



ORIGINAL ARTICLE

A novel route for waste water treatment: Photocatalytic degradation of rhodamine B

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Abstract The direct photocatalytic degradation of rhodamine B (RB) has been reported by thiocyanate complex of iron and hydrogen peroxide. The rate determining parameters like, pH of the medium, concentration of the complex and dye, amount of H₂O₂, and light intensity on the degradation process were studied in detail. The rate of photocatalytic degradation of the dye was observed spectrophotometrically and it follows pseudo-first-order kinetics.

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1. Introduction

Dyes are extensively used in the textile industry. They are the copious source of colored organics emanating as a waste from

the textile dyeing process. Due to the high concentration of organics in the effluents and the higher stability of modern synthetic dye, the conventional biological treatment methods are ineffective for the complete color removal and degradation of organics and dyes (Souther et al., 1957; Hamza et al., 1980). Other conventional methods of color removal from an aqueous medium include techniques like coagulation, filtration, adsorption by activated carbon, and treatment with ozone (Lorimer et al., 2001). Some promising applications of homogeneous transition metal photocatalysis have been reported in areas such as organic synthesis, micro imaging coating technology, biology, medicines, pollution remediation, and energy storage (Liou et al., 2005; Kong and Lemley, 2006). In homogeneous photocatalysis, the substrate and the photocatalyst, both are in the same phase. Dyes and coordination compounds are some of the good examples of homogeneous photocatalysis and heterogeneous photocatalysis; both the substrate and the photocatalyst are in different phases. Each method has its own advantages and disadvantages. For example, the use of charcoal is technically easy but has a high waste disposal cost. While in filtration, low-molar-mass dyes can pass through the filter system. Coagulation, using alum, ferric

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salts, or lime is a low cost process. However, the disposal of toxic sludge is a severe drawback in all the above methods. Lastly, the ozone treatment does not require disposal but suffers from high cost. Advanced oxidation processes are of ample interest currently for the effective oxidation of a wide variety of organics and dyes (Kang and Hoffman, 1998; Boye et al., 2002). Among them, top priority goes to like photo-Fenton- and photocatalytic methods-assisted photocatalytic degradation. The Fenton reagent is an established reagent for the degradation of dyes but the main disadvantage of the reagent is that the reaction ceases after complete consumption of Fe^{2+} , whereas, in the photo-Fenton reaction, Fe^{2+} are regenerated from Fe^{3+} with the additional requirement of light. This makes the process cyclic in nature and the photochemical degradation proceeds smoothly (Jain et al., 2007). Degradation of dyes employing the photo-Fenton reagent provides a newer method for the treatment of waste water containing dye effluents. In addition to the involvement of $\cdot\text{OH}$, some results on the mechanism of the Fenton reaction suggest the participation of a ferryl complex (Pignatello et al., 1999). Chen et al. (2002) investigated the photo-Fenton degradation of malachite green catalyzed by aromatic compounds under visible light irradiation. Xie et al. (2002) studied the photo-assisted degradation of dyes in the presence of Fe^{3+} and H_2O_2 under visible irradiation. Photocatalytic degradation of direct Yellow 12 dye using UV/ TiO_2 in a shallow pond slurry reactor was studied by Toor et al. (2006). Nerud et al. (2001) reported the decolorization of synthetic dyes by the Fenton reagent and the Cu/Pyridine/ H_2O_2 system. Comparative photocatalytic studies of degradation of a cationic and an anionic dye were done by Hasnat et al. (2005). Chen et al. (2003) observed the electrochemical degradation of bromo-pyrogallol red in the presence of cobalt ions. Garcia et al. (2007) investigated the comparative study of the degradation of real textile effluents by the photocatalytic reactions involving UV/ TiO_2 / H_2O_2 and UV/ Fe^{2+} / H_2O_2 systems. Photocatalytic degradation of dye sulforhodamine B with photosensitization was studied by Liu et al. (Zhao, 2000).

In a literature survey, no attention was found to have been paid to the photocatalytic degradation of RB dye using thiocyanate complex of iron and H_2O_2 . Therefore, in the present investigation an attempt was made to carry out photochemical degradation of RB dye in a homogeneous medium using thiocyanate complex and H_2O_2 , which generates $\cdot\text{OH}$ (Fig. 1).

