

## **Use of Photo-Fenton Reagent for Photocatalytic Degradation of Reactive Red 45**

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**Abstract:** *Advanced oxidation processes (AOPs) are widely used for the removal of health hazardous organic pollutants from industrial and municipal wastewater. Reactive Red 45, which has a complex molecular structure with azo aromatic groups, is widely used in textile industry. Degradation of Reactive Red 45 by Photo-Fenton reagent has been investigated under irradiation of visible light in aqueous solution. The parameters that influence degradation such as concentration of reactive Red 45, FeSO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, light intensity and pH of the experimental solution were studied. The optimum condition for the photocatalytic degradation of dye was established. The degradation of dye in the dilute solution follows first order kinetics.*

**Keywords:** *Photocatalytic Degradation, Reactive Red 45, Photo-Fenton.*

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### **1. INTRODUCTION**

In recent years, many different types of synthetic dyes such as azo, vat, nitro, indigo, etc., are widely used for different purposes in paper and pulp manufacturing plastics, printing and textile industries [1-2]. The effluent from these industries, when it contains substantial amounts of such dyes, causes not only coloration of water, but also poses a threat to aquatic life [3]. Furthermore; their presence in drinking water constitutes a potential human health hazard [4-5]. Many azo dyes and their intermediate products are toxic mutagenic or carcinogenic to aquatic life and human [6]. It is therefore essential either to remove the dyes from water or to treat them in such a way so as to minimize their effects on the environment and also to decolorize the water.

In the past two decades, advanced oxidation processes (AOPs) have been proven to be powerful and efficient treatment methods for degrading recalcitrant materials or mineralizing stable, inhibitory, or toxic contaminants. These technologies could be applied for contaminated groundwater, surface water, and wastewaters containing recalcitrant, inhibitory, and toxic compounds with low biodegradability as well as for the purification and disinfection of drinking water.

Advanced oxidation processes are those groups of technologies that lead to hydroxyl radical ( $\cdot\text{OH}$ ) generation as the primary oxidant (second highest powerful oxidant after the fluorine). These radicals are produced by means of oxidizing agent such as H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>, ultraviolet irradiation, ultrasound, and homogeneous or heterogeneous catalysts.

Common AOPs which are widely used are H<sub>2</sub>O<sub>2</sub>/UV [7], TiO<sub>2</sub>/UV [8], Ozonation [9], O<sub>3</sub>/UV [10], Fenton reagent [11], UV-Fenton [12] process electron beam irradiation [13], sonolysis [14], wet-air oxidation [15] and various combination of these methods [16]. Photocatalytic degradation has been proved to be a promising method for the treatment of wastewater contaminated with organic and inorganic pollutants [17-20]. Fenton and Fenton type processes have proven to yield very good results either for complete mineralization of azo dyes or for their transformation into less complex structures that are more easily biodegradable. It can be used to degrade many pesticides [21], harmful chemicals [22-23] and dyes [24-26]. It has been shown that Photo-Fenton reagent cleaves the conjugated bonds of azo-dyes chromophores, leading to color removal and enhancing the biodegradability of the treated wastewater. It has the advantages of coagulation and catalytic oxidation, as well as being able to generate oxygen in water.

Reactive Red 45 (RR45) is widely used in textile industries. As, it causes great potential of pollution of water environment, a proper treatment is necessary before discharge into the environment. Therefore, it is planned to undertake the title investigation. The objective of the present study is to

evaluate the dependence factors for the color removal rate such as concentration of Dye (RR45), photo catalyst (Fenton reagent),  $H_2O_2$  and pH of the experimental solutions.

## 2. EXPERIMENTAL

### 2.1. Materials

For the present studies the commercial azo dye Reactive Red 45 was used. Photocatalyst  $FeSO_4$  (Merck, 99% purity) and  $H_2O_2$  (Merck, 30% purity) were used for photocatalytic degradation. For the photo bleaching process,  $1 \times 10^{-3} M$  stock solution of dye Reactive Red 45 was prepared in double distilled water and diluted as required. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions. All laboratory reagents were of analytical grade.

