solozhenko et al. [7], Zhang et al. [18] and Kang et al. [19]). Following 30 min of precipitation, the supernatant was decanted. The pH of the decanted supernatant was adjusted to 7. After 2 h of precipitation, the supernatant was decanted for UV absorbance, COD and TOC measurements.

COD determination was performed after the Fenton's coagulation stage, i.e. after the overall treatment, whereas UV absorbance and TOC of the samples were measured after both Fenton's oxidation and Fenton's coagulation stages. The reason for this is that if a water or wastewater sample includes hydrogen peroxide, the standard COD test will be interfered since the dichromate ions react with H_2O_2 in an acidified solution [6,20,21]. Therefore, COD measurements were performed only after the Fenton's coagulation stage. Since hydrogen peroxide is unstable in basic solution, after raising the pH above 7 for the initiation of Fenton's coagulation, it decomposes to give oxygen and water and looses its oxidation ability [6] so that no interference is of importance. On the other hand, neither TOC measurement nor absorbency determination has the problem of interference of H_2O_2. Therefore, TOC measurements and absorbency determination could be performed after both stages of Fenton's treatment and were conducted immediately after sampling.

All the experiments conducted were carried out in duplicate sets. All measurements were performed in parallels in each set. COD and TOC removals reported are the average of the parallel
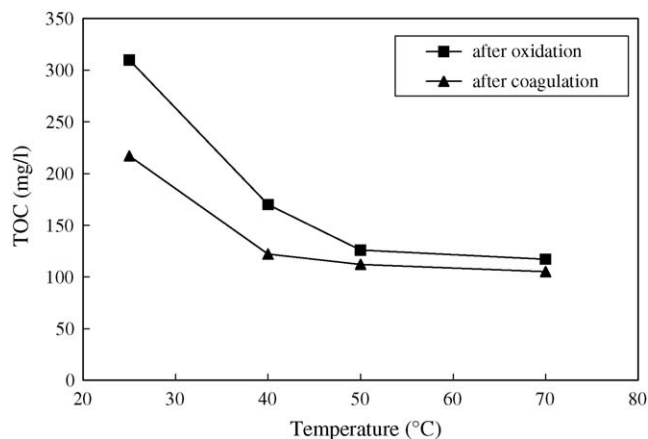

Fig. 1. Effect of temperature on TOC removal (initial TOC = 2000 mg/l; $FeSO_4$ and H_2O_2 were 5.5 and 385 g/l, respectively; pH 3).

measurements of the duplicate sets in which duplicates were close to each other by 15% at most.

2.3. Reagents

H_2O_2 (35%; density: 1.13 kg/l) and $FeSO_4 \cdot 7H_2O$, used during experiments, were purchased from Merck KGaA (Germany).

2.4. Analysis

COD of the samples were measured according to an EPA approved reactor digestion method (for a COD range of 0–1500 mg/l) using HACH DR2000. TOC of the samples were measured using TOC analyser, Schimadzu 5000. BOD_5 and other wastewater parameters presented in Table 2, were analysed according to standard method of analysis [22]. The absorbency of the samples was determined with Secomam 750 (France) spectrometer at wavelength intervals of 5 nm, from 200 to 400 nm. The pH measurements were performed using a pH meter (Model 2906, Jenway Ltd., UK) and a pH probe (G-05992-55, Cole Parmer Inst. Co., USA).

3. Results and discussion

3.1. Effect of temperature

Typical temperature for dyeing wastewater of carpet mill is around 50 °C. Therefore, a temperature range of 25–70 °C was studied in order to observe the effect of temperature on Fenton's treatment (Fig. 1). The obtained TOC removal efficiencies after oxidation and coagulation are 89.1, 93.9, 94.4 and 94.7% at 25, 40, 50 and 70 °C, respectively, for the initial TOC value of 2000 mg/l. No optimal temperature was detected as opposed to most of the literature reports [11,23,24] in which 30 °C is stated as optimal temperature for Fenton's oxidation. Alaton and Teksoy [25] also reported that there is an optimal temperature, but, at 50 °C for the acid dyebath effluent (with a COD of 2700 mg/l). On the other hand, Ramirez et al. [24] reported the temperature of 29 and 50 °C as optimal for color and TOC removal, respectively, in a study investigating the degradation of the synthetic

dye Orange II (TOC 58 mg/l). Despite different optima figures reported for the temperature, what is common to all above mentioned literature studies is that removal performance declined above the optimal value due to hydrogen peroxide decomposition into oxygen and water being very significant at above 40–50 °C, which is not observed in our study. In our study, there was almost no change in the TOC removal efficiency above 40 °C. However, our observation was in accordance with the findings of Dutta et al. [26] who stated that there was practically no difference in the rate and extent of degradation of the reaction in the temperature between 40 and 75 °C.

