Photo-degradation Treatment of Reactive Blue 13 in Aqueous Solution by Photo-Fenton Reagent

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Abstract

The Non-biodegradable and or hazardous organic constituents from textile industry and Industrial waste water can be removed by the use of photo-Fenton oxidation treatment (AOPs). Azo dyes like Reactive Blue 13 have complex molecular structure and are being used widely in dyeing and printing industries. Photo-degradation treatment of Reactive Blue 13 was carried out in an aqueous solution under irradiation of visible light by using Fenton system. The optimum doses of the parameters like concentration of dye, amount of hydrogen peroxide, pH etc. that are necessary for complete mineralization of Reactive Blue 13 were also investigated in detail. The optimum condition for the photo-degradation of dye RB 13 was established. The kinetics of photo-Fenton oxidation treatment in the dilute solution of Reactive Blue 13 follows first order kinetics.

Keywords: *Photo-degradation, Reactive Blue 13, Photo-Fenton.*

1. INTRODUCTION

Textile, paper and pulp manufacturing plastics, printing industries are using different synthetic dyes such as azo, vat, nitro, indigo, etc., for different purposes [1, 2]. Many azo dyes and their intermediate products are toxic mutagenic or carcinogenic to aquatic life and human [6]. When the effluent from these industries contains substantial amounts of such dyes in water, can be a threat to aquatic life [3] and a potential human health hazard [4, 5]. It is therefore become essential either to remove these dyes completely from water or to treat them in such a way so as to minimize their hazardous effects on the environment and also to decolorize the water.

Advanced oxidation processes (AOPs) are those groups of technologies that lead to hydroxyl radical (˙OH) generation by means of oxidizing agent such as H_2O_2 and O_3, ultraviolet irradiation, ultrasound, and homogeneous or heterogeneous catalysts as the primary oxidant (second highest powerful oxidant after the fluorine).

AOPs are powerful and efficient treatment methods for degrading Non-biodegradable and hazardous organic constituents from Industrial waste water or mineralizing stable, inhibitory, or toxic contaminants. These

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methods could be applied to the purification and disinfection of drinking water as well as to treat the contaminated groundwater, surface water, and wastewaters containing recalcitrant, inhibitory, and toxic compounds with low biodegradability.

Common AOPs which are widely used are H_2O_2 / UV [7] , TiO_2 / UV [8], Ozonation [9], O_3 / 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].

Photo-Fenton reagent cleaves the conjugated bonds of azo-dyes chromophore, 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 Blue 13 (RB13) is a dye used widely in textile industries and as it causes great potential of water pollution, therefore, a proper treatment is necessary before discharge into the aquatic environment.

MATERIALS AND METHODS

2.1 Reagents Used

In the present Investigation the commercial azo dye Reactive Blue 13, Photo-catalyst $FeSO_4$ (Merck, 99% purity) and H_2O_2 (Merck, 30% purity) were used. All laboratory reagents were of analytical grade. A stock solution $1x10^{-3}$ M of dye Reactive Blue 13 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.

2.2 Procedure and Analysis

A 30.0 mL of reaction mixture in double distilled water was prepared by taking 1.0 mL of Reactive Blue 13 dye solution ($1x10^{-3}$ M), 1.0 mL of $FeSO_4$ ($1x10^{-3}$ M) and 1.0 mL of H_2O_2 (30%) at pH 2.8. The pH of the solution was measured by pH meter (Hanna Instrument, Italy). For photo-degradation of RB 13 the reaction mixture was exposed to light source (200W Tungsten lamp). Water filter was used to cut off thermal radiation. The rate of decrease of color with time was continuously monitored by measuring Absorbance using spectrophotometer (Systronics Double Beam Spectrophotometer 2203) at λ_{max} = **583 nm** at definite time intervals**.** After complete mineralization in 23 minutes, the presence of end products NO_2^-, NO_3^-, SO_4^{2-} ions and evolution of CO_2 in the

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reaction mixture were tested by chemical tests. 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.

2. RESULTS AND DISCUSSION

Control experiments in absence of $FeSO_4$, light were carried out to confirm the necessity of photocatalyst, light for photo-degradation of RB 13 dye. The photo-degradation of Reactive Blue 13 was observed at 583 nm. The optimum conditions obtained for the photo-degradation of RB 13 were [Dye] = 3.33 x10^{-5} M, [$FeSO_4$] = 3.33 x10^{-5} M, H_2O_2 = 1.0 mL and pH = 2.8. The results with optimum conditions are summarized in Table-1.