### 2.2. Procedure and Analysis

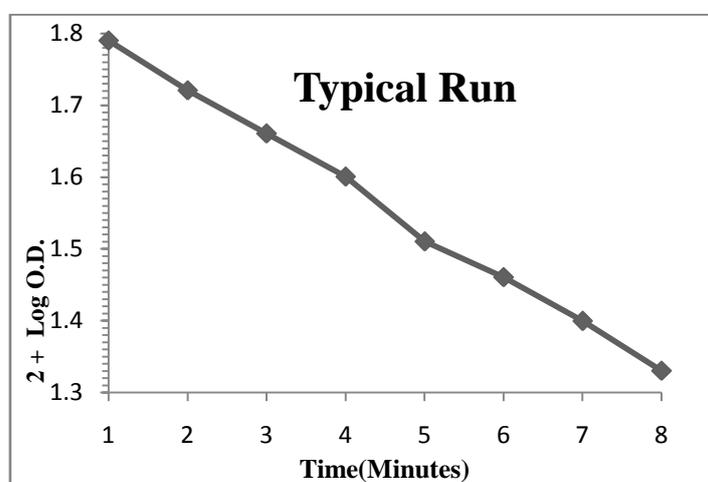
The reaction mixture was prepared by taking 1.0 mL of Reactive Red 45 dye solution ( $1 \times 10^{-3} M$ ), 1.0 ml of  $FeSO_4$  ( $1 \times 10^{-3} M$ ) and 1.0 ml of  $H_2O_2$  (30%) in a beaker at pH 2.9. The total volume of the reaction mixture was made 30 ml by adding double distilled water. To carry out the photobleaching, the reaction mixture was irradiated under light source (200 W Tungsten lamp). Water filter was used to cut off thermal radiation. The pH of the solution was measured by pH meter (Systronics, 335). The progress of the reaction was observed at definite time intervals by measuring absorbance using spectrophotometer (Systronics Double Beam Spectrophotometer 2203) at **521.9 nm**. The rate of decrease of color with time was continuously monitored. After complete mineralization, the presence of  $NO_2^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$  ions and evolution of  $CO_2$  were tested by standard procedure.

### 2.3. Results and Discussion

**Table1.** Typical Run of Photocatalytic degradation of Reactive Red 45

[Reactive Red 45] =  $3.33 \times 10^{-5} M$ ; pH = 2.9;  $[Fe^{2+}] = 3.33 \times 10^{-5} M$ ;  $H_2O_2 = 1.0 mL$ ;  $\lambda_{max} = 521.9 nm$  Light Intensity =  $60 mWcm^{-2}$ ;

Time (minutes)	O.D	2 + log O.D.
0	0.616	1.7902
1	0.526	1.7209
2	0.458	1.6608
3	0.399	1.6009
4	0.324	1.5105
5	0.289	1.4608
6	0.251	1.3996
7	0.214	1.3304



**Figure1.** Typical Run of Photocatalytic degradation of Reactive Red 45 in Photo-Fenton Process

Control experiments (in absence of photocatalyst, light) confirm the necessity of photocatalyst, light to follow the photocatalytic path for the photobleaching of dye. The photocatalytic degradation of

Reactive Red 45 was observed at **521.9 nm**. The optimum conditions for the photobleaching of dye were **[Dye] = 3.33 x10<sup>-5</sup> M**, **[FeSO<sub>4</sub>] = 3.33 x10<sup>-5</sup> M**, **H<sub>2</sub>O<sub>2</sub> = 1.0 mL** and **pH = 2.9**. The result of photocatalytic bleaching of Reactive Red 45 is presented in Table 1. It was observed that absorbance (Abs.) decreases with the increase in time of irradiation indicating that the dye is degraded on irradiation. A graph between 2 + log O.D. and time has been plotted. The linearity of the plot indicates that the photocatalytic bleaching of Reactive Red 45 follows a first order kinetics. The rate constant of this photobleaching process was determined using the expression Rate Constant (k) = 2.303 x Slope.

#### 2.4.Effect of pH Variation on Photo degradation of Dye

To study the effect of pH on photodegradation, experiments are conducted for **3.33 x 10<sup>-5</sup>M** Reactive Red 45 in presence of **Fe<sup>2+</sup>: 3.33 x 10<sup>-5</sup> M** and **1.0 ml H<sub>2</sub>O<sub>2</sub>** at different initial pH values (2.5-3.2). The values of k are given in Table 2:

**Table2.** Kinetic of photo degradation of Reactive Red 45 at different initial variation of pH

[Reactive Red 45] = 3.33 × 10<sup>-5</sup> M; [Fe<sup>2+</sup>] = 3.33 × 10<sup>-5</sup>M; H<sub>2</sub>O<sub>2</sub> = 1.0 mL; Light Intensity = 60 mWcm<sup>-2</sup>; λ<sub>max</sub> = 521.9 nm

pH	k×10 <sup>-2</sup> s <sup>-1</sup>
2.5	7.13
2.6	8.16
2.7	9.67
2.8	11.28
<b>2.9</b>	<b>14.96</b>
3.0	13.58
3.1	10.13
3.2	8.75

Fenton oxidation is known as a highly pH dependent process since pH plays an important role in the mechanism of OH production in the Fenton's reaction. At high pH (pH > 3.2) the generation of ·OH gets slower because of the formation of the ferrichydroxo complexes. On the other hand, at very low pH values (<2.5) hydrogen ions act as OH radical-scavengers. The reaction is slowed down due to the formation of complex species [Fe (H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>, which reacts more slowly with peroxide compared to that of [Fe(OH)(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup>.