In order to observe the relative efficiencies of Fenton's oxidation and Fenton's coagulation, TOC measurements were conducted at the end of corresponding stages. As seen from Fig. 1, as the temperature increased from 25 to 50 °C, efficiency of oxidation stage in the overall treatment increased. At 50 °C, almost all of the TOC removal was from the oxidation stage.

3.2. Effect of initial pH

Fenton oxidation is known as a highly pH dependent process since pH plays an important role in the mechanism of $OH^\bullet$ production in the Fenton's reaction [5–7,12–17]. At high pH (pH > 4), the generation of $OH^\bullet$ gets slower because of the formation of the ferric hydroxo complexes; the complexes would further form $[Fe(OH)_4]$ when the pH value is higher than 9.0 [6]. On the other hand, at very low pH values (<2.0) the reaction is slowed down due to the formation of complex species $[Fe(H_2O)_6]^{2+}$, which reacts more slowly with peroxide compared to that of $[Fe(OH)(H_2O)_5]^{2+}$. In addition, the peroxide gets solvated in the presence of high concentration of H^+ ion to form stable oxonium ion $[H_3O_2]^+$. An oxonium ion makes peroxide electrophilic to enhance its stability and presumably reduces substantially the reactivity with Fe^{2+} ion [27]. Therefore, the initial pH value has to be in the acidic range (2–4) to generate the maximum amount of $OH^\bullet$ to oxidize organic compounds [5–7,12–17,28].

Fig. 2 depicts the effect of pH on TOC removal. In parallel to the above mentioned literature findings, pH 3 resulted in the highest TOC removal. However, the TOC removals attained for other pH values were not significantly different from each other (91–94%), which was attributed to the almost completion
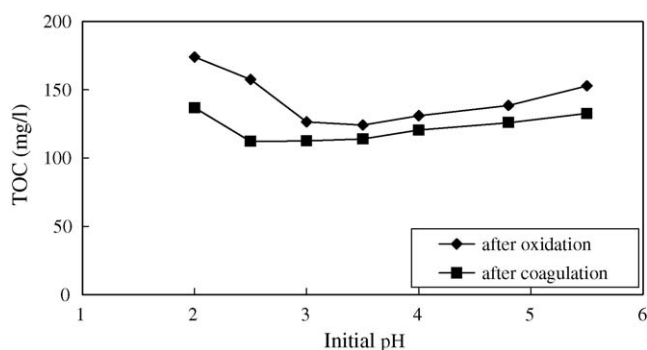
of the reaction within 30 min. Similarly, Alaton and Teksoy [25] applied a 30 min of reaction period to oxidize acid dyebath effluent with a COD of 2700 mg/l and reported that COD removal efficiencies were not sensitive to pH. Nevertheless, the TOC removal attained at pH 2 was the lowest and deviated most from the others, probably due to the oxonium ion formation which reduces substantially the reactivity of peroxide with Fe^{2+}. So, this may indicate the reaction was not complete at the end of 30 min at this pH.

When the relative efficiencies of Fenton's oxidation and Fenton's coagulation were examined, TOC removals showed that as the pH deviated from the pH range of 3–3.5 toward more acidic conditions, the removal of TOC by Fenton's oxidation becomes less as compared to the removal after Fenton's coagulation (Fig. 2). This was attributed to the scavenging effect of high hydrogen ion concentration. However, in and above pH 3, the overall removal of TOC is by Fenton's oxidation mainly.

3.3. Effect of FeSO4 and H2O2 concentrations

The effect of $FeSO_4$ concentration on COD and TOC removals was examined by changing the $FeSO_4$ concentration between 1.1 and 10.9 g/l while keeping the concentration of H_2O_2, pH and temperature constant at 385 g/l, 3 and 50 °C, respectively (Fig. 3). As seen from Fig. 3a, as $FeSO_4$ doses were increased from 1.1 to 5.5 g/l, COD removal efficiencies increased from about 40 to 95%. Hence, it can be said that higher ferrous doses lead to the generation of more $OH^\bullet$ radicals and not only made the redox reaction complete but also caused coagulation resulting in improved COD removal. At higher doses, the

