Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2011 Desalination Publications. All rights reserved
doi: 10/5004/dwt.2011.2234

28 (2011) 260–264
April

Fenton oxidation of carpet dyeing wastewater for removal of COD and color

Pradeep Kumar[a], Tjoon Tow Teng[b], Shri Chand[c], Kailas L. Wasewar[d,*]

[a]*Department of Chemical Engineering and Technology, Institute of Technology, Banaras Hindu University, Varanasi 221005, India*
[b]*Environmental Technology Division, School of Industrial Technology, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia*
[c]*Department of Chemical Engineering, Indian Institute of Technology, Roorkee 247667, India*
[d]*Department of Chemical Engineering, Visvesvaraya National Institute of Technology (VNIT), Nagpur 440011, Maharashtra, India*
Tel. +91 712 2801561; email: k_wasewar@rediffmail.com

Received 24 August 2010; Accepted 30 January 2011

ABSTRACT

The decolorization and chemical oxygen demand (COD) removal of carpet dyeing wastewater by Fenton oxidation process was investigated at various reaction conditions. The initial COD of carpet dyeing wastewater was 2760 mg/l and its color in term of absorbance was 2.7. The effect of various parameters such as pH, ferrous sulphate concentration, hydrogen peroxide concentration, reaction time, and temperature on COD and color removal of carpet dyeing wastewater by Fenton oxidation were studied. Using Fenton oxidation, the optimum operating conditions of pH of 4, $FeSO_4$ concentration 4 g/l, H_2O_2 concentration 30 g/l, temperature 25°C, and 30 min reaction time at atmospheric pressure, giving maximum color and COD removals of 93% and 98%, respectively, were found. The carpet dyeing wastewater can be satisfactorily treated by adopting this process. The calorific value of dried residue obtained after thermal treatment was 12.8 MJ/kg, which is about 76% to that of lignite coal and thus could be used as a solid fuel. Also the dye degradation kinetics was studied.

Keywords: Carpet dyeing wastewater; COD removal; Color removal; Fenton oxidation

1. Introduction

The wastewater generated from carpet dyeing industries is a large source of organic and inorganic matters, colors, surface active materials, additives, suspended solids (SS), chelating agents, etc. with high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) [1–3]. Furthermore, the compositions of carpet dyeing wastewater vary greatly from day to day and hour to hour, and concentration of fixing compounds which are added. Dyes usually present have high stability under sunlight and is visible even at low concentrations and can cause environmental damage to living organisms by stopping the reoxygenation capacity of water and also blocking sunlight, thereby disturbing the natural growth activity of aquatic life [4–7].

Various methods for color and COD removals, such as aerobic and anaerobic microbial degradation, coagulation, chemical oxidation, electrochemical methods, filtration, softening and membrane separation process have been proposed from time to time. The satisfactory results of carpet dyeing wastewater treatments are difficult to obtain by the traditional processes or any combination of the activated sludge process and chemical and physical methods [6,8].

Fenton oxidation is a homogeneous catalytic advanced oxidation process. The Fenton oxidation mixture is a mixture of hydrogen peroxide and ferrous salt to induce a complex redox reaction in acidic environment. Ferrous ion initiates and catalyses the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals, $^{\bullet}OH$ [9–12].

---

*Corresponding author.

$$FeSO_4 \cdot 7H_2O \rightarrow Fe^{2+} + SO_4^{2-} + 7H_2O \quad (1)$$

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

Formed Fe(III) can react with H_2O_2 in the so-called Fenton-like reactions regenerating Fe^{2+} and thus supporting the Fenton process:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^{2\bullet} + H^+ \quad (3)$$

$$Fe^{3+} + HO^{2\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \quad (4)$$