Table: 1. Photodegradation of Reactive Blue 13

[Reactive Blue 13] = 3.33 ×10^{-5} M;   pH = 2.8;   [Fe^{2+}] = 3.33 ×10^{-5} M;

H_2O_2 = 1.0 mL λ_{max} = 583 nm   Light Intensity = 60 mWcm^{-2};

Time (minutes)	Absorbance (A)	2 + log A
0	0.592	1.7723
1	0.515	1.7118
2	0.453	1.6560
3	0.401	1.6031
4	0.362	1.5587
5	0.302	1.4800
6	0.265	1.4232
7	0.243	1.3856
8	0.206	1.3138
9	0.185	1.2671
10	0.161	1.2068
11	0.142	1.1522

A decrease in the absorbance (A) was found with the increase in time of irradiation indicating that the dye is degrading on irradiation. A graph between 2 + log A and time was plotted. The linearity of the curve shows that the photo-degradation of Reactive Blue 13 follows a first order kinetics. The rate constant of this process was determined using the expression (k) = 2.303 x Slope.
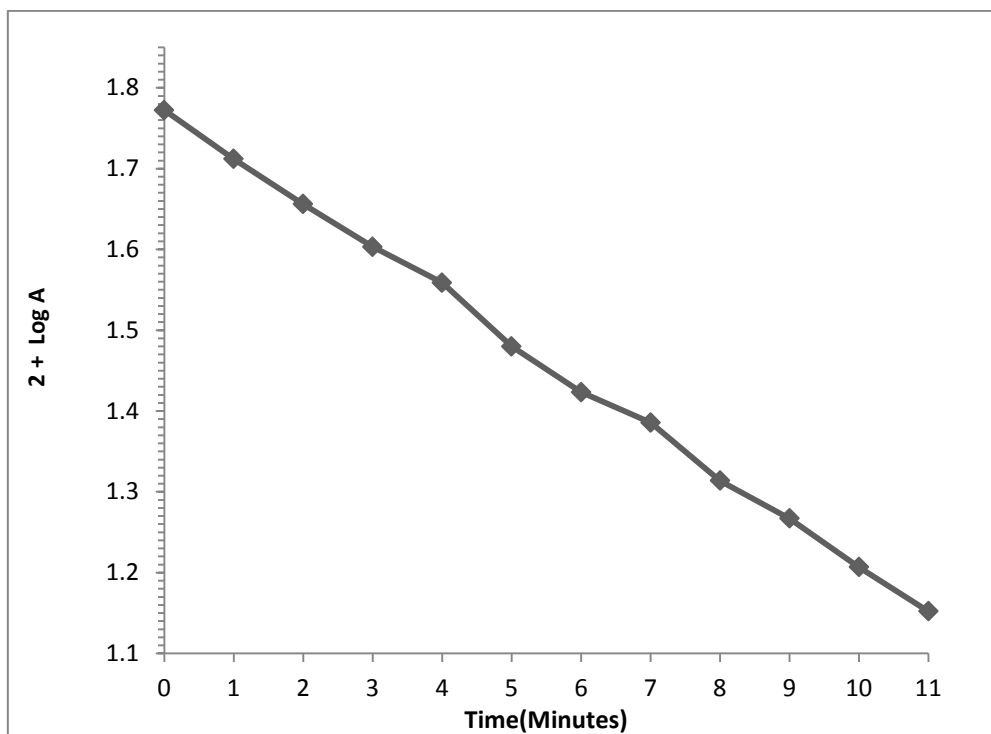
Fig.: 1- Photodegradation of Reactive Blue 13 with time

3.1 Effect of Variation of pH on Photodegradation of Reactive Blue 13

The effect of pH on photodegradation experiments were conducted at different initial pH values (2.5 - 3.2) for Reactive Blue 13 (3.33 x 10^{-5} M) in presence of Fe^{2+} = 3.33 x 10^{-5} M and 1.0 ml H_2O_2. The results are given in Table- 2:

Table-2: Effect of Variation of pH on Photodegradation of Reactive Blue 13

[Reactive Blue 13] = 3.33 $\times10^{-5}$ M   [Fe^{2+}] = 3.33 $\times10^{-5}$ M;

H_2O_2 = 1.0 mL;   Light Intensity = 60 mWcm^{-2};

λ_{max}=583 nm

pH	k×10^{-2}s^{-1}
2.5	8.91
2.6	9.21
2.7	9.90
2.8	**10.82**
2.9	9.44
3.0	8.98
3.1	8.06
3.2	7.59

Fenton oxidation is a highly pH dependent process because pH plays an important role in the mechanism of ˙OH production [27]. In this study maximum color removal efficiencies were obtained at pH 2.8 for the RB 13 dye.

