



## Optimization of Fenton's Process for the Decolourization of Azo Dyes

AIZA SHOUKAT<sup>1,2,\*</sup> and SHOUKAT ALI<sup>2</sup>

<sup>1</sup>Department of Industrial Chemistry, Government College University, Faisalabad-38000, Pakistan

<sup>2</sup>Department of Chemistry & Biochemistry, University of Agriculture, Faisalabad-38040, Pakistan

\*Corresponding author: E-mail: aizachemist@yahoo.com

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Coloured azo dye effluents from different dyeing units, poses a threat to the aquatic environment due to their non-biodegradable, toxic and carcinogenic nature. It is imperative to treat these effluents before discharging in to water bodies. In the present research, Fenton's process was employed to treat the industrial effluents and further different working parameters like pH, temperature and doses of H<sub>2</sub>O<sub>2</sub> and Fe(II) were also optimized to achieve the better efficiency of process. Decolourization efficacy of process was evaluated by measuring the absorbance spectrophotometrically. It was observed that the degradation rate of azo dyes was mainly dependent on pH, temperature and doses of Fe(II) and H<sub>2</sub>O<sub>2</sub>. Furthermore, water quality parameter, COD was conducted through standard methods the extent of mineralization. These investigations can provide a fundamental knowledge for the treatment of wastewater containing red azo dye by Fenton oxidation process.

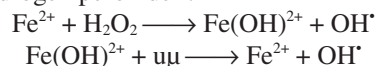
**Key Words:** Fenton's reagent, Reactive dyes, Oxidation, Decolourization efficacy.

### INTRODUCTION

Dyes in waste water create aesthetic problems, limit the possible use of the water and reduce the efficacy of microbial treatment of waste water due to toxicity towards microorganisms<sup>1</sup>. The treatment of textile wastewaters is difficult task because of highly complex structures of dyes used in dyeing units of textile industries and requires special advanced treatment technologies like sedimentation, ozonation, adsorption electrochemical oxidation and photo catalytic discoloration<sup>2-4</sup>. The non-biodegradability of textile effluents is due to the higher content of dyestuff; a very complex structure organic molecules and additives<sup>5</sup>. Most of these dyes are not readily degraded under the aerobic conditions prevailing in biological treatment plants due to the inhibitory nature of dye molecules.

Advanced oxidation processes (AOPs) encompass a number of emergent methodologies viewing production of free hydroxyl radicals, non-selective oxidizing agent capable of destroying recalcitrant pollutants<sup>6-8</sup>. Therefore, AOPs have been growing during the last decade since they are able to deal with the problem of dye destruction in aqueous systems<sup>9</sup>. Due to the instability of OH radical, it must be generated continuously "in situ" through chemical or photochemical reactions. The versatility of AOP is enhanced by the fact that they offer different possible ways for hydroxyl radical production thus allowing a better compliance with a specific treatment<sup>10</sup>.

Fenton's reagent is a solution of hydrogen peroxide and an iron catalyst that is used to oxidize contaminants of waste water. This is suitable for the treatment of effluents which are resistant to biological treatment. In advanced oxidation processes organic compounds are transformed with reactions involving hydroxyl radicals. Fenton's oxidation produces •OH from Fenton's reagent (Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>). Fenton's oxidation, catalyzed with ferrous iron (Fe<sup>2+</sup>), is successful in removing organics from water but requires the continuous addition of dissolved Fe(II). Fe(II) is oxidized by hydrogen peroxide to Fe(III), a hydroxyl radical and a hydroxyl anion. Fe(III) is then reduced back to Fe(II), peroxide radical and a proton by the same hydrogen peroxide<sup>11</sup>.



The advantage of the Fenton reagent is that no energy input is required necessarily to activate hydrogen peroxide. Therefore, this method offers a cost-effective source of hydroxyl radicals, using easy-to-handle reagents. Therefore, this research was designed to optimize the Fenton's oxidation process to deodorization of azo dyes as an effort to solve the problem that might be established as an effective technique to treat the azo dyes containing textile effluents.