$$Fe^{3+} + RH \rightarrow Fe^{2+} + R^{\bullet} + H^+ \quad (5)$$

$$Fe^{3+} + R \rightarrow Fe^{2+} + R^+ \quad (6)$$

$$R^+ + H_2O \rightarrow ROH + H^+ \quad (7)$$

$$RH \rightarrow \text{Dye molecule (Organic substance)} \quad (8)$$

Side reaction

$$2H^+ + SO_4^{2-} \rightarrow H_2SO_4 \quad (9)$$

${}^{\bullet}OH$ is able to react with organic pollutants to mineralize these pollutants into CO_2, water and inorganic ions [12]. Wei et al. [12] studied the treatment of 2-phenylamino-3-methyl-6-di-*n*-butylaminofluoran production effluent by combination of biological treatments and Fenton's oxidation. They observed that the best oxidation efficiency is achieved when neither H_2O_2 nor Fe^{2+} is overdosed, so that the maximum amount of $\bullet OH$ radicals must be available for the oxidation of organics. Many authors [9,10,12] suggested Fe^{2+} to H_2O_2 mass ratio to be optimal in the range of 1–10. But it must be optimized for particular wastewater to minimize scavenging effects. The Fenton reaction has a short reaction time among all advanced oxidation processes and it has many other important advantages. Iron and H_2O_2 are cheap and non-toxic, there is no mass transfer limitations due to its homogenous catalytic nature, energy is not involved as catalyst and the process is easy to run and control. It has been widely used for treatment of highly polluted textile and paper mill wastewaters.

In view of the effect of carpet dyeing wastewater on environment, it is essential to treat this wastewater before discharging to the environment. Hence, it has been though desirable to study the removal of color and COD from carpet dyeing wastewater using Fenton oxidation. The effect of various parameters such as pH, ferrous sulphate concentration, hydrogen peroxide concentration, reaction time, temperature on COD and color removal of carpet dyeing wastewater by Fenton oxidation were studied. Also the dye degradation kinetics was studied.

2. Materials and methods

2.1. Carpet dyeing wastewater

Carpet dyeing wastewater was collected from a Carpet Dyeing Industry at Bhadohi, UP, India. There are various dyes present in the dyeing wastewater such as acid blue 264, basic blue 69, acid blue 25, basic red 22, basic green 4, acid yellow 36, acid violet, ethyl orange, etc. Table 1 shows the characteristics of carpet dyeing wastewater. It consists of dye, acid, salt and other leveling agents. The wastewater collected from the plant was stored in deep freezer and used without any dilution and treatment for study.

2.2. Reagents

All the chemicals used were of analytical grade and used without any further purification. $CuSO_4 \cdot 5H_2O$ and Ag_2SO_4 were procured from Qualigens Fine Chemicals, Mumbai, India. Hg_2SO_4 and H_2SO_4 were obtained from Loba Chemicals, Mumbai, India. NaOH was procured from Thomas Baker (Chemicals), Mumbai, India and $K_2Cr_2O_7$ from S.D. Fine, Mumbai, India. $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ purchased from Reidel (India) Chemicals, Hapur, India, $FeSO_4 \cdot 7H_2O$ from RCFL New Delhi, India and H_2O_2 was procured from Polypharm, Mumbai, India. Deionized water was used throughout this study. The chemical used are of the purity >99.5%.

2.3. Analytical methods

The COD value was measured by a COD analyzer (S.M. Scientific Instruments) using the standard dichromate open reflux method. The color was measured by UV–VIS spectrophotometer 159 in terms of absorbance. The total suspended solid was evaluated by TDScan WP1, made in Singapore. The pH was measured using

Table 1
Characteristics of carpet dyeing wastewater

Characteristics	Value[a]
pH (at 29°C)	8.5
COD	2760
BOD	1790
Color (absorbance)	2.80
Total dissolved solid	810
Turbidity (NTU)	1400
Appearance	Brown
Total iron (as Fe)	1.76
Chlorides (as Cl)	545
Oil and grease	260
Sulphate (as SO_4)	148

[a] All values except pH, color and turbidity are in mg/l.

