

Photochemical treatment of rhodamine-B wastewater by photo-Fenton reagent

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Oxidation by photo-Fenton like reaction is an economically feasible process for degradation of a variety of hazardous pollutants in wastewater from dyeing and printing industries. Oxidation of rhodamine-B, (an acid dye of xanthene series) using photo-Fenton reagent has been carried out under ambient conditions. The effect of different parameters like the concentration of ferric ion, rhodamine-B, pH, hydrogen peroxide, light intensity etc. on the reaction rate has been observed. A tentative mechanism for the degradation of rhodamine-B by photo-Fenton's reaction has been proposed.

Keywords: Photochemical degradation, Photo-Fenton, Rhodamine-B, AOPs

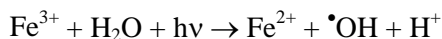
The world is facing the challenge of purification of water and air resources. In spite of many uses, the organic compounds are toxic in nature and environmental contamination by these toxic chemicals is emerging as a serious global problem. Organic compounds containing industrial effluents from textile, dyeing and printing industries may cause skin cancer due to photosensitization and photodynamic damage. On the contrary, degradation products of these organic compounds are relatively less toxic and in some cases, these are almost harmless. Secondly, polluted water is of almost no use, but if these organic compounds are degraded to smaller fragments, then this treated water may be used for washing, cooling, irrigation and cleaning purposes.

In recent years, innovative technologies such as the Advance Oxidation Processes (AOPs) have emerged for the destruction of organic compounds¹. Some systems e.g. UV-H₂O₂ and UV-O₃, are widely known and are in practical use also^{2,3}. Another treatment method using the Fenton reaction⁴, utilizes hydroxyl radicals produced by interaction of H₂O₂ with ferrous salts

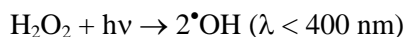


In the dark, this reaction is stopped after complete conversion of Fe²⁺ to Fe³⁺. It has also been found that illumination of the Fe²⁺-Fe³⁺-H₂O₂ system increases the rate of degradation of many organic substances, e.g. nitrophenols⁵, nitrobenzene, anisole⁶ and di-*n*-

butyl-*ortho*-phosphate⁷. The reasons for the rate enhancement of degradation on irradiation include the photoreduction of Fe³⁺ ions back to Fe²⁺ ions, which produce new •OH radicals with H₂O₂ as shown above or according to the following mechanism⁸.



The direct photolysis of H₂O₂ also generates •OH radicals.



Chen *et al.*⁹ studied the photochemical degradation of azo dyes, namely red MX-5B, reactive black-5 and orange-G using low iron concentrations in Fenton and Fenton like systems. An environmental assessment of different photo-Fenton approaches for commercial reactive dye removal has been made by Garcia-Montane *et al.*^{10,11}. Daneshvar and Khataee¹² decolorized the solution containing a common textile and leather dye, C.I. acid red 14 (AR14), at pH 3 using Fenton, UV/H₂O₂/O₂, UV/H₂O₂/Fe²⁺, UV/H₂O₂/Fe³⁺ and UV/H₂O₂/Fe³⁺/oxalate processes. Papamerou *et al.*¹³ studied the decolorization kinetics of procion H dye from textile dyeing using photo-Fenton reaction. The influence of alizarin violet 3B dye on the Fenton reaction of organic compounds under visible irradiation ($\lambda > 450 \text{ nm}$) was examined by Tang *et al.*¹⁴. The degradation of acid orange 7 dye (AO7) by three different

photochemical processes (photoperoxidation, Fenton, photo-Fenton) was observed by Martins *et al.*¹⁵. Use of photo-Fenton process for color removal from textile wastewaters was also investigated by different workers from time to time¹⁶⁻²⁰.