(a)

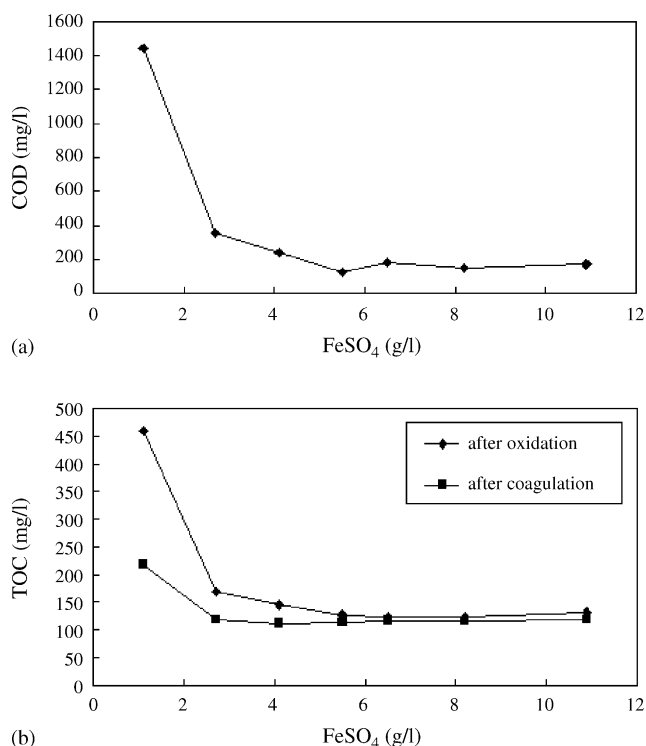Fig. 3. Dependence of (a) COD and (b) TOC removal on $FeSO_4$ concentration (initial COD = 2400 mg/l; initial TOC = 2000 mg/l; 385 g/l H_2O_2; 50 °C; pH 3).
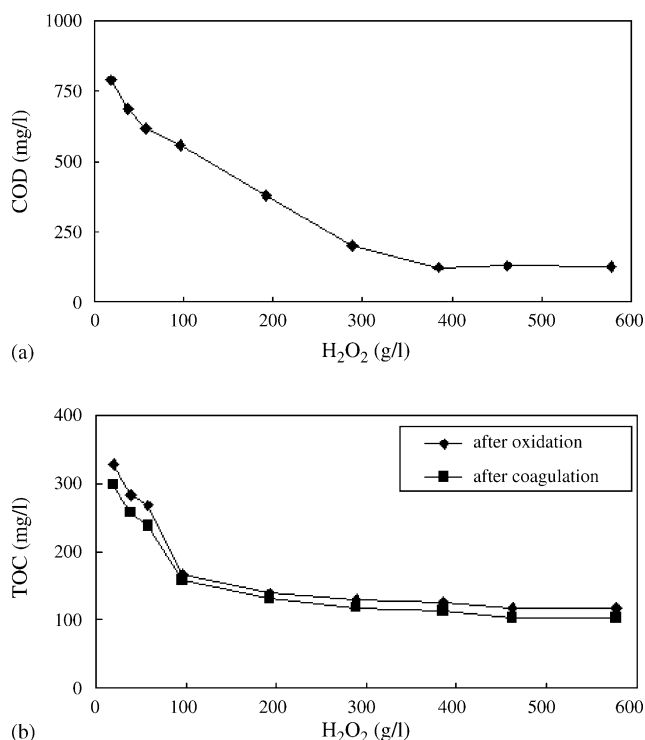

Fig. 2. Effect of initial pH on TOC removal (initial TOC = 2000 mg/l; $FeSO_4$ and H_2O_2 were 5.5 and 385 g/l, respectively; 50 °C).

Fig. 4. Dependence of (a) COD and (b) TOC removal on H_2O_2 concentration (initial COD = 2400 mg/l; initial TOC = 2000 mg/l; 5.5 g/l $FeSO_4$; 50 °C; pH 3).

Fig. 5. UV spectral profiles of carpet industry wastewater before and after Fenton's treatment (385 g/l H_2O_2; 5.5 g/l $FeSO_4$; 50 °C; pH 3).

COD removal efficiency remained constant at around 94–95%, indicating that H_2O_2 became the limiting for further $OH^\bullet$ generation.