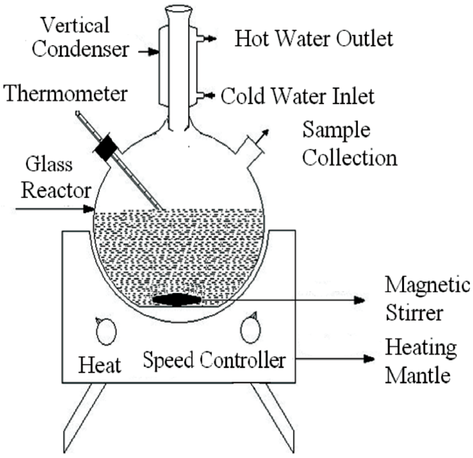

Fig. 1. Experimental set up for Fenton oxidation.

a microprocessor based pH meter. Turbidity was measured by digital nephelo-turbidity meter 132. The calorific value of dried residue was determined using Bomb calorimeter.

2.4. Experimental

The Fenton oxidation studies were conducted in a three-necked glass reactor. The glass reactor was equipped with a vertical condenser, heating device, magnetic stirrer and a sample withdrawal assembly. The initial pH of the wastewater was adjusted using either 0.1 N H_2SO_4 or 0.1 N NaOH. The effectiveness of Fenton oxidation reagent was found out by optimization of pH, $FeSO_4$ concentration, H_2O_2 concentration, reaction time and temperature at atmospheric pressure using 100 ml wastewater in each experiment. The experimental set up has been illustrated in Fig. 1.

3. Results and discussion

3.1. Effect of pH

The effect of initial pH of solution on the color and COD removal of carpet dyeing wastewater by Fenton oxidation was studied in the pH range of 2–5. Fenton oxidation is highly pH dependent process since pH plays an important role in the mechanism of OH generation in the Fenton reaction. The pH of samples was adjusted by 0.1 N NaOH and 0.1 N H_2SO_4. The experiments were carried out at atmospheric pressure and room temperature, keeping ferrous sulphate concentration of 2 g/l, hydrogen peroxide concentration of 30 g/l and reaction time of 30 min. The pH of the treated samples was adjusted to 7, the neutral pH. Thereafter, it was left for 2 h to settle. The oxidized carpet dyeing wastewater may result in an additional coagulation and precipitation effect. These samples were filtered and analyzed for color and COD. The experiments were run in the absence of light to prevent the photo Fenton oxidation.

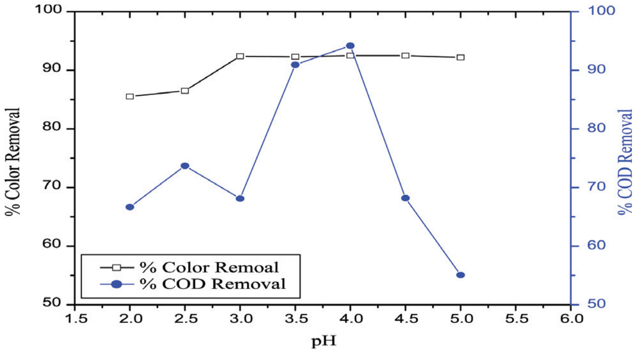

Fig. 2. Effect of pH on removal of color from carpet dyeing wastewater by Fenton oxidation. Temp. = 25°C, $FeSO_4$ conc. = 2 g/l, H_2O_2 concentration = 30 g/l, reaction time = 30 min.

Fig. 2 shows the effect of pH on the color and COD removal efficiencies by Fenton oxidation. With decrease in initial pH from 4 to 2, the color and COD removal decreased from 93% and 94% to 86 % and 67 %, respectively. This can be explained due to the formation of oxonium ion $[H_3O_2^+]$ which enhanced the stability of hydrogen peroxide and restricted the generation of OH at low pH. In addition, the scavenging of the OH ion by excessive H^+ ions may be another reason for low color and COD removal.

At pH above 4, the color and COD removal efficiencies by oxidation decreased rapidly, not only by decomposition of hydrogen peroxide, but also by deactivation of ferrous sulphate catalyst with the formation of ferric hydroxo complexes which result in smaller amount of •OH generation. Complex molecules have lower activity and will not react with hydrogen peroxide and ferric ions in solution that can react with hydrogen peroxide to reduced. The maximum color and COD removal were 93% and 94%, respectively. The optimum pH was observed as 4.