Thus, it may be concluded that step (i) dominates over step (ii) in the pH range below 2.9. However, retardation of the reaction above pH 2.9 suggests the dominance of step (ii) over step (i). In addition, the peroxide gets solvated in the presence of high concentration of H<sup>+</sup> ions to form stable oxonium ion [H<sub>3</sub>O<sub>2</sub>]<sup>+</sup>. An oxonium ion makes peroxide electrophilic to enhance its stability and presumably substantially reduces the reactivity with Fe<sup>2+</sup> ion. Maximum color removal efficiencies were obtained at pH 2.9, for the dye in case of photo-Fenton processes.

#### 2.5.Dye Concentration Variation

The effect of initial dyes concentration on the decolorization degree at the optimum pH, Fenton reagent concentration and H<sub>2</sub>O<sub>2</sub> dosage, were studied in photo-Fenton processes see. As an example, Dyes concentrations were varied from 2.66 x10<sup>-5</sup> M, to 4.33 x 10<sup>-5</sup>M for Reactive Red 45. The results are given in Table-3. The rate of photochemical degradation was found to increasing with increase in the concentration of RR45 up to 3.33×10<sup>-5</sup>M. On further increasing its concentration, a sudden decrease in the rate of degradation was observed. This may be explained on the basis that on initially increasing the concentration of RR45, more molecules of RR45, are available for degradation. However on increasing the concentration above 3.33×10<sup>-5</sup>M, the reaction rate was found to decrease. It may be attributed to the fact that as the concentration of RR45 was increased, it started acting like a filter for the incident light, where its large concentration will not permit the desired light intensity to react the dye molecule in the bulk of the solution and thus a decrease in the rate of photochemical bleaching of Reactive Red 45 has observed. At the optimum conditions for the dye, the best dye concentration was equal to 3.33 x 10<sup>-5</sup> M.

**Table3.** Kinetic of photodegradation at different initial concentrations of Reactive Red 45 Effect of initial  $Fe^{2+}$  concentration  $pH = 2.9$ ;  $[Fe^{2+}] = 3.33 \times 10^{-5}M$ ;  $H_2O_2 = 1.0$  mL; Light Intensity =  $60$  mWcm $^{-2}$ ;  $\lambda_{max} = 521.9$  nm

[Dye] $\times 10^{-5}M$	$k \times 10^{-2} s^{-1}$
2.66	7.13
3.0	9.44
3.33	14.96
3.66	12.20
4.0	10.13
4.33	8.52

Dye degradation efficiency by Photo-Fenton process is influenced by the concentration of  $Fe^{2+}$  ions which catalyze hydrogen peroxide decomposition resulting in OH radical production and consequently the degradation of organic molecule. The effect of concentration of  $Fe^{2+}$  on the rate of photochemical degradation of Reactive Red 45 was observed by keeping all other factors constant. The results are given in Table 3. Increasing ferrous salt concentration, degradation rate of organic compound also increases, to certain level while a reverse trend was observed beyond this limit. This may be explained on the basis that on increasing the  $Fe^{2+}$  ions in the reaction mixture is accompanied by enhanced generation of .OH radicals, consequently increasing the rate of photodegradation. After the optimal  $Fe^{2+}$  ions addition, the higher concentration of  $Fe^{2+}$  resulted in a brown turbidity due to recombination of .OH radicals and here  $Fe^{2+}$  ions act as a scavenger, therefore, the rate decreases.

**Table3.** Kinetic of photodegradation of Reactive Red 45 at different initial concentrations of  $FeSO_4$  [Reactive Red 45] =  $3.33 \times 10^{-5}M$ ;  $pH = 2.9$ ;  $H_2O_2 = 1.0$  mL; Light Intensity =  $60$  mWcm $^{-2}$ ;  $\lambda_{max} = 521.9$  nm

$[FeSO_4] \times 10^{-5}M$	$k \times 10^{-2} s^{-1}$
1.66	6.21
2.0	7.15
2.33	9.90
2.66	10.80
3.0	12.66
3.33	14.96
3.66	11.05
4.0	9.44
4.33	8.06

## 2.6. Effect of $H_2O_2$ Concentration

Concentration of  $H_2O_2$  plays a more crucial role in the overall efficiency of the degradation processes. Usually it has been observed that the percentage degradation of the Reactive Red 45 increases with an increase in the dosage of  $H_2O_2$ , but excess quantities are not recommended.