As seen from Fig. 3b, for $FeSO_4$ concentrations of 5.5 g/l and higher, the dominant process was Fenton's oxidation and the role of Fenton's coagulation is almost negligible. However, as the concentration of $FeSO_4$ was decreased, the amount of TOC removed by Fenton's oxidation decreased and percent removal by coagulation increased as compared to higher concentrations. This is most probably due to less $OH^\bullet$ production when amount of Fe^{2+} is smaller.

The effect of H_2O_2 concentration on Fenton's treatment was investigated in a H_2O_2 concentration range between 19.3 and 577.5 g/l, while keeping the $FeSO_4$ dose, pH and temperature constant at 5.5 g/l, 3 and 50 °C, respectively. The results obtained are presented graphically in Fig. 4. As seen from Fig. 4a, at 19.3 g/l H_2O_2, COD removal was 67% and it increased to 95% when H_2O_2 was raised to 385 g/l, due to increase in the formation of $OH^\bullet$. However, for H_2O_2 doses higher than 385 g/l, no further increase in the COD removal was observed since ferrous ion concentration became deficient for reacting with H_2O_2.

When TOC measurements are concerned, increase in H_2O_2 concentrations increased the overall TOC removal and almost all of the TOC was removed in the oxidation stage (Fig. 4b). For all H_2O_2 concentrations studied, the efficiency of Fenton's coagulation in the overall treatment is almost negligible. On the contrary, Bae et al. [9] reported that great part of the COD present in their textile wastewater was removed by ferric coagulation rather than Fenton oxidation. This could be due to differences in dyes in wastewaters. Moreover, they did apply Fenton's process
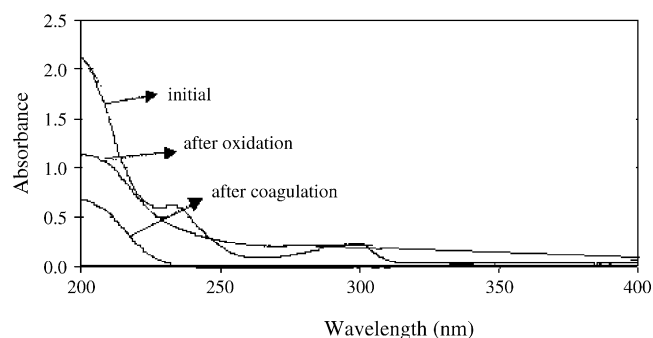
to the biologically treated wastewater which could also change the characteristics of the organic structure(s) of the wastewater. The efficiency of Fenton's oxidation stage also increased with increasing H_2O_2 doses between 19.3 and 288 g/l. This increase is similar to the findings presented by Kang and Hwang [29], stating that increasing the dosage of H_2O_2 increased both the overall removal efficiency and the efficiency by oxidation.

The concentrations of H_2O_2 and $FeSO_4$ (i.e. 385 and 5.5 g/l, respectively), determined as required for achieving 95% COD removal, are appreciably higher than those stated in the literature for treatment of artificial dye wastewater with Fenton's reagent. In their study, Kang and Chang [5] reported 90 and 84% COD removal for synthetic dye wastewater when H_2O_2 and Fe^{2+} doses were 300 mg/l. Similarly, Kuo [6] mentioned using H_2O_2 doses of 292–584 mg/l and $FeSO_4$ doses of 82–500 mg/l for different artificial dyeing wastewaters and achieving around 90% COD removal. On the other hand, Kuo [6] also reported that the effective amount of H_2O_2 and $FeSO_4$ did increase from 292 to 2042 mg/l and from 333 to 666 mg/l, respectively, when dispersants were present in wastewater containing 0.3 g/l dye. Hence, requirement of much higher doses, in our study, is most probably due to the consumption of $FeSO_4$ and H_2O_2 by not only dispersants but also dye auxiliaries, pH adjusters, dye carriers, sequestrants and surfactants found in the carpet dyeing wastewater. Supportingly, Guedes et al. [11] found that very high dose of H_2O_2 (10.6 g/l) is required for the Fenton oxidation of cork cooking (real) wastewater having a COD of 5000 mg/l.

In addition, degradation of organic compounds was monitored by recording UV absorbance in the range from 200 to 400 nm (Fig. 5). As can be seen from this figure, original wastewater sample had three peaks at 200, 235 and 300 nm, among which the absorbance at 200 nm was the highest. After Fenton's oxidation, these peaks diminished and a continuous decrease in the absorbance was observed from 200 to 400 nm, indicating that Fenton's oxidation effectively removed these organics. Further, UV scans after Fenton's coagulation suggested that Fenton's coagulation removed organic compounds that were not removed by Fenton's oxidation.