3.2. Effect of ferrous sulphate concentration

The effect of ferrous sulphate concentration on the color and COD removal was examined by varying the ferrous sulphate concentration from 1 to 6 g/l, while keeping the concentration of hydrogen peroxide 30 g/l, pH 4, reaction temperature 25°C and 30 min reaction time. It is clear from Fig. 3 that color and COD removal efficiencies were increased with increased in ferrous sulphate concentration up to 4 g/l. Therefore, increase in concentration of ferrous sulphate generates not only more OH radicals but also give faster oxidation and coagulation, giving higher color and COD removals.

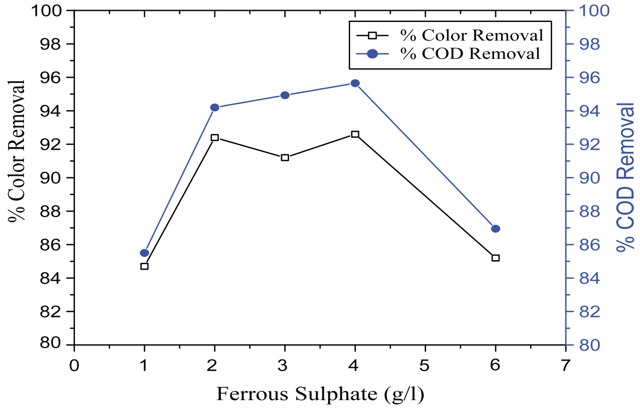

Fig. 3. Effect of ferrous sulphate concentration on removal of COD and color from carpet dyeing wastewater by Fenton oxidation. Temp. = 25°C, pH = 4, H_2O_2 concentration = 30 g/l, reaction time = 30 min.

At higher doses, the color and COD removal efficiencies do not increase further, indicating that hydrogen peroxide became limiting for further OH radicals generation. However, as concentration of ferrous sulphate is decreased, the amount of color and COD removal decreased. This may be most probably due to less OH radical generation when amount of Fe^{2+} is smaller. The color and COD removals at above-mentioned conditions were 93% and 96% at optimum 4 g/l $FeSO_4$ concentration.

3.3. Effect of hydrogen peroxide concentration

The effect of hydrogen peroxide concentration on Fenton treatment was investigated in a hydrogen peroxide concentration range between 15 and 180 g/l, while keeping other parameters constant as above. The color and COD removal at 15 g/l were found to be 79% and 86%, which increased to 93% and 96%, respectively, when hydrogen peroxide was increased to 30 g/l (Fig. 4). This may again be due to the increase in the formation of OH radicals. However, at hydrogen peroxide dose higher than 30 g/l, no increase in color and COD removal were observed since ferrous sulphate concentration became deficient for hydrogen peroxide. Hence the optimum dose of H_2O_2 concentration was found as 30 g/l.

3.4. Effect of reaction time

Fig. 5 shows the effect of reaction time on color and COD removal of carpet dyeing wastewater by varying the reaction time from 10 min to 50 min. It is observed that the removal of color and COD were increased with increased in reaction time up to 30 min. The optimum color and COD removal at 30 min were 93% and 98%, respectively. With increase in reaction time above 30 min, however, there is no considerable change in color and COD removal. The optimum treatment time was found as 30 min.

3.5. Effect of temperature

The temperature was varied in the range of 25–65°C to observe its effect on Fenton oxidation. The other parameters were kept constant at ferrous sulphate dose of 4 g/l, pH 4, reaction time 30 min and hydrogen peroxide 30 g/l. The results are shown in Fig. 6. The maximum color and COD removal of 93% and 98% was observed at 25°C, respectively. The color and COD removal were found to decrease with increasing temperature. This may be due to less oxidation stability and higher decomposition of hydrogen peroxide at higher temperature. Hydrogen peroxide decomposes to give oxygen and water.