It can be observed from the data given in Table-4 that the rate of reaction increases on increasing the amount of  $H_2O_2$  up to 1.0 mL. Thereafter, the rate of degradation decreases on with the increase in the amount of the  $H_2O_2$ . This can be explained on the basis that at optimum amount of  $H_2O_2$ , more hydroxyl radicals are produced by  $Fe^{2+}$  ions which degrade more dye molecules. On further increasing the amount of  $H_2O_2$ , the rate of reaction was found to decrease because of the fact that as the amount of  $H_2O_2$  increased along its optimum condition (1.0 mL) the rate of the reaction [Eq. (3) and Eq.(4) of mechanism] become fast and .OH radicals are consumed rapidly due to more availability of  $H_2O_2$  molecule. The peroxide radical are utilized and  $H^+$  ions are produced. The production of  $H^+$  ions is confirmed by a slight decrease in pH of the reaction mixture at the end of reaction. As a consequence, the rate of photodegradation decreases.



This may be due to recombination of hydroxyl radicals and also hydroxyl radicals react with  $H_2O_2$  contributing to the OH scavenging capacity.

**Table4.** Kinetic of photodegradation of Reactive Red 45 at different initial amounts of H<sub>2</sub>O<sub>2</sub>

[Reactive Red 45] = 3.33 × 10<sup>-5</sup> M; pH = 2.9; [Fe<sup>2+</sup>] = 3.33 × 10<sup>-5</sup> M; Light Intensity = 60 mWcm<sup>-2</sup>; λ<sub>max</sub> = 521.9 nm

H <sub>2</sub> O <sub>2</sub> (ml)	k × 10 <sup>-2</sup> s <sup>-1</sup>
0.5	5.98
0.6	6.45
0.7	7.59
0.8	9.90
0.9	12.43
<b>1.0</b>	<b>14.96</b>
1.1	11.05
1.2	9.67

### 2.7. Effect of Light Intensity

The effect of light intensity on the photodegradation of Reactive Red 45 was also observed. The results obtained are given in Table 5. A linear plot was obtained between the rate constant and light intensity, which indicates that an increase in the light intensity increase the rate of reaction because an increase in the intensity of light will increase the number of photons striking catalyst particles per unit time per square cm. As a result, more photons reacts with Fe<sup>3+</sup> ions and there is an increase in the number of active species, the hydroxyl radicals and corresponding increases in the rate of reaction.



**Table5.** Kinetic of photodegradation of Reactive Red 45 at different Variation in Light Intensity

[Reactive Red 45] = 3.33 × 10<sup>-5</sup> M; pH = 2.9; [Fe<sup>2+</sup>] = 3.33 × 10<sup>-5</sup> M; H<sub>2</sub>O<sub>2</sub> = 1.0 mL; λ<sub>max</sub> = 521.9 nm

Light Intensity (mWcm <sup>-2</sup> )	k × 10 <sup>-2</sup> s <sup>-1</sup>
10	3.45
20	4.14
30	5.06
40	5.98
50	11.51
60	<b>14.96</b>

### 3. MECHANISM

In presence of Fe<sup>2+</sup>, the peroxide breaks down to ·OH and OH<sup>-</sup>, according to the following reaction



#### Consumption of ·OH radicals



The participation of the ·OH radicals as an active oxidizing species was confirmed using the hydroxyl radical scavenger 2-Propanol, Which reduced rate of Photo-degradation.

After continuous irradiation, the complete mineralization of dye occurred via converting into end products. The end products are simple molecules or ions and less harmful to the environment.



The end products were detected in the reaction mixture by chemical test. Nitrate ions were detected and confirmed by a chemical test using H<sub>2</sub>SO<sub>4</sub> and FeSO<sub>4</sub>. A positive test for presence of nitrite ions is indicated by a dark brown solution, arising from the iron nitric oxide complex. Sulphate ions are

precipitated as BaSO<sub>4</sub>. CO<sub>2</sub> was confirmed by introducing the gas to freshly prepared limewater. The lime water turns milky indicates its presence.

#### 4. CONCLUSION

Photodegradation efficiency of dye was negligible when photolysis was carried out in the absence of H<sub>2</sub>O<sub>2</sub> and UV light. Photo-Fenton reaction increased the production of ·OH radicals and led to 65.25% mineralization of the dye in 7 minutes. The experimental data demonstrated that photo-Fenton process is promising techniques for the degradation of Reactive Red 45 dye from aqueous solution. This process is environmental friendly due to generation of biodegradable end products.

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