### EXPERIMENTAL

Red azo dye, used in this research, was of laboratory grade, donated by Sandal Bar Dyes Stuff (Pvt) Faisalabad, Pakistan.

All other chemicals like hydrogen peroxide (35 %), ferrous sulphate, sodium hydroxide and sulfuric acid *etc.*, were of analytical grade procured from Merck, Germany and used without any further purification.

**Screening for the dye concentration:** Dye solution of different concentrations *i.e.*, 0.003, 0.004, 0.005, 0.006 *etc.*, were prepared. The maximum absorbance wavelength of dye solution was found 518 nm by using UV/vis spectrophotometer and a graph (abs. *versus* concentration) was made to select the one concentration with linear trend.

**Optimization of parameters:** The parameter like pH, temperature and doses of FeSO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> were optimized for the efficiency of Fenton's process of decolourization. Four experiments in duplicate were conducted with 50 mL dye solution (0.004 %), 50 mL FeSO<sub>4</sub> ( $3.5 \times 10^{-5}$  M) and 50 mL H<sub>2</sub>O<sub>2</sub> ( $0.1 \times 10^{-2}$  M) to optimization pH. The pH of each duplicate experiment was adjusted from 3-6 using sodium hydroxide (1 M) and sulfuric acid (1 M). Each experiment was proceeded for 50 min on the electromagnetic stirrer at 40 °C. The aliquot of samples were drawn periodically (after each 10 min) with pipette and immediately analyzed at 518 nm using UV/vis. spectrophotometer. The decolourization efficiency was calculated by the following formula;

$$\text{Decolourization of dye (\%)} = \left[ \frac{\text{Abs. at 0 min} - \text{Abs. at t min}}{\text{Abs. at 0 min}} \right] \times 100$$

Moreover, the optimization of dose of H<sub>2</sub>O<sub>2</sub> ( $1.0 \times 10^{-3}$ - $4.0 \times 10^{-2}$  M), dose of FeSO<sub>4</sub> ( $5.0 \times 10^{-5}$ - $3.5 \times 10^{-5}$  M) and temperature (30-50 °C) were also performed in the same fashion.

#### Evaluation of Fenton's process by estimating COD:

The chemical oxygen demand (COD) to study the toxicity of samples treated with Fenton's reagent was analyzed according to standard procedure<sup>11</sup>. Briefly, 5-50 mL of treated and control samples were taken in a conical flask (250 mL) with a ground glass joint. Added 10 mL of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.25 N) solution in 18 N H<sub>2</sub>SO<sub>4</sub>, 1 g Ag<sub>2</sub>SO<sub>4</sub> and 1 g HgSO<sub>4</sub> and refluxed the samples for 6 h, cooled and titrated the excess amount of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with 0.1 N H<sub>2</sub>SO<sub>4</sub> using 8-10 drops of Ferroin (1.485 g 1,10-phenanthroline + 0.695 g FeSO<sub>4</sub>·7H<sub>2</sub>O dissolved in 100 mL water) as an indicators.

**Statistical analysis:** All the observations were carried in triplicate of duplicate samples and data are reported as mean  $\pm$  standard deviation<sup>12</sup>.

## RESULTS AND DISCUSSION

**$\lambda_{\text{max}}$  of red azo dye:** Dye solutions of different concentrations *i.e.*, 0.001, 0.0002, 0.003, 0.004, 0.005 %, prepared in distilled water were used for the scanning of  $\lambda_{\text{max}}$  on UV/vis. spectrophotometer in the visible range. All the dye solutions gave maximum absorbance at 518 nm and this wavelength was selected to study the process of decolourization. 0.004 % dye concentration was selected to optimize the various parameters due to its maximum linear trend<sup>13</sup>.