3.6. Dye degradation kinetics

Considering the degradation of dye as a *n*th order reaction

$$-r = dC/dt = k\,C^n$$

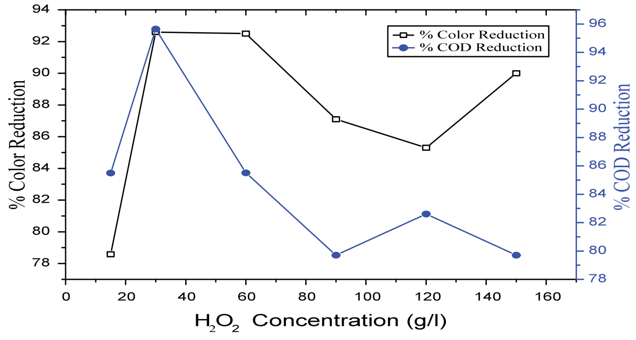

Fig. 4. Effect of hydrogen peroxide concentration on removal of COD and color from carpet dyeing wastewater by Fenton oxidation. Temp. = 25°C, pH = 4, $FeSO_4$ conc. = 4 g/l, reaction time = 30 min.

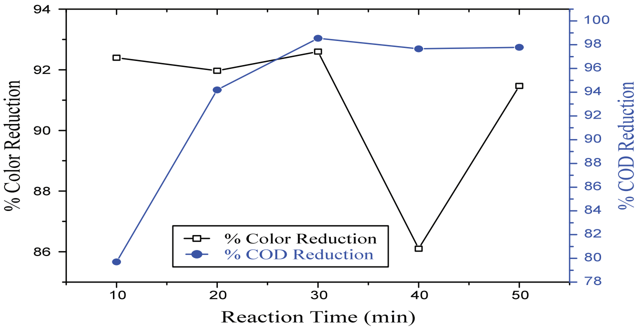

Fig. 5. Effect of reaction time on removal of COD and color from carpet dyeing wastewater by Fenton oxidation. Temp. = 25°C, $FeSO_4$ conc. = 4 g/l, H_2O_2 concentration = 30 g/l, pH = 4.

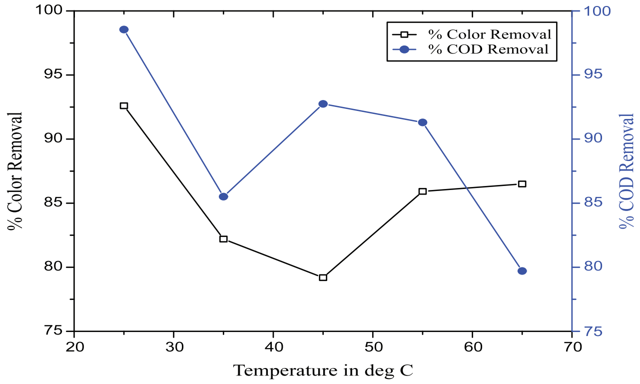

Fig. 6. Effect of temperature on removal of color from carpet dyeing wastewater by Fenton oxidation. $FeSO_4$ concentration = 4 g/l, H_2O_2 concentration = 30 g/l, pH = 4, reaction time = 30 min.

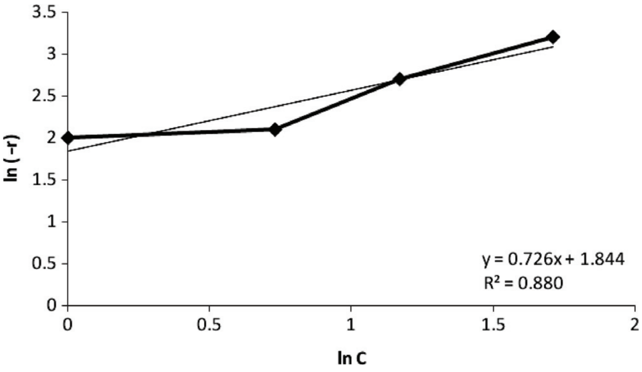

Fig. 7. ln (–r) vs ln C for Fenton oxidation.

where, C is the dye concentration, $-r$ is the dye degradation rate, k is the rate constant, and n is the order of the reaction. The slope of the tangents on C v/s t curve $(-r)$ were estimated at various values of C. Fig. 7 shows that the degradation of dye by Fenton oxidation is of 0.73 order and the degradation rate of dye is $-r = 6.32\ C^{0.73}$.