Experimental Procedure

Materials and Methods

Rhodamine-B (SDS), FeCl₃ (CDH) and H₂O₂ (30%, Merck), were used in the present investigations. The dye solution of rhodamine-B was prepared in doubly distilled water. The photochemical degradation of rhodamine-B was studied in the presence of Fe³⁺ ion, H₂O₂ and light. 0.0479 g of rhodamine-B was dissolved in 100 mL of doubly distilled water (1.0×10⁻⁴ M) and 0.4055 g of anhydrous FeCl₃ was dissolved in 500 mL of doubly distilled water so that the concentration of the FeCl₃ solution was 5.0×10⁻³ M. These were used as stock solutions. The photochemical degradation of rhodamine-B was studied taking 50 mL of dye solution (2.0×10⁻⁶ M) and 8.0 mL of FeCl₃ solution (1.0×10⁻³ M). The reaction mixture was exposed to light (Intensity 80.0 mWcm⁻²). A 200-watt tungsten lamp (Sylvania Laxman) was used for irradiation purpose. Sunlight was used for higher intensities of light. The intensity of light at various distances was measured by Suryamapi (CEL Model SM 201). A water filter was used to cut off thermal radiations. The pH of the solution was measured by a digital pH meter (Systronics Model 335). The desired pH of the solution was adjusted by the addition of previously standardized HCl and NaOH solutions. The necessary conditions for the correct measurement of optical density is that the solution must be free from suspension. Centrifuge machine (Remi-1258) and Whatman filter paper was used to remove the suspension but both were not found suitable. Thus, G-3 sintered glass crucible was used for filtration to obtain the desired accuracy in measurement of optical density at different time intervals, whereas λ_{max} of the dye was determined with the help of Ultraviolet-visible recording spectrophotometer (Shimadzu U.V. 240).

Results and Discussion

The photochemical degradation of rhodamine-B was observed at λ_{max} 545 nm. The results for a typical run are given in Fig. 1. It was observed that optical density of rhodamine-B solution decreases with the increase in the time of irradiation; thus, indicating that

rhodamine-B is consumed on irradiation. A plot of 2 + logOD against time was linear and it followed pseudo-first order kinetics. The rate constant was measured with expression $k = 2.303 \times \text{slope}$. The optimum rate constant for this reaction was determined as $k = 5.12 \times 10^{-4} \text{ s}^{-1}$

Effect of pH

The effect of pH on the rate of degradation of rhodamine-B was investigated in the pH range of 2.0 to 5.5. The photochemical degradation depends strongly on the pH of the reaction medium as it is evident from Fig. 2 that the rate of photochemical degradation of rhodamine-B increases with increase in pH upto 2.5 and then the rate of reaction decreases with increasing pH. The hydroxyl radicals are generated by two steps: (i) The reaction between

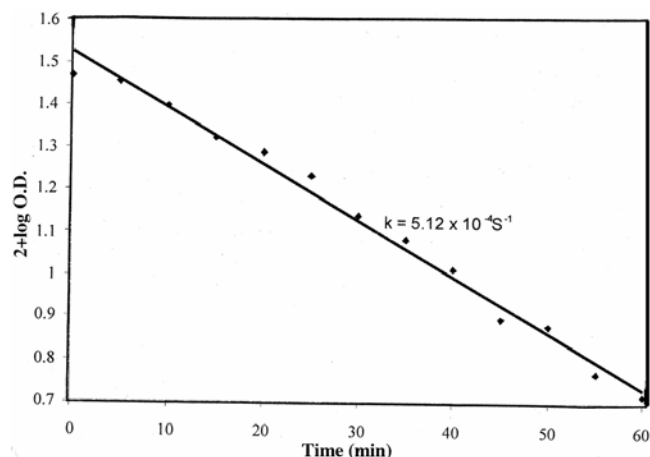


Fig. 1 — A typical run [Rhodamine-B] = 2.0×10⁻⁶ M; pH = 2.5; [Fe³⁺] = 1.60×10⁻⁴ M; H₂O₂ = 1.5 mL; Light intensity = 80.0 mWcm⁻²