**Optimization of pH for decolourization of red dye solution:** The pH has pronounced affects the oxidation of organic substances. Fenton's reactions are strongly pH dependent as they influence the generation of hydroxyl radicals and oxidation efficacy. The effect of initial pH value of solutions

on the decolourization of red dye by Fenton oxidation process was studied in the pH range of 3.0-7.0 and the data obtained is recorded in Fig. 1. A direct influence of initial pH on the decolourization of red dye could be observed and the best decolourization efficiency was obtained at pH of 3.0. At initial pH of 7.0, the decolourization of red dye almost was not observed appreciable even after 50 min of reaction. It is principally due to the formation of ferrous/ferric hydroxide complexes that may lead to the deactivation of ferrous catalyst and subsequently least production of  $\cdot\text{OH}$ . When the initial pH was decreased from 7.0 to 3.0, the decolourization efficiency of red dye within 50 min increased significantly from 10.3 to 75.7 %, respectively. However, the decolourization efficiency of red dye slowed down to 68.9 % as a further increase of the initial pH from 3.0 to 4.0. A diminishing efficiency of H<sub>2</sub>O<sub>2</sub>/Fe process at pH 4 was in accordance with another report that near and above pH 4 rapid hydrogen peroxide decomposition, probably on the surface of ferric hydroxide and would not produce appreciable amounts of available hydroxyl radicals in the solution<sup>14</sup>. Hence, a suitable initial pH for the decolourization of red dye by Fenton oxidation process was recommended as 3.0.

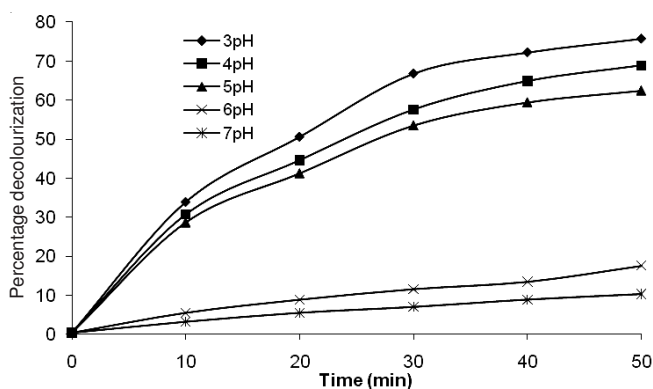


Fig. 1. Effect of initial pH values on the decolourization of red azo dye by Fenton oxidation

**Effect of H<sub>2</sub>O<sub>2</sub> dosage on the decolourization of red dye:** H<sub>2</sub>O<sub>2</sub> plays an important role as a source of  $\cdot\text{OH}$  generation in Fenton's reaction. The effect of H<sub>2</sub>O<sub>2</sub> dosage on the decolourization of red dye was examined by varying initial concentration of H<sub>2</sub>O<sub>2</sub> from  $1.0 \times 10^{-3}$  to  $4.0 \times 10^{-2}$  M and the data obtained is shown in Fig. 2. It was observed that by increasing the dosage of H<sub>2</sub>O<sub>2</sub> ( $1.0 \times 10^{-3}$ - $4.0 \times 10^{-2}$  M) the decolourization of red dye was achieved from 53.6-96.3 %, respectively within 50 min of reaction time. However, by further increase of the dosage of H<sub>2</sub>O<sub>2</sub> above  $4.0 \times 10^{-2}$  M, the decolourization of investigated dye was not improved significant. Addition of H<sub>2</sub>O<sub>2</sub> is known to influence the decomposition of organic compounds through Fenton like reaction. Generally, the degradation rate of organic compounds increases as the H<sub>2</sub>O<sub>2</sub> concentration increases until a critical H<sub>2</sub>O<sub>2</sub> concentration is achieved. However, when the concentration higher than the critical concentration is used, the degradation rate of organic compounds will decrease as a result of the so-called scavenging effect<sup>2,3</sup>.