At high pH value (pH > 3.2) the generation of ˙OH gets slower because of the formation of the ferric hydroxo complexes and at very low pH values (< 2.5) hydrogen ions act as ˙OH radical-scavengers. The formation of complex species $[Fe(H_2O)_6]^{2+}$ slowed down the reaction which reacts more slowly with peroxide compared to that of $[Fe(OH)(H_2O)_5]^{2+}$.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad \textbf{... (1)}$$

$$Fe^{3+} + H_2O + h\nu \rightarrow \cdot OH + H^+ + Fe^{2+} \qquad \textbf{... (2)}$$
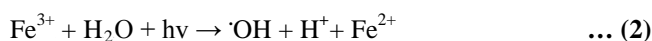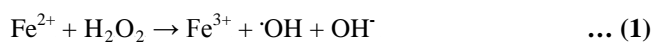
Thus, it may be concluded that in the pH range below 2.8, step (1) dominates over step (2). However, above pH 2.8 retardation of the reaction suggests the dominance of step (2) over step (1). In addition, the peroxide gets solvated in the presence of high concentration of H^+ ions to form stable oxonium ion $[H_3O_2]^+$ that makes peroxide electrophilic, to enhance its stability and presumably substantially reduces the reactivity with Fe^{2+} ion.

3.2 Effect of concentration of Reactive Blue 13

The optimum concentration of RB 13 dye for photo-degradation was determined by taking different

concentration and the results are given in Table 3.

Table 3: Effect of concentration of Reactive Blue 13

$[Fe^{2+}] = 3.33 \times 10^{-5}$ M;   pH = 2.8; $H_2O_2 = 1.0$ mL;
Light Intensity = 60 mWcm^{-2}; $\lambda_{max}= 583$ nm

[Dye] $\times 10^{-5}$ M	$k \times 10^{-2}$ s^{-1}
2.66	7.36
3.0	8.75
3.33	**10.82**
3.66	8.52
4.0	7.83
4.33	6.90

Initially the rate of photo-degradation was found to increase with increase in the concentration of RB13 up to 3.33×10^{-5} M then a decrease was observed. This may be due to the fact that initially an increase in the concentration of RB13 means more molecules of dye are available for photo-degradation so the rate was found to increase. After optimum concentration 3.33×10^{-5} M the increased concentration of RB13 started acting like a filter for the incident light and its large concentration will not permit the light to react the dye molecules and thus a decrease in the rate of photo-degradation was observed.

3.3 Effect of variation of Fe^{2+} concentration

The efficiency of Photo-Fenton process is influenced by the concentration of Fe^{2+} ions which catalyze decomposition of H_2O_2 resulting in ˙OH radical production and consequently the degradation of organic

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molecule [27]. The results of study of variation in concentration of Fe^{2+} on the rate of photo-degradation of Reactive Blue 13 by keeping all other factors constant are given in Table 4.

Table 4: Effect of Fe^{2+} concentration

[Reactive Blue 13] = 3.33 ×10^{-5} M;   pH = 2.8; λ_{max}=583 nm

H_2O_2 = 1.0 mL;   Light Intensity = 60 mWcm^2;

[FeSO$_4$]×10^{-5} M	k×10^{-2}s^{-1}
1.66	5.52
2.0	6.21
2.33	7.13
2.66	9.67
3.0	9.97
3.33	**10.82**
3.66	8.29
4.0	7.59
4.33	6.67

The Increase in ferrous salt concentration increases the degradation rate of RB 13 to certain level (3.33 x 10^{-5} M) but a reverse trend was observed beyond this limit. This may be due to the fact that initially an increase in the Fe^{2+} ions in the reaction mixture is accompained by enhanced generation of $^{.}OH$ radicals, consequently increases the rate of photo-degradation. After the optimum concentration of Fe^{2+} ions the addition 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.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {^{.}OH} + OH^- \qquad \textbf{... (3)}$$
$$Fe^{2+} + {^{.}OH} \rightarrow Fe^{3+} + OH^- \qquad \textbf{... (4)}$$

3.4 Effect of amount of H_2O_2

The hydrogen peroxide plays an important role in the overall efficiency of the degradation processes. Usually it has been observed that the percentage degradation of the Reactive Blue 13 increases with an increase in the dosage of H_2O_2, but excess quantities are not recommended. The results of effect of amount of hydrogen peroxide on photo-degradation of Reactive Blue 13 are presented in Table 5.

Table 5: Effect of amount of H_2O_2

[Reactive Blue 13] = 3.33 ×10^{-5} M;   pH = 2.8;   [Fe^{2+}] = 3.33 ×10^{-5}M;

Light Intensity = 60 mWcm^{-2}; λ_{max}= 583 nm

H_2O_2(ml)	k×10^{-2}s^{-1}
0.5	5.98
0.6	6.45
0.7	7.83
0.8	9.44
0.9	9.90
1.0	**10.82**
1.1	9.67
1.2	7.36
1.3	6.21