3.7. Proximate analysis and calorific value of dried residue

Color and other impurities in the carpet dyeing wastewater were precipitated during the treatments. The precipitate was collected and dried in sunlight. The calorific value of dried residue was estimated to be 12.8 MJ/kg which is about 76% to that of lignite coal. Thus it can be used as a solid fuel. The dried residue has a high content of volatile matter, which makes it easier to convert into gas, than higher ranking coals. The proximate analysis of dried residue is given below:

Moisture content = 4.2%
Ash content = 42.7%
Volatile matter = 43.8%
Fixed carbon = 9.3%

4. Conclusion

The treatment of carpet dyeing wastewater from a carpet industry was carried out using Fenton oxidation. The decolorization and COD removal of carpet dyeing wastewater by Fenton oxidation process was investigated at varying reaction conditions. The optimum operating conditions were observed at pH 4, $FeSO_4$ 4 g/l, H_2O_2 30 g/l, temperature 25°C and reaction time of 30 min at atmospheric pressure. The maximum color and COD removal at these conditions were 93% and 98%, respectively. The carpet dyeing wastewater can be satisfactorily treated by this process. The calorific value of dried residue obtained after thermal treatment was 12.8 MJ/kg, which is about 76% to that of lignite coal and thus could be used as a solid fuel.

References

[1] A. Yasar, N. Ahmad, A.A.A. Khan and A. Yousaf, Decolorization of Blue CL-BR dye by AOPs using bleach wastewater as source of H_2O_2, J. Environ. Sci., 19 (2007) 1183.
[2] J.M.P. Hernandez, Y.M. Vong, F.J. Rodrıguez, T.W. Chapman, M.I. Maldonado and L.A. Godınez, Comparison of hydrogen peroxide-based processes for treating dye-containing wastewater: Decolorization and destruction of Orange II azo dye in dilute solution, Dyes Pigments, 76 (2008) 656.
[3] S. Figuero, L. Vazquez and A.A. Gallegos, Decolorizing textile wastewater with Fenton's reagent electro-generated with a solar photovoltaic cell, Water Res., 43 (2009) 283.
[4] Y. Flores, R. Flores and A.A. Gallegos, Heterogeneous catalysis in the Fenton-type system reactive black 5/H_2O_2, J. Mol. Catal. A: Chem., 281 (2008) 184.
[5] J.H. Sun, S.P. Sun, J.Y. Sun, R.X. Sun, L.P. Qiao, H.Q. Guo and M.H. Fan, Degradation of azo dye Acid black1 using low concentration iron of Fenton process facilitated by ultrasonic irradiation, Ultrason. Sonochem., 14 (2007) 761.
[6] S. Wang and Z.H. Zhu, Characterisation and environmental application of an Australian natural zeolite for basic dye removal from aqueous solution, J. Hazard. Mater., B136 (2006) 946.
[7] H.J. Hsing, P.C. Chiang, E.E. Chang and M.Y. Chen, The decolorization and mineralization of Acid Orange 6 azo dye in aqueous solution by advanced oxidation processes: A comparative study, J. Hazard. Mater., 141 (2007) 8.
[8] M.S. Lucas and J.A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, Dyes Pigments, 71 (2006) 236.
[9] A. Ozcan, Y. Sahin, A.S. Koparal and M.A. Oturan, Carbon sponge as a new cathode material for the electro-Fenton process: Comparison with carbon felt cathode and application to degradation of synthetic dye basic blue 3 in aqueous medium, J. Electroanal. Chem., 616 (2008) 71.
[10] J.G. Montano, N. Ruiz, I. Munoz, X. Domenech, Jose A. Garcıa-Hortal, Francesc Torrades and Jose Peral, Environmental assessment of different photo-Fenton approaches for commercial reactive dye removal, J. Hazard. Mat., A138 (2006) 218.
[11] Y.H. Huang, S.T. Tsai, Y.F. Huang and C.Y. Chen, Degradation of commercial azo dye reactive Black B in photo/ferrioxalate system, J. Hazard. Mater., 140 (2007) 382.
[12] D. Wei, G.Y. Xin, Y. Min, D. Ran and Z. Yu, Treatment of 2-phenylamino-3-methyl-6-di-*n*-butylaminofluoran production effluent by combination of biological treatments and Fenton's oxidation, J. Environ. Sci., 19 (2007) 1178.