**Effect of Fe<sup>2+</sup> dosage on the decolourization of red dye:** Fe<sup>2+</sup> is another main parameter in Fenton's reaction that cataly-

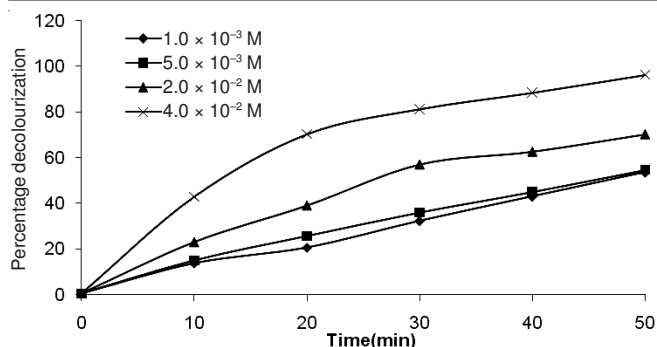


Fig. 2. Effect of H<sub>2</sub>O<sub>2</sub> dosage on the decolourization of red azo dye by Fenton oxidation

tically decomposes H<sub>2</sub>O<sub>2</sub> to generate  $\cdot\text{OH}$ . The data regarding the effect of initial concentration of Fe<sup>2+</sup> ( $5.0 \times 10^{-6}$ - $3.5 \times 10^{-5}$  M) on the decolourization of red dye has been presented in Fig. 3. It was observed that the decolourization was limited at  $5.0 \times 10^{-6}$  M of Fe<sup>2+</sup> and only 41.2 % of red dye was degraded within 50 min of reaction time. In the presence of  $1.5 \times 10^{-5}$ ,  $2.5 \times 10^{-5}$  and  $3.5 \times 10^{-5}$  M of Fe<sup>2+</sup>, a great improvement of the decolourization of red dye was observed and the decolourization efficiencies within 50 min of reaction achieved were 65.6, 89.1 and 92.4 %, respectively. The maximum decolourization efficiency achieved at high Fe<sup>2+</sup> dosage may be attributed to the higher production of  $\cdot\text{OH}$  with more Fe<sup>2+</sup> in Fenton's reaction. The decolourization of dye began to decrease by further increasing the concentration of Fe<sup>2+</sup>. As Fe<sup>2+</sup> has catalytic effect on H<sub>2</sub>O<sub>2</sub>, when its concentration is increased, the catalytic effect also increases accordingly up to a specific level of Fe<sup>2+</sup> concentration beyond which there was no significant development in the decolourization. Hence,  $3.5 \times 10^{-5}$  M of Fe<sup>2+</sup> was considered to be a suitable dosage for the decolourization of red dye. It is important to detect the optimum molar ratio of [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>], because the ratio can directly affect the production of  $\cdot\text{OH}$  in Fenton's reaction. The optimal molar ratio of [H<sub>2</sub>O<sub>2</sub>]/[Fe<sup>2+</sup>] proposed for the degradation of different pollutants in aqueous solutions after these investigations is 1:1 to 400:1<sup>14</sup>.

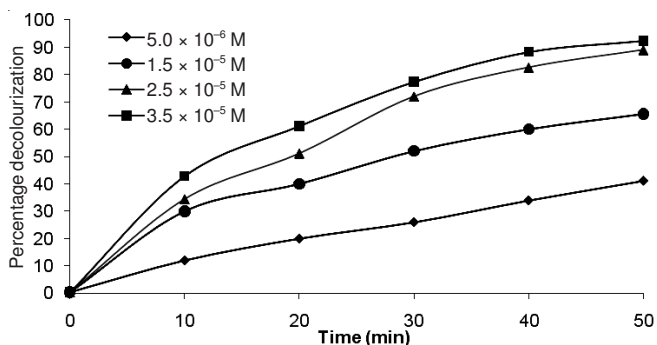


Fig. 3. Effect of Fe<sup>2+</sup> dosage on the decolourization of red azo dye by Fenton oxidation

**Effect of temperature on the decolourization of red dye:** The effect of temperature on the decolourization of red dye was studied at different temperatures *i.e.*, 30, 40, 50 and 60 °C and the observations recorded has been shown in Fig. 4. It was found that a rising trend in temperature has a positive impact on the decolourization of red dye. The decolourization