3.4. Effect of H_2O_2/Fe^{2+} ratio

In order to find the optimal H_2O_2/Fe^{2+} ratio (g/g), COD removals were plotted against the H_2O_2/Fe^{2+} ratios calculated

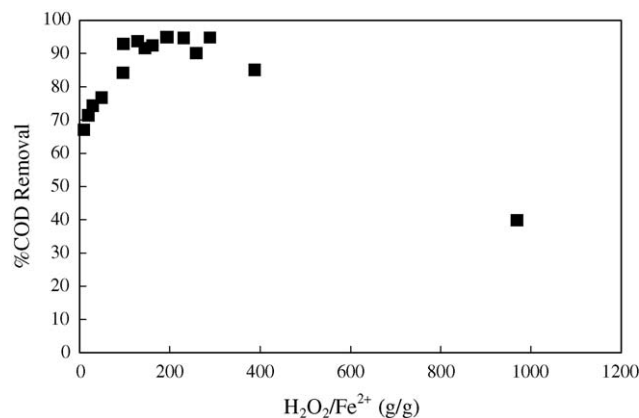Fig. 6. Effect of H_2O_2/Fe^{2+} ratio on COD removal (50 °C; pH 3).

for the experiments (Fig. 6). It was seen that COD removal increased as the ratio increased to 95 and did not change in between 95 and 290 while ratio above 290 caused a decrease in COD removal. The lower COD removals were observed where either ferrous ions or H_2O_2 concentration was superfluous, i.e. where ratio was the lowest or the highest. Hence, the H_2O_2/Fe^{2+} ratio giving highest COD removal for carpet dyeing composite wastewater appeared to be between 95 and 290 (g/g) which corresponds to 153–470 as molar ratio.

Several groups working with different systems have also reported different H_2O_2/Fe^{2+} ratios for efficient dye degradation. Casero et al. [30] found that the required molar ratio for the oxidation of amine (COD 1200 mg/l) is around 5–40. Solozhenko et al. [7] worked with a quite wide range of molar ratios (5.8–340) for the removal of azo dye active yellow light-fast 2KT (40 mg/l) and observed a distinct maximum at the molar ratio of 340 at constant reaction time. Barbeni et al. [31] studied the chlorophenols oxidation and found the ratio to be 100 (w/w). In his study with five different artificial dyeing wastewaters (1100–2700 mg/l COD), Kuo [6] worked with ratios between 3 and 9 (w/w) and reported about 90% COD removal. Tang and Huang [15] reported the ratio for chlorinated aliphatic organics to be about 5 to 11 (w/w) whereas Tang and Tassos [16] suggested molar ratio of H_2O_2/Fe^{2+} 2:1–5:1 for bromoform (49.2–295 µg/l) oxidation. Kochany and Lugowski [17] suggested that optimum conditions for treatment require H_2O_2/Fe^{2+} molar ratio of 10:2.5. As seen from these literature figures, H_2O_2/Fe^{2+} ratio shows a great variation depending on the types of organics as well as their loads. When comparison was made, it was seen that the ratio found in this study is remarkably higher than those reported in the literature. This would be attributed to the relatively higher organic load and/or different composition of the organic matter used in this study. Furthermore, unlike others, the presence of auxiliary chemicals in the real wastewater used in this study could be another factor leading to this higher ratio.