2. Materials and methods

The photochemical degradation of RB was studied in the presence of an iron complex, i.e., $[\text{Fe}(\text{SCN})]^{2+}$, H_2O_2 , and light. A stock solution of RB (1.0×10^{-3} M) was prepared in doubly distilled water. The complex $[\text{Fe}(\text{SCN})]^{2+}$ was prepared by mix-

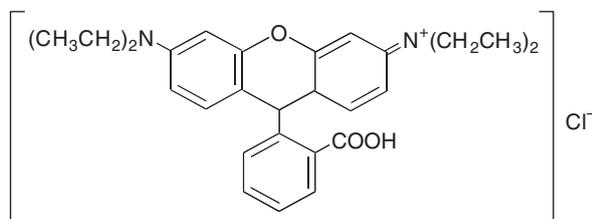
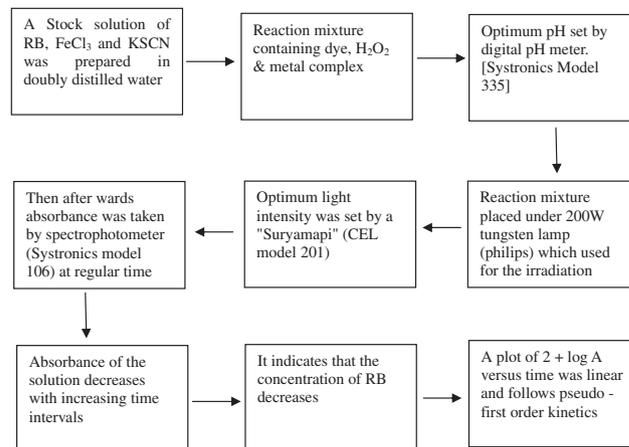


Figure 1 Rhodamine B.

ing FeCl_3 (1.0×10^{-3} M, Himedia) and KSCN (1.0×10^{-3} M, Himedia) in a 1:1 ratio. H_2O_2 (30%, Merck) was a commercial product and was used as received. The reaction mixture containing dye (10^{-5} M), complex (10^{-5} M), and hydrogen peroxide was exposed to light for a certain period depending on the employed complex. A 200 W tungsten lamp (Philips) was used for the irradiation. The intensity of light at various distances was measured by a "Suryamapi" (CEL Model 201). The pH of the solution was measured using a digital pH meter (Systronics Model 335). The desired pH of the solution was adjusted by the addition of previously standardized 0.05 M sulphuric acid and 1.0 M sodium hydroxide solutions. A visible spectrophotometer (Systronics Model 106) was used for measuring the absorbance of the reaction mixture at regular time intervals.



3. Results and discussion

Photocatalytic degradation of RB by the iron complex/ H_2O_2 system was studied by taking 40.0 mL reaction mixture containing 1.50×10^{-5} M dye solution, 0.3 mL hydrogen peroxide, and 2.18×10^{-5} M FeCl_3 solution in a 100 mL beaker for untreated solution and 1.50×10^{-5} M dye, 0.3 mL hydrogen peroxide and 4.37×10^{-5} M iron complex in a 100.0 mL beaker for treated solution. The pH of the both the reaction mixtures was adjusted to 4.0.

An aliquot of 3.0 mL was taken out from the reaction mixture at regular time intervals and the absorbance was measured spectrophotometrically at $\lambda_{\text{max}} = 560$ nm. It was observed that the absorbance of the solution decreases with increasing time intervals, which indicates that the concentration of RB decreases with increasing time of exposure. A plot of $2 + \log A$ versus time was linear and follows pseudo-first-order kinetics. The rate constant was measured using the following expression:

$$k = 2.303 \times \text{Slope}$$

Typical run has been graphically represented in Fig. 2.