The rate of photo-degradation increases up to 1.0mL of H_2O_2, thereafter, a decrease in the rate was observed. This can be explained on the basis that at optimum amount of H_2O_2, more $\cdot$OH are produced by Fe^{2+} ions which degrade more dye molecules. On further increasing the amount of H_2O_2, the rate was found to decrease because of the fact that as the amount of H_2O_2 increased after optimum condition (1.0 mL) the rate of the reaction [Eq. (5) and Eq.(6)] become fast and $\cdot$OH radicals are consumed rapidly due to more availability of H_2O_2 molecule. The peroxide radical are utilized and H^+ ions are produced [27]. 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 photo-degradation decreases.

$$Fe^{3+} + H_2O_2 + hv \rightarrow Fe^{2+} + \cdot OOH + H^+ \qquad ....(5)$$

$$H_2O_2 + \cdot OH \longrightarrow H_2O + \cdot OOH \qquad ....(6)$$

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

3.5 Effect of Light Intensity

The results obtained for the effect of light intensity on the photo-degradation of Reactive Blue 13 are given in Table 6.

Table 6: Effect of Light Intensity

[Reactive Blue 13] = 3.33×10^{-5} M;   pH = 2.8; $[Fe^{2+}] = 3.33 \times 10^{-5}$M;
H_2O_2 = 1.0 mL; λ_{max}=583 nm

Light Intensity (mWcm^{-2})	$k \times 10^{-2} s^{-1}$
10	2.99
20	3.91
30	4.83
40	5.52
50	9.21
60	**10.82**

A linear plot obtained between the rate constant and light intensity indicates that on increasing the light intensity will increase the number of photons striking catalyst particles per unit time per square cm therefore more photons will react with Fe^{+3} ions to increase in the number of active species (hydroxyl radicals) and hence the photo-degradation rate also.

$$Fe^{3+} + H_2O + hv \rightarrow \cdot OH + H^+ + Fe^{2+} \qquad ... (7)$$
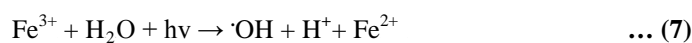
3. **Mechanism**

The peroxide breaks down to $\cdot$OH and OH$^-$ in presence of Fe^{2+} as shown in the following reactions-

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$$Fe^{2+} + H_2O_2 \quad \rightarrow \quad Fe^{3+} + \cdot OH + OH^- \qquad \dots (8)$$

$$Fe^{3+} + H_2O_2 + hv \quad \rightarrow \quad \cdot OOH + H^+ + Fe^{2+} \qquad \dots (9)$$

$$Fe^{3+} + H_2O + hv \quad \rightarrow \quad Fe^{2+} + \cdot OH + H^+ \qquad \dots (10)$$

$$\cdot OH + H_2O_2 \quad \rightarrow \quad H_2O + \cdot OOH \ \ (\text{Highly Unstable}) \qquad \dots (11)$$

$$Fe^{2+} + \cdot OH \quad \rightarrow \quad Fe^{3+} + OH^- \qquad \dots (12)$$

$$Fe^{3+} + \cdot OOH \quad \rightarrow \quad O_2 + Fe^{2+} + H^+ \qquad \dots (13)$$
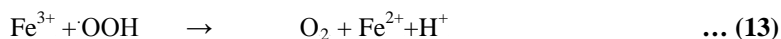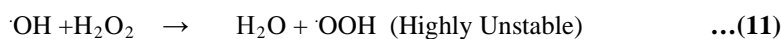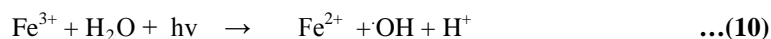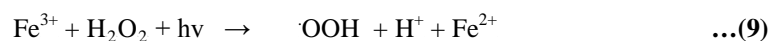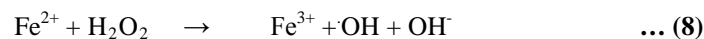
Consumption of $\cdot OH$ radicals

$$H_2O_2 + \cdot OH \quad \rightarrow \quad \cdot OOH + H_2O \qquad \dots (14)$$

$$\cdot OH + \cdot OH \quad \rightarrow \quad H_2O_2 \qquad \dots (15)$$

$$\cdot OH + \text{Dye (RB 13)} \quad \rightarrow \text{Colorless Degraded end Product} \qquad \dots (16)$$

The end products ($CO_2 + H^+ + H_2O + NO_2^- + NO_3^- + SO_4^{-2}$) are simple molecules or ions and less harmful to the environment.

5. Conclusion

Photo-Fenton reaction increased the production of $\cdot OH$ radicals and led to 76.01% mineralization of the dye in 11 minutes and complete mineralization in 23 minutes. It is clear from the experimental data in the present investigation that photo-Fenton process is promising techniques for the degradation of Reactive Blue 13 dye in aqueous solution. This process is environmental friendly due to generation of biodegradable end products CO_2, H^+, H_2O, NO_2^-, NO_3^-, SO_4^{-2} that are simple molecules or ions and less harmful to the environment.

6. Acknowledgement

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