A series of experiments were further conducted in order to find out the level up to which the concentrations of H_2O_2 and FeSO$_4$ added can be decreased or tuned up on the condition that the ratio is kept constant. To this purpose, three values of H_2O_2/Fe^{2+} were selected from the predetermined ratio
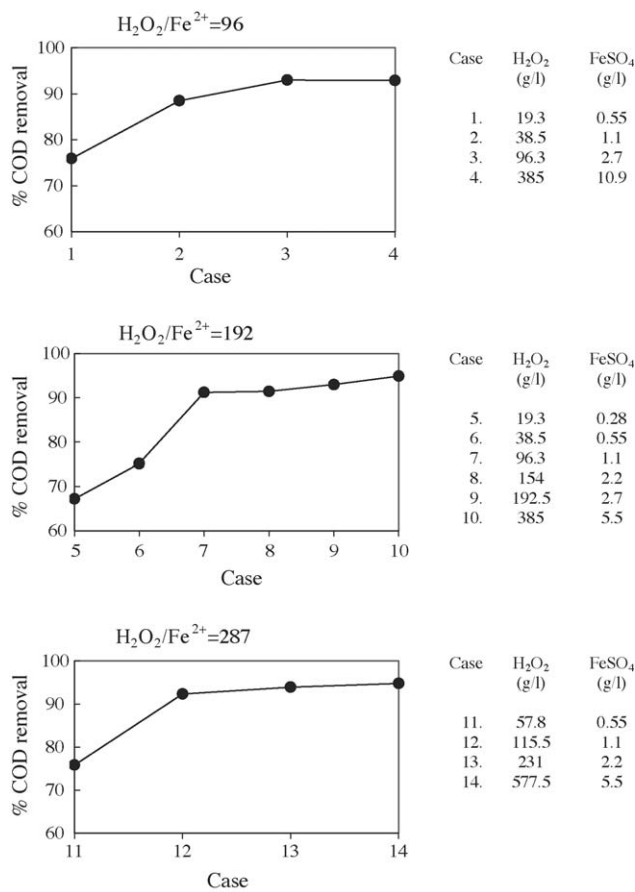

Fig. 7. Dependence of COD removal on H_2O_2 and FeSO$_4$ concentrations at different H_2O_2/Fe^{2+} ratios (g/g).

range (95–290). H_2O_2/Fe^{2+} ratios of 96, 192 and 287 (g/g) as to correspond to about the minimal, middle and maximal values, respectively, were selected within the range. Then, different doses of H_2O_2 and FeSO$_4$ were selected which yielded the same H_2O_2/Fe^{2+} ratio. The results obtained can be seen in Fig. 7. According to this figure, in general, COD removal remained almost constant (90–95%) for H_2O_2 concentrations of 96.3–385 g/l and FeSO$_4$ concentrations of 1.1–5.5 g/l. For doses lower than these ranges, COD removal decreased although the ratio was kept constant. This result indicates that, in order to achieve maximum COD removal, as well as a required H_2O_2/Fe^{2+} ratio, sufficient amount of Fenton's reagent is also needed to produce adequate amount of OH$^\bullet$. In addition, provided that the required H_2O_2/Fe^{2+} ratio is satisfied, required H_2O_2 and FeSO$_4$ doses can be reduced or tuned up significantly. This observation was noteworthy as it allowed observing that it is possible to decrease H_2O_2 and FeSO$_4$ concentrations from 385 to 96.3 g/l and from 5.5 to 1.1 g/l, respectively, for nearly the same treatment efficiency.

For a constant percent COD removal, i.e. 90–95%, the amount of Fenton's reagent required was 96.3 g/l H_2O_2 and 2.7 g/l FeSO$_4$ for a H_2O_2/Fe^{2+} ratio of 96; 96.3 g/l H_2O_2 and 1.1 g/l FeSO$_4$ for a H_2O_2/Fe^{2+} ratio of 192 and 115.5 g/l H_2O_2 and 1.1 g/l FeSO$_4$ for a H_2O_2/Fe^{2+} ratio of 287 (g/g) (Fig. 7). It is clear that the least amount of Fenton's reagent required was

for the ratio of 192. Therefore, it should also be considered that the effective doses of Fenton's reagent vary with respect to the selected ratio. In order to achieve maximum removal with minimum doses, effect of ratio should be given importance. Improvement in the biodegradability of the wastewater was also followed in terms of the change in the BOD_5/COD ratio and it was seen that, after Fenton's treatment (at a H_2O_2/Fe^{2+} ratio of 192), the biodegradability of the wastewater was increased by about 1.3–1.4 times, depending on the doses applied.

4. Conclusions

The following general conclusions can be drawn from this study:

- H_2O_2/Fe^{2+} is a critical parameter for improving the efficiency of the Fenton's process. Keeping the H_2O_2/Fe^{2+} ratio constant within the specified range, it is possible to decrease $FeSO_4$ and H_2O_2 concentrations remarkably, still achieving nearly the same COD removal efficiency.
- Fenton's coagulation removes organic compounds which were not removed by Fenton's oxidation, indicating that the Fenton's coagulation act as a polishing step.

Considering the relatively high $FeSO_4$ and H_2O_2 concentrations required, Fenton's treatment may be rated as uneconomical for the large volumes of dyeing wastewater. However, degradation of the pollutant organics into biodegradable products by relatively low Fenton's reagent doses and applying biological treatment following it, might be a more economical and effective method to achieve discharge standards.

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