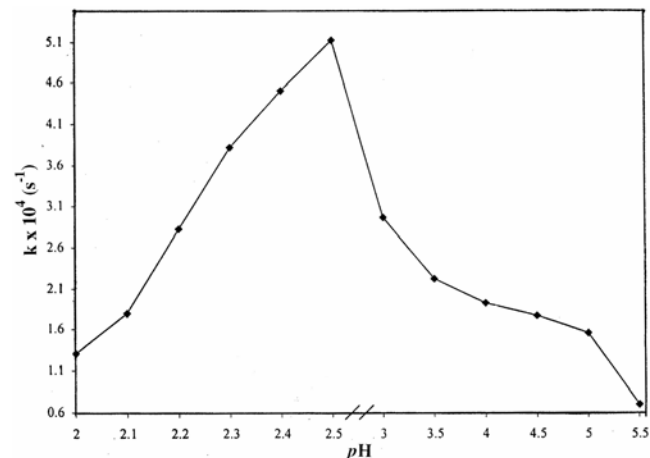


Fig. 2 — Effect of pH [Rhodamine-B] = 2.0×10⁻⁶ M; H₂O₂ = 1.5 mL; [Fe³⁺] = 1.60×10⁻⁴ M; Light intensity = 80.0 mWcm⁻²

ferrous ions and hydrogen peroxide, (ii) Photochemical reaction of ferric ions and water.

The increase in the pH of the medium will favour the step, (i) where OH^- ions are formed along with hydroxyl radicals, whereas protons are generated in step (ii); thus, it may be concluded that the step (i) dominates over step (ii) in the pH range below 2.5. However, retardation of the reaction above pH 2.5 suggests the dominance of step (ii) over step (i).

Effect of rhodamine-B concentration

Effect of variation of dye concentration on rate of reaction was also studied by taking different concentrations of rhodamine-B solution. The results are given in Fig. 3. The rate of photochemical degradation was found to increase with increasing concentration of rhodamine-B upto 2.0×10^{-6} 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 increasing the concentration of rhodamine-B, more molecules of rhodamine-B are available for degradation. However, on increasing the concentration above 2.0×10^{-6} M, the reaction rate was found to decrease. It may be attributed to the fact that as the concentration of rhodamine-B was increased, it started acting like a filter for the incident light, where its larger concentration will not permit the desired light intensity to reach the dye molecule in the bulk of the solution and thus, a decrease in the rate of photochemical bleaching of rhodamine-B was observed.

Effect of ferric ion concentration

The effect of concentration of Fe^{3+} ions on the rate of photochemical degradation of rhodamine-B was observed by keeping all other factors constant. The

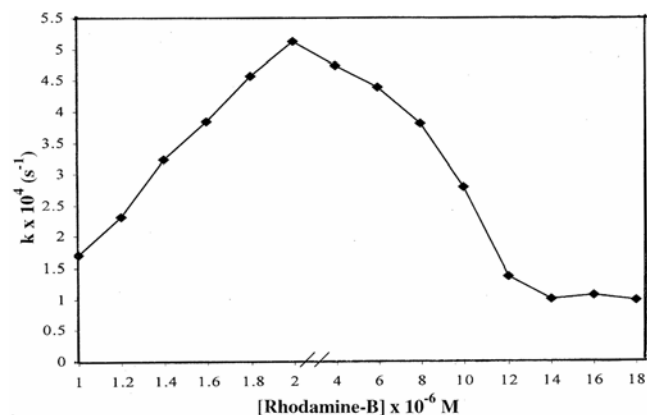


Fig. 3 — Effect of rhodamine-B concentration $pH = 2.5$; $H_2O_2 = 1.5$ mL; $[Fe^{3+}] = 1.60 \times 10^{-4}$ M; Light intensity = 80.0 mWcm⁻²

results are presented in Fig. 4. It is clear from Fig. 4 that the rate of photodegradation increases on increasing concentration of Fe^{3+} ions upto 1.60×10^{-4} M, while a reverse trend was observed beyond this limit. This may be explained on the basis that on increasing the Fe^{3+} ions in the reaction mixture, the concentration of Fe^{2+} ions also increases, which is accompanied by enhanced generation of the active species $\bullet OH$ radicals and as a consequence, the rate of photodegradation also increases. However, on increasing the concentration of Fe^{3+} ions further, the rate of the reaction was found to decrease. This is because of the fact that the Fe^{3+} ions imparts a yellow colour to the solution and at larger concentrations, it may also act as a filter for the incident light. As the concentration of Fe^{3+} was increased above its optimum concentration, the rate of the reaction of [Eq. (2)] and [Eq. (6)] (see mechanism) become very fast. Now in [Eq. (2)] hydroperoxyl radicals ($\bullet OOH$) are generated, which consumed more amount of Fe^{3+} ions and hence, Fe^{3+} ions are now less available [Eq. (1)] and as a consequence less $\bullet OH$ radicals are generated and the rate of photodegradation also decreases.