The reaction mixture containing the same concentration of dye, H_2O_2 , and complex was kept in dark and the absorbance of the solution was measured at interval of 15.0 min. The result obtained is graphically given in Fig. 3. From the data in Figs. 2 and 3, it has been observed that with increase in time, the absorbance of dye solution decreases and hence, bleaching of

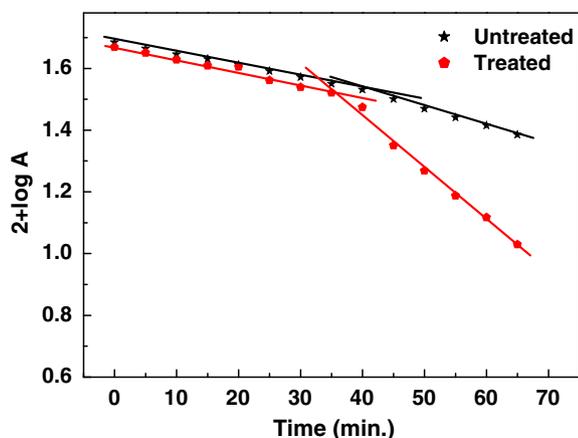


Figure 2 A typical run. Treated system – degradation of RB: pH, 4.0; (H₂O₂), 0.30 ml; complex concentration, 4.37×10^{-5} M; dye concentration, 1.50×10^{-5} ; light intensity, 50 mW cm^{-2} , $k_1 = 2.30 \times 10^{-4} \text{ s}^{-1}$, $k_2 = 5.76 \times 10^{-4} \text{ s}^{-1}$. Untreated system – degradation of RB: pH, 4.0. (H₂O₂), 0.30 ml; FeCl₃ concentration, 2.18×10^{-5} M; dye concentration, 1.50×10^{-5} ; light intensity, 50 mW cm^{-2} , $k_1 = 1.55 \times 10^{-4} \text{ s}^{-1}$, $k_2 = 2.32 \times 10^{-4} \text{ s}^{-1}$.

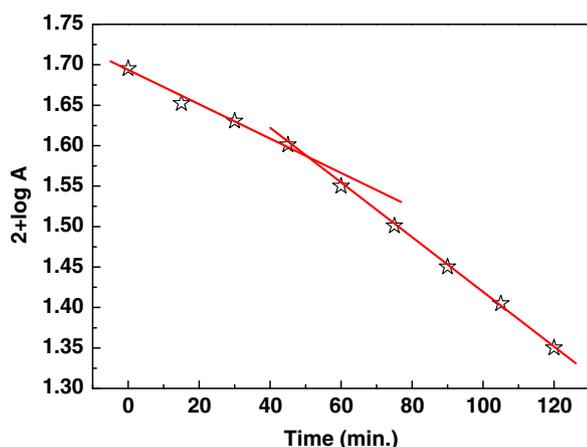


Figure 3 A typical run (in dark). Treated system – degradation of RB in dark: pH, 4.0; (H₂O₂), 0.30 ml; complex concentration, 4.37×10^{-5} M; dye concentration, 1.50×10^{-5} ; $k_1 = 0.38 \times 10^{-4} \text{ s}^{-1}$; $k_2 = 0.64 \times 10^{-4} \text{ s}^{-1}$.

dye takes place under both the conditions i.e. in the presence and absence of light. From the k values, it is clear that rate of bleaching of dye is greatly accelerated in the presence of light as compared to dark.

In this degradation process, the reaction proceeded in two phases. The first phase was an induction period (Chen et al., 2002), in which radicals were generated, whereas the major degradation of the dye occurred in second step, as shown by the sharp decrease in the absorbance, so we considered only second step i.e. k_2 (sharp absorbance).

3.1. Effect of pH

The effect of pH on photocatalytic degradation was investigated in the pH range 2.0–5.5. The result is given in Table 1. The photochemical degradation of RB was maximum at pH

4.0. The photochemical degradation depends strongly on the pH of the reaction medium. It was observed that rate of degradation of dye increased on decreasing pH from 5.5 to 4.0. It may be due to dominance of Eq. (1) over Eq. (2), where OH[−] ions are generated. These OH[−] ions are removed by increasing H⁺ ion concentration on decreasing pH. This will facilitate the Eq. (1) forming more ·OH radicals, which will be utilized for oxidative degradation of RB as well as thiocyanate radical. On decreasing the pH further i.e. below 4.0, the reaction rate decreases again. It may be attributed to the fact that Eq. (2) starts dominating over Eq. (1) as Fe(OH)₃ is less soluble than Fe(OH)₂ and the generation of ·OH radicals by Eq. (2) is retarded at lower pH than 4.0 (Dean, 1978).