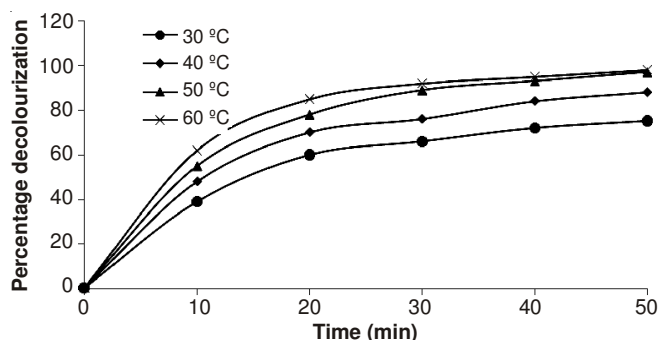


Fig. 4. Effect of temperature on the decolourization of red azo dye by Fenton oxidation

efficiency within 10 min of reaction increased from 39.0 to 62.0 % as the temperature was raised from 30 to 60 °C, respectively. But after a certain level of temperature the improvement in the decolourization efficiency for dye becomes non-significant *e.g.*, at 50 min, the different in decolourization at 30-50 °C were 75.1-98.0 %, respectively. The literature reports also support the present investigation that by increasing the temperature, the decolourization of red dye become very fast but up to certain level<sup>15</sup>. This can be explained that Fenton's reaction could be accelerated by raising temperature which improved the rate of generation of  $\cdot\text{OH}$  and therefore, enhance the decolourization efficiency of red dye.

**Characterization of waste water by chemical oxygen demand (COD) test:** Chemical oxygen demand (COD) is a very good parameter to access the degradation of organic matter in water. Chemical oxygen demand tests were performed according to standard method. The data regarding the COD values of treated and original solutions of azo dye has been presented in Fig. 5. The reduction of COD value of treated sample showed the maximum removal of COD of red dye solution by Fenton/H<sub>2</sub>O<sub>2</sub> treatment that indicate the advanced oxidation processes as valuable approach to eliminate the COD, regarded as representative parameter for the quality of water. It might be assumed that the reduction of COD is due to the reduction of total organic carbon (TOC) and partial oxidation of organic substrates. Decolourization of the dyestuff does not always result in complete degradation to CO<sub>2</sub> and H<sub>2</sub>O. Some colourless reaction intermediates may be formed during

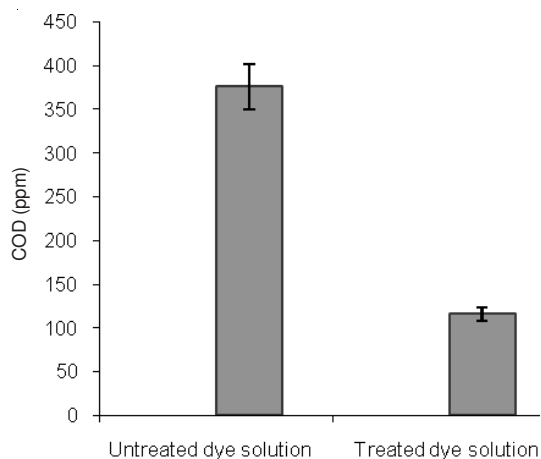


Fig. 5. COD of treated and untreated red azo dye solution

degradation of dyestuffs<sup>16</sup>. Therefore, it is important to know the degree of mineralization or total organic carbon removal during decolourization of azo-dyes. The utility of this approach is attractive particularly because the Fenton oxidation process is a developmental complex technology and this technique might be helpful to study the relative significance of the various experimental factors under actual operating levels, aiding the design of optimal processes. The formation of by-products during the oxidation processes results in less reduction of COD in all the dye effluents.

### Conclusion

It was concluded from the present investigation that Fenton oxidation process is a valuable approach for the decolourization of aqueous solutions of azo dyes. The performance of the process was found best at various operating parameters *i.e.*, pH value 3,  $4.0 \times 10^{-2}$  M dosage of  $H_2O_2$ ,  $3.5 \times 10^{-5}$  M dosage of  $Fe^{2+}$ , 40 °C temperature and 50 min as reaction time. It was possible to achieve 95.4 % decolourization of azo dye at the above operating parameters. Therefore, it suggested that the industries which are using azo dyes as colourant must treat their effluents by using this approach before discharging into water bodies.

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