Effect of hydrogen peroxide

The effect of amount of hydrogen peroxide on photodegradation of rhodamine-B was also investigated. The results are presented in Fig. 5. It was observed that the rate of reaction increases on increasing the amount of H_2O_2 and it attained an optimum value at $H_2O_2 = 1.5$ mL. Thereafter, the rate of degradation decreases on increasing the amount of the hydrogen peroxide above 1.5 mL. This can be

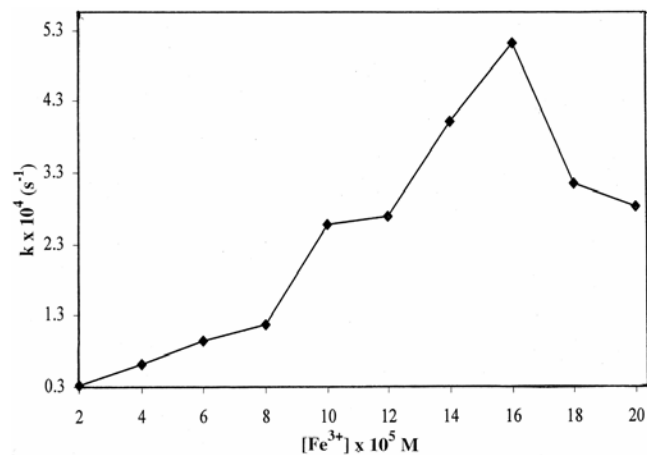


Fig. 4 — Effect of ferric ion concentration [Rhodamine-B] = 2.0×10^{-6} M; $pH = 2.5$; $H_2O_2 = 1.5$ mL; Light intensity = 80.0 mWcm⁻²

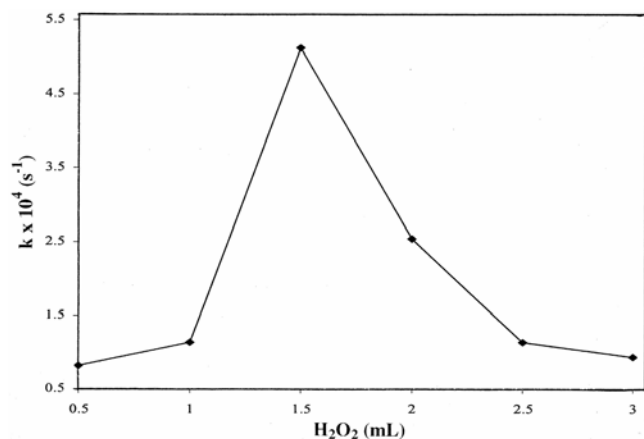


Fig. 5 — Effect of hydrogen peroxide [Rhodamine-B] = 2.0×10^{-6} M; pH = 2.5; $[\text{Fe}^{3+}] = 1.60 \times 10^{-4}$ M; Light intensity = 80.0 mWcm^{-2}

explained on the basis that more H_2O_2 molecules are available for Fe^{2+} ions to react, which increases the number of $\cdot\text{OH}$ radicals. Therefore, the rate of reaction also increases. On further increasing the amount of H_2O_2 more than 1.5 mL, the rate of reaction was found to decrease. It is because of the fact that as the amount of H_2O_2 was increased along its optimum condition (1.5 mL) the rates of the reaction [Eq. (2)] and [Eq. (4)] become fast and $\cdot\text{OH}$ radicals are consumed rapidly [Eq. (4)] due to more availability of H_2O_2 molecules. From [Eq. (2)] and [Eq. (4)], $\cdot\text{OOH}$ radicals generated in more amount. This $\cdot\text{OOH}$ radical is utilized [Eq. (6)] 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.

Effect of light intensity

The effect of light intensity on the photodegradation of rhodamine-B was also observed. The results obtained are given in Fig. 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. This may be attributed to the increased number of photons reacting with Fe^{3+} ions and as a result, there is an increase in the number of active species, the hydroxyl radicals and corresponding increase in the rate of reaction.