3.2. Effect of hydrogen peroxide

The effect of varying amount of H₂O₂ on the rate of photocatalytic degradation of RB was also investigated. The result is reported in Table 2. The photochemical degradation of RB was maximum at 0.3 mL. It may be explained on the basis that the increasing amount of H₂O₂ will provide more ·OH radicals responsible for oxidative degradation of RB. But after a fixed amount of H₂O₂ (0.3 mL) further increment in amount of H₂O₂ will produce more ·OH ion along with ·OH radicals and as a result, the pH of the medium increases, resulting into a decrease in the rate of degradation (Jain et al., 2007).

Table 1 Effect of pH.

pH	$k_1 \times 10^4 \text{ (s}^{-1}\text{)}$	$k_2 \times 10^4 \text{ (s}^{-1}\text{)}$
2.0	0.24	0.44
2.5	0.48	0.60
3.0	0.72	1.48
3.5	2.29	4.22
4.0	2.30	5.76
4.5	0.91	1.37
5.0	0.38	0.55
5.5	0.29	0.49

[Rhodamine B] = 1.50×10^{-5} M, [complex] = 4.37×10^{-5} M, H₂O₂ = 0.3 mL, light intensity = 50.0 mW cm^{-2} .

Table 2 Effect of hydrogen peroxide.

H ₂ O ₂ [mL]	$k_1 \times 10^4 \text{ (s}^{-1}\text{)}$	$k_2 \times 10^4 \text{ (s}^{-1}\text{)}$
0.0	0.28	0.94
0.1	0.77	2.93
0.2	1.04	3.96
0.3	2.30	5.76
0.4	2.15	4.91
0.5	1.74	4.72
0.6	1.11	4.53
0.7	1.04	3.40

[Rhodamine B] = 1.50×10^{-5} M, pH 4.0, [complex] = 4.37×10^{-5} M, light intensity = 50.0 mW cm^{-2} .

3.3. Effect of concentration of complexes

The effect of concentration of complexes on the rate of photocatalytic degradation of RB was observed by keeping all other factors identical. The result is reported in Table 3. It is clear from the data that the rate of photocatalytic degradation increases on increasing concentration of complexes. The rate was determined up to the concentration 4.37×10^{-5} M, because beyond this limit the rate was extremely fast and it was not possible to record the observation correctly due to the experimental limitations. This increasing trend may be explained on the basis that on increasing the concentration of complex more molecules of complex were available to take part in the reaction. This results in an enhanced generation of the $\cdot\text{OH}$ radicals and as a consequence the rate of photocatalytic degradation of dye also increases.

3.4. Effect of sunset yellow FCF concentration

The effect of RB concentration on the rate of photochemical degradation was observed and the result is given in Table 4. The rate of degradation was found to increase with increasing concentration of RB up to 1.50×10^{-5} M. Further increase in concentration beyond this limit decreases the rate of degradation. This may be explained on the basis that on increasing the concentration of RB, the reaction rate increases as more molecules of dye were available for degradation, but further increase in concentration after certain limit causes retardation of the reaction. It is because at the higher concentration, the dye molecules themselves act as filter for incident light, thus proper intensity of the light does not reach the molecules present in the interior of the reaction mixture, which results in de-

Table 3 Effect of concentration of complex.

[Complex] $\times 10^5$ M	$k_1 \times 10^4$ (s ⁻¹)	$k_2 \times 10^4$ (s ⁻¹)
0.00	0.60	1.27
0.62	0.77	1.81
1.25	0.93	2.68
1.87	1.61	3.35
2.50	1.94	3.62
3.12	2.02	3.81
3.75	2.22	5.16
4.37	2.30	5.76

[Rhodamine B] = 1.50×10^{-5} M, pH 4.0, H₂O₂ = 0.3 mL, light intensity = 50.0 mW cm⁻².

