



Photocatalytic degradation of Reactive Red 24 in Aqueous Media by Photo-Fenton Reagent

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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 24, which has a complex molecular structure with azo aromatic groups, is widely used in textile industry. Degradation of Reactive Red 24 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 24, FeSO₄, H₂O₂, 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 the first order kinetics.

Keywords: Photocatalytic Degradation; Reactive Red 24; Photo-Fenton.



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1. INTRODUCTION

Water is one of the fundamental requirements of life and any undesired addition of chemical substances leads to its contamination and makes it unfit for human utility. Generally, various dyes found in industrial effluents, ultimately, enter the aquatic ecosystem and create various environmental hazards. These have very adverse and sometimes irreversible effects on other animals and plants as well. The main purpose of wastewater treatment is the removal of these toxic substances and colour and try to make the water usable for industrial or domestic use [1]. Many azo dyes and their intermediate products are toxic, mutagenic or carcinogenic to aquatic life and human [2]. 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. 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_2O_2 and O_3 , ultraviolet irradiation, ultrasound, and homogeneous or heterogeneous catalysts.

Common AOPs which are widely used are $\text{H}_2\text{O}_2/\text{UV}$ [3], TiO_2/UV [4], Ozonation [5], O_3/UV [6], Fenton reagent [7], UV-Fenton process [8] electron beam irradiation [9], sonolysis [10], wet-air oxidation [11] and various combination of these methods [12]. Photocatalytic degradation has been proved to be a promising method for the treatment of wastewater contaminated with organic and inorganic pollutants [13-16]. Fenton and Fenton type processes give 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 [17], harmful chemicals [18-19] and dyes [20-22]. 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 24 (RR24) is widely used in textile industries. As, it causes great potential of pollution to aquatic environment, hence 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 (RR24), photocatalyst (Fenton reagent), H_2O_2 , Light intensity and pH of the experimental solutions.

2. EXPERIMENTAL

2.1. Materials

For the present experimental studies the commercial azo dye Reactive Red 24 was used. Photocatalyst FeSO_4 (Merck, 99% purity) and H_2O_2 (Merck, 30% purity) were used for photocatalytic degradation. For the photobleaching process, $1 \times 10^{-3} \text{ M}$ stock solution of dye Reactive Red 24 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 24 dye solution ($1 \times 10^{-3} \text{ M}$), 1.5 ml of FeSO_4 ($1 \times 10^{-3} \text{ M}$) and 0.8 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 visible light source (200 W Tungsten filament 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 (Systronic Double Beam Spectrophotometer 2203) at 514.7 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.

3. RESULTS AND DISCUSSION

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 24 was observed at 514.7 nm. The optimum conditions for the photobleaching of dye were $[\text{Dye}] = 3.0 \times 10^{-5} \text{ M}$, $[\text{FeSO}_4] = 4.0 \times 10^{-5} \text{ M}$, $\text{H}_2\text{O}_2 = 0.8 \text{ mL}$ and $\text{pH} = 2.9$. The result of photocatalytic bleaching of Reactive Red 24 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 $2 + \log \text{O.D.}$ and time has been plotted. The linearity of the plot indicates that the photocatalytic bleaching of Reactive Red 24 follows a first order kinetics. The rate constant of this photobleaching process was determined using the expression. **Rate Constant (k) = 2.303 x Slope**



Table 1. Typical Run of Photocatalytic degradation of Reactive Red 24

[Reactive Red 24] = 3.0×10^{-5} M ;
[Fe²⁺] = 4.0×10^{-5} M;
 λ_{max} =514.7nm;

pH = 2.9;
H₂O₂ = 0.8 mL;
Light Intensity = 60 mWcm⁻²;

Time(minutes)	O.D	2+log O.D.
0	0.614	1.7881
1	0.511	1.7084
2	0.416	1.6190
3	0.389	1.5899
4	0.323	1.5092
5	0.295	1.4698
6	0.238	1.3765
7	0.201	1.3031
8	0.169	1.2278
9	0.148	1.1702

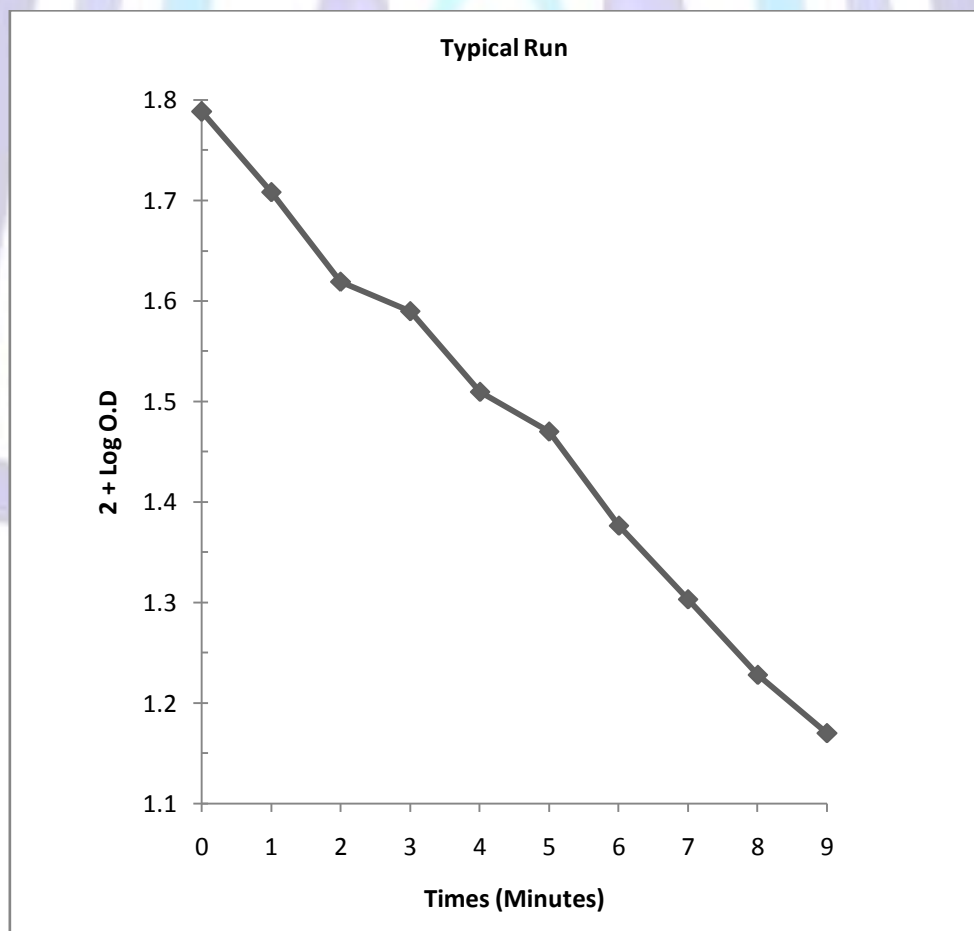


Fig. 1. Typical Run of Photocatalytic degradation of Reactive Red 24 Rate Constant (k) = $15.43 \times 10^{-2} \text{s}^{-1}$



3.1. Effect of pH Variation on Photodegradation of Dye

To study the effect of pH on photodegradation experiments are conducted for 3.0×10^{-5} M Reactive Red 24 in presence of Fe^{2+} : 3.0×10^{-5} M and 0.8 mL H_2O_2 at different pH values (2.5-3.2). The values of k at different pH are given in Table 2:

Table-2. Kinetics of photodegradation of Reactive Red 24 at different pH

[Reactive Red 24] = 3.0×10^{-5} M [Fe^{2+}] = 4.0×10^{-5} M;
 H_2O_2 = 0.8 mL; λ_{max} = 514.7nm; Light Intensity = 60 mWcm^{-2} ;

pH	$k \times 10^{-2} \text{ s}^{-1}$
2.5	5.29
2.6	6.63
2.7	9.90
2.8	10.98
2.9	15.43
3.0	11.97
3.1	8.98
3.2	5.98

Fenton oxidation is known as a highly pH dependent process since pH plays an important role in the mechanism of $\cdot\text{OH}$ production in the Fenton's reaction. At high pH ($\text{pH} > 3.2$) the generation of $\cdot\text{OH}$ gets slower because of the formation of the ferrichydroxo complex. 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 $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, which reacts more slowly with peroxide compared to that of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$. The reaction is slowed down due to the formation of complex species $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, which reacts more slowly with peroxide compared to that of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$.



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^+ ions to form stable oxonium ion $[\text{H}_3\text{O}_2]^+$. An oxonium ion makes peroxide electrophilic to enhance its stability and presumably substantially reduces the reactivity with Fe^{2+} ion. Maximum color removal efficiencies were obtained at pH 2.9, for the dye in case of photo-Fenton processes.

3.2 Dye Concentration Variation

The effect of initial dyes concentration on the decolorization degree at the optimum pH (2.9), Fe^{2+} ion (4.0×10^{-5} M) and H_2O_2 (0.8 mL 30%), was studied in photo-Fenton process. As an example, concentrations of dye Reactive Red 24 were varied from 2.66×10^{-5} M to 4.66×10^{-5} M. The results are summarized in Table- 3. The rate of photochemical degradation was found to increase with increase in the concentration of RR24 up to 3.0×10^{-5} 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 RR24, more molecules of RR24 are available for degradation. However on increasing the concentration above 3.0×10^{-5} M, the reaction rate was found to decrease. It may be attributed to the fact that as the concentration of RR24 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 24 was observed.

**Table - 3. Kinetics of photodegradation at different concentrations of Reactive Red 24**

pH = 2.9; $[\text{Fe}^{2+}] = 4.0 \times 10^{-5} \text{ M};$
 $\text{H}_2\text{O}_2 = 0.8 \text{ mL};$ $\lambda_{\text{max}} = 514.7\text{nm};$ Light Intensity = $60 \text{ mWcm}^{-2};$

[Reactive Red 24] $\times 10^{-5} \text{ M}$	$k \times 10^{-2} \text{ s}^{-1}$
2.66	3.5
3.0	15.43
3.33	14.27
3.66	12.89
4.0	9.44
4.66	7.36

3.3 Effect of Fe^{2+} concentration Variation

Dye degradation efficiency by Photo-Fenton process is influenced by the concentration of Fe^{2+} ions which catalyze hydrogen peroxide decomposition resulting in $\cdot\text{OH}$ radical production and consequently the degradation of organic molecule.

The effect of Fe^{2+} concentration on color removal was examined by changing the Fe^{2+} concentration between $2.66 \times 10^{-5} \text{ M}$ to $5.0 \times 10^{-5} \text{ M}$, while keeping the concentration of H_2O_2 , pH and dyes constant [($[\text{H}_2\text{O}_2]$ = 0.8 ml , pH = 2.9, for Reactive Red 24 = $3.0 \times 10^{-5} \text{ M}$], On the basis of the data reported in table-4, it can be said that initially on increasing ferrous salt concentration, degradation rate of organic compound also increases up to $4.0 \times 10^{-5} \text{ M}$ 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 $\cdot\text{OH}$ 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 $\cdot\text{OH}$ radicals and here Fe^{2+} ions act as a scavenger, therefore, the rate decreases.

**Table- 4. Kinetics of photodegradation of Reactive Red 24 at different concentrations of Fe^{2+}**

[Reactive Red 24] = $3.0 \times 10^{-5} \text{ M};$ pH = 2.9;
 $\text{H}_2\text{O}_2 = 0.8 \text{ mL};$ $\lambda_{\text{max}} = 514.7\text{nm};$ Light Intensity = $60 \text{ mWcm}^{-2};$

$[\text{Fe}^{2+}] \times 10^{-5} \text{ M}$	$k \times 10^{-2} \text{ s}^{-1}$
2.66	4.3
3.00	10.36
3.33	11.51
3.66	14.04
4.0	15.43
4.33	9.21
4.66	6.44
5.0	6.21

3.4 Effect of H_2O_2 Variation

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 24 increases with an increase in the dosage of H_2O_2 , but excess quantities are not recommended. During the determination of optimum H_2O_2 dose, studies were conducted at constant Fe^{2+} concentration $4.0 \times 10^{-5} \text{ M}$, pH 2.9 and dye concentration $3.0 \times 10^{-5} \text{ M}$. Varied dosage of H_2O_2 from 0.5 to 1.3 ml were applied. As demonstrated from the results shown in table- 5 It was observed that the rate of reaction



increases on increasing the amount of H₂O₂ up to 0.8 mL. Thereafter, the rate of degradation decreases with the increase in the amount of the H₂O₂. This can be explained on the basis that at optimum amount of H₂O₂, more hydroxyl radicals are produced by Fe²⁺ ions which degrade more dye molecules. On further increasing the amount of H₂O₂, the rate of reaction was found to decrease because of the fact that as the amount of H₂O₂ increased along its optimum condition (0.8 mL) the rate of the reaction [Eq. (5) and Eq.(6)] become fast and ·OH radicals are consumed rapidly due to more availability of H₂O₂ 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 H₂O₂ contributing to the ·OH radicals scavenging capacity.

Table - 5: Kinetics of photodegradation of Reactive Red 24 at different amount of H₂O₂

[Reactive Red 24] = 3.0 × 10⁻⁵ M; pH = 2.9; [Fe²⁺] = 4.0 × 10⁻⁵ M;
 λ_{max} = 514.7nm; Light Intensity = 60 mWcm⁻²;

H ₂ O ₂ [ml]	k×10 ⁻² s ⁻¹
0.5	9.67
0.6	11.51
0.7	13.81
0.8	15.43
0.9	14.73
1.0	8.29
1.2	7.59
1.3	6.90

3.5 Effect of Light Intensity

The effect of light intensity on the photodegradation of Reactive Red 24 was also observed. The results obtained are given in Table - 6. A linear plot was obtained between the rate constant and light intensity, which indicates that an increase in the light intensity increases 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⁺³ ions and there is an increase in the number of active species, the hydroxyl radicals and corresponding increases in the rate of reaction.

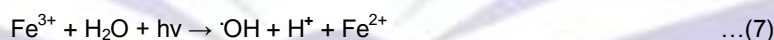


Table- 6: Kinetics of photodegradation of Reactive Red 24 at different Variation in Light Intensity

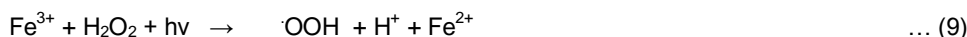
Reactive Red 24] = 3.0 × 10⁻⁵ M; pH = 2.9;
 [Fe²⁺] = 4.0 × 10⁻⁵ M; λ_{max} = 514.7nm; H₂O₂ = 0.8 mL;

Light Intensity(mWcm ⁻²)	k×10 ⁻² s ⁻¹
10	5.52
20	5.75
30	6.21
40	7.13
50	10.36
60	15.43



4 MECHANISM

In presence of Fe^{2+} , the peroxide breaks down to $\cdot\text{OH}$ and OH^- , according to the following reaction

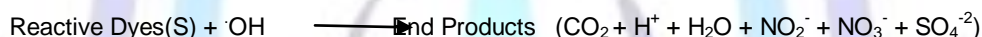


Consumption of $\cdot\text{OH}$ radicals



The participation of the $\cdot\text{OH}$ 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_2SO_4 and FeSO_4 . 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_4 . CO_2 was confirmed by introducing the gas to freshly prepared limewater. The lime water turns milky indicates its presence.

5 CONCLUSION

Photo-Fenton reaction increased the production of $\cdot\text{OH}$ radicals and led to 76% mineralization of the dye in 9 minutes. The experimental data demonstrated that photo-Fenton process is promising techniques for the degradation of Reactive Red 24 dye from aqueous solution. This process is environmental friendly due to generation of biodegradable end products.

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