Mechanism

On the basis of experimental observations and corroborating the existing literature, a tentative

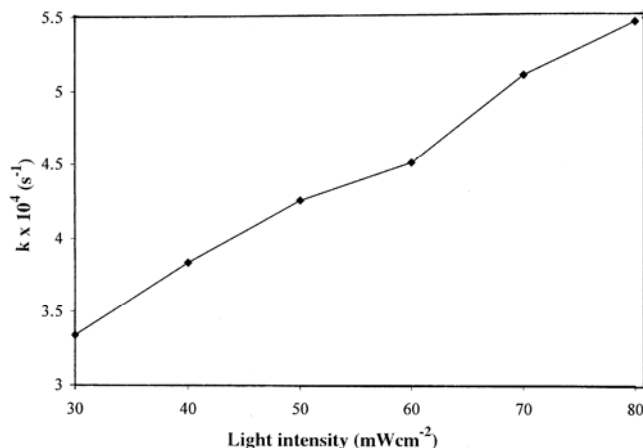
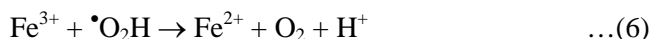
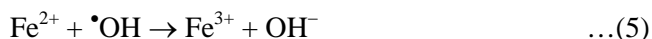
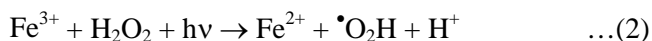
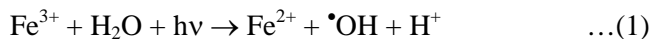


Fig. 6 — Effect of light intensity [Rhodamine-B] = 2.0×10^{-6} M; pH = 2.5; $[\text{Fe}^{3+}] = 1.60 \times 10^{-4}$ M; $\text{H}_2\text{O}_2 = 1.5 \text{ mL}$

mechanism has been proposed for photodegradation of rhodamine-B with photo-Fenton reagent.



The aqueous solution of ferric ions on exposure to light dissociates water into a proton and $\cdot\text{OH}$ radical and ferric ions are reduced to ferrous ions. These ferrous ions will decompose H_2O_2 into hydroxyl ion and hydroxyl radical, while ferrous ions undergo oxidation to ferric ions. The ferric ions generates $\cdot\text{OOH}$ radical due to dissociation of H_2O_2 in presence of light. The incorporation of $\cdot\text{OH}$ with H_2O_2 also produces $\cdot\text{OOH}$ radicals. Ferrous ions will undergo oxidation to ferric ions by addition of $\cdot\text{OH}$ radicals, while ferric ions get reduced to ferrous ions by incorporation of $\cdot\text{OOH}$ radical and producing H^+ ion. $\cdot\text{OOH}$ Radicals are highly unstable in water and undergo facile disproportionation rather than reacting slow with dye molecules. The participation of

hydroxyl radical as an active oxidizing species was confirmed by using hydroxyl radical scavenger like isopropanol, where the rate of photodegradation was drastically reduced.

Now there are two possibilities for the consumption of $\cdot\text{OH}$ radicals. First hydroxyl radicals may dissociate H_2O_2 into $\cdot\text{OOH}$ and water or combine together to form H_2O_2 molecules and secondly, it may react with rhodamine-B to give the colourless degradation products.

The main advantage of using photo-Fenton reagent is the regeneration of the consumed Fe^{2+} ions on illumination. Every Fe^{2+} ion can produce many $\cdot\text{OH}$ radicals in contrast with dark Fenton reaction as this process is cyclic in nature, where only a single $\cdot\text{OH}$ radical is formed by one ferrous ion. It means that the amount of ferrous salt required in photo-Fenton conditions is small as compared to Fenton condition, where one has to add ferrous ions at require intervals otherwise the reaction will stop after conversion of ferrous ions to ferric ions. It is important for industrial use as further separation of the ferric ions is not required after wastewater treatment²¹⁻²⁶.

Conclusion

Photo-Fenton reaction is capable of oxidizing dyes like rhodamine-B into colourless degradation products. Degradation of dyes by photo-Fenton as oxidizing agent may open new avenues for the treatment of waste water from dyeing, printing and textile industries. The treated waste water may be used for cooling, cleaning, waste land irrigation etc., which is not possible otherwise with coloured water.

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