Table 4 Effect of rhodamine B concentration.

[Dye] $\times 10^5$ M	$k_1 \times 10^4$ (s ⁻¹)	$k_2 \times 10^4$ (s ⁻¹)
1.00	2.28	4.43
1.50	2.30	5.76
2.00	1.65	4.43
2.50	1.61	4.25
3.00	1.60	4.08
3.50	1.55	3.72
4.00	1.45	3.37

H₂O₂ = 0.3 mL, pH 4.0, [complex] = 4.37×10^{-5} M, light intensity = 50.0 mW cm⁻².

crease in the rate of degradation. Moreover, at the higher concentration the number of collisions between dye molecules increases whereas, the collisions between dye and $\cdot\text{OH}$ radicals decreases. As a consequence, the rate of reaction is retarded. Unsuitable steric orientation is also one of the major factors for decrement in the rate of reaction (Laidler, 1994; Jain et al., 2007).

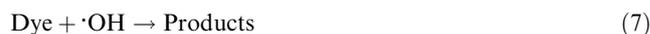
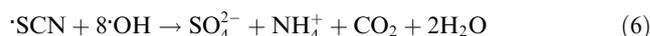
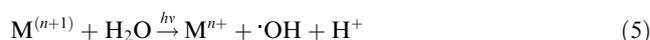
3.5. Effect of light intensity

The effect of light intensity on the photocatalytic degradation of RB was investigated. The result is reported in Table 5. The figure indicates that an increase in the light intensity, increases the rate of reaction and the maximum rate has been found at 50.0 mW cm⁻². It may be explained on the basis that as the light intensity was increased, the number of photons striking per unit area also increased, resulting into a higher rate of degradation.

Further increase in the light intensity beyond this limit results in decrease in the rate of reaction. It may be probably due to thermal side reactions.

4. Mechanism

On the basis of the experimental observations and corroborating the existing literature a tentative mechanism has been proposed for the degradation of RB in the presence of iron complex, H₂O₂, and light (Lang et al., 2002).



(Here M stands for iron)

The Photo-Fenton reaction is one of the examples of classical photocatalytic process in homogeneous system that

Table 5 Effect of light

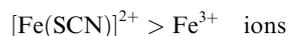
Light intensity (mW cm ⁻²)	$k_1 \times 10^4$ (s ⁻¹)	$k_2 \times 10^4$ (s ⁻¹)
10.0	1.36	2.52
20.0	1.41	4.33
30.0	1.46	4.33
40.0	1.48	4.70
50.0	2.30	5.76
60.0	1.80	5.42
70.0	1.70	5.04
80.0	1.39	4.70

[Rhodamine B] = 1.50×10^{-5} M, [complex] = 4.37×10^{-5} M, H₂O₂ = 0.3 mL, pH 4.0.

involves H_2O_2 -iron (III)-visible radiations. The thiocyanate complex of Fe^{3+} gives Fe^{2+} and thiocyanate radical on exposure to light. Fe^{2+} ion decomposes hydrogen peroxide into $\cdot\text{OH}$ radical, ^-OH ion, and itself oxidized to Fe^{3+} ions. Fe^{3+} ion decomposes water photochemically to give $\cdot\text{OH}$ radical and Fe^{2+} ions. Thiocyanate radical and dye are decomposed by hydroxyl radicals to simpler ions/molecules like sulphates ion and ammonium ions, carbon dioxide, water, etc.

5. Conclusion

The rate of photocatalytic degradation of RB is enhanced by an iron complex. The increasing order of the rate with different iron complex and Fe^{3+} ions is as follows



The hydroxyl radicals degrade the RB. The participation of $\cdot\text{OH}$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavengers, like 2-propanol, where the rate of photo degradation was drastically reduced.

Further, this method is more advantageous over other methods, since it does not add to pollution, any further. The active oxidizing species, the hydroxyl radicals, will dimerise to give hydrogen peroxide, which may degrade ultimately to water and